CHAPTER II

SECTION I

SYNTHESIS AND PHOTOREACTIONS OF 5,5'-DIMETHOXY-2,2'-DINITRO-
DIPHENYLMETHANE AND ITS 4,4'-DIHALO DERIVATIVES IN
NEUTRAL MEDIUM

INTRODUCTION

The photolysis of 2,2'-dinitrodiphenylmethane experimented by Joshua and coworkers in these laboratories is acquiring greater synthetic utility. It proved to be a feasible and easier method for arriving at the dibenzo[c,f][1,2]diazepine derivatives, benzisoxazoles, acridones and N-hydroxyacridones which are otherwise difficult to obtain by conventional methods.

Some psychopharmacological drugs\textsuperscript{231-234} of the diazepine group were shown to have marked antiepileptic action. Certain chlorodiazepoxides also were found to exhibit anticonvulsant action\textsuperscript{231} and sedative effect.\textsuperscript{235,236} Similarly the role of acridines and its derivatives in medicine is deep rooted since many decades. 3,6-Diamino-10-methylacridiniumchloride was found to be active against cholera. Many acridine derivatives were found to have antibacterial properties. Proflavine as well as Acriflavine which are acridine derivatives were used as wound-disinfectants during both world wars.\textsuperscript{238-240} The National Institute of Health, U.S.A. in their screening of various organic compounds for anticancer activity have found that N-hydroxy-acridones are moderately active.
The above mentioned applications of various compounds obtained in the photoreaction of 2,2'-dinitrodiphenylmethane prompted us to examine more of its derivatives.

Earlier dibenzo[ε,ε][1,2]diazepine and its derivatives were prepared by various workers\textsuperscript{241-249} adopting different procedures.

Synthesis of a dibenzo[ε,ε][1,2]diazepine derivative was reported as early as in 1905 by Duval.\textsuperscript{241-244} The author obtained 3,8-disubstituted-11H-dibenzo[ε,ε][1,2]diazepin-5-oxides, when the reduction of appropriate disubstituted 2,2'-dinitrodiphenylmethanes was carried out with zinc dust and ammonium chloride, in alcoholic medium. The azoxy compounds so obtained were subsequently reduced in alcoholic potassium hydroxide using zinc dust to get the diazepine derivative.

\[
\text{X} \quad \text{Zn} \quad \text{KOH} \quad \text{NH}_4\text{Cl} \quad \text{X} \quad \text{N} = \text{N}
\]

In connection with the preparation of a model compound for the study of 14\textsuperscript{π} electron systems containing heteroatoms, Allinger and Youngdale\textsuperscript{245,246} prepared 11H-dibenzo[ε,ε][1,2]-diazepin-5-oxide which was then reduced to 11H-dibenzo[ε,ε][1,2]-diazepine by sodium sulfide or lithium aluminium hydride. The diazepine was also prepared by Theilacker and Korndorfer\textsuperscript{247} by
the lithium aluminium hydride reduction of 2,2'-dinitrodiphenylmethane in ether solution, in better yield. Catala and Popp extended this method to the preparation of 3,6-dihalo derivatives of 11H-dibenzo[c,e][1,2]diazepines.

Attempts made by Johns and Markham for the preparation of 11H-dibenzo[c,e][1,2]diazepin-11-one by lithium aluminium hydride reduction of 2,2'-dinitrobenzophenone met with failure. However they succeeded in its preparation when alkaline glucose was used for its reduction.

Catala and Popp failed to get the dihalodibenzo[c,e][1,2]-diazepin-11-one by the alkaline glucose reduction of the dihalodinitrobenzophenones. They therefore used the chromic anhydride oxidation of the corresponding 3,8-dihalo-11H-dibenzo[c,e][1,2]diazepines for their preparation.
The yield of diazepinone was found to be low and a total failure was observed when the benzene ring carried easily oxidizable groups.

It has been shown that photochemical intramolecular hydrogen abstraction and internal coupling of the two proximal nitro groups in 2,2'-dinitrodiphenylmethanes could be used as a method for the preparation of this 14 σ electron system. The irradiation of 2,2'-dinitrodiphenylmethanes in 2-propanol resulted, mainly, in the formation of dibenzo [c,f][1,2] diazepin-11-one-5-oxides and dibenzo [c,f][1,2] diazepin-11-one-5,6-dioxides. Both the N-oxide and the N,N-dioxide were easily converted to the dibenzo [c,f][1,2] diazepin-11-one derivatives by reduction with magnesium in ethanol or isopropanol.

Continued interest in the study of the photochemistry of nitroarenes prompted the examination of the effect of substituents in 2,2'-dinitrodiphenylmethanes on the photoreaction. It was also thought that more insight into the mechanism of these photoreactions would come out of these studies. Hence a study of the photoreactions of some methoxy and halogen substituted 2,2'-dinitrodiphenylmethanes, in neutral (protic and aprotic) and acidic media were taken up.

**PREPARATION OF THE STARTING MATERIALS**

As early as in 1935 Scanlan described a method for the preparation of 4,4'-diaminodiphenylmethane by the condensation of formaldehyde with aniline in the presence of an acid.
A similar condensation of formaldehyde with \( \alpha \)-anisidine appeared to be a feasible route to \( 4,4' \)-diamino-3,3'-dimethoxydiphenylmethane.

Present attempt to synthesise the compound by the condensation of formaldehyde with \( \alpha \)-anisidine was successful. The condensation yielded a white compound which could be purified by fractional precipitation from dilute hydrochloric acid using ammonia. On crystallisation of the compound from alcohol, white flakes with melting point 88\( ^\circ \)C and molecular composition \( C_{15}H_{18}O_2N_2 \) were obtained. The compound has been assigned structure (1) in analogy with the structure of \( 4,4' \)-diaminodiphenylmethane. Spectral data confirmed the structure (1) assigned to this diamino compound.

\[
\begin{align*}
\text{CH}_3 & \quad \text{H}_2\text{N} \\
\text{H}_2\text{N} & \quad \text{OCH}_3 \\
\text{NH}_2 & \quad \text{H}_2\text{N} \\
\end{align*}
\]

(1)

Nitration of (1) in 98% sulphuric acid at -5 to 5\( ^\circ \)C with anhydrous potassium nitrate dissolved in 98% sulphuric acid yielded an yellow compound, m.p. 166\( ^\circ \)C with a molecular composition \( C_{15}H_{16}O_6N_4 \) indicating that it is dinitro compound (2).

The isomers which could represent the dinitro compound are the following.
(2a) \[ \text{Diagram 2a} \]

(2b) \[ \text{Diagram 2b} \]

(2c) \[ \text{Diagram 2c} \]

(2d) \[ \text{Diagram 2d} \]

(2e) \[ \text{Diagram 2e} \]

(2f) \[ \text{Diagram 2f} \]

(2g) \[ \text{Diagram 2g} \]

(2h) \[ \text{Diagram 2h} \]

(2i) \[ \text{Diagram 2i} \]
The structure of the product obtained was arrived at from its chemical reactions and spectral data.

The derivatives of the nitro compound (2) obtained by deamination and Sandmeyer reaction were found to be photoactive. The photosensitiveness of these compounds suggest that at least one of the two nitro groups is ortho to the methylene, or methoxy group. Further it was observed that these derivatives when treated with LiAlH₄ in ethereal solution gave yellow compounds which were identified as dibenzo [g,f][1,2] diazepines. The formation of a diazepine ring requires the presence of one ortho nitro group each on each aromatic ring.

The n.m.r. spectrum of the compound (2) showed only a single signal for the methoxy protons suggesting a symmetrical structure. Structure 2g as well as 2i have nitro groups in o,o' positions and have symmetrically placed methoxy groups. The correct structure 2g for the compound was arrived at from n.m.r. spectral data. The spectrum showed two singlets (2 protons each) in the aromatic region which could be accounted only by structure 2g.

Diazotisation of the diaminodinitro compound (2) in hypophosphorous acid in presence of cuprous oxide afforded 5,5'-dimethoxy-2,2'-dinitrodiphenylmethane (3a). The 4,4'-dihalo derivatives (3b-d) were obtained from (2) by Sandmeyer reactions. The following scheme represents the conversion of the diamino derivatives to the various products.
RESULTS OF PHOTOLYSIS IN ISOPROPANOL

Exposure of a solution of 5,5'-dimethoxy-2,2'-dinitro-diphenylmethane (3a) and its dihalo derivatives (3b-d) in isopropanol (1 gm in 500 ml) in sunlight was found to result in a rapid photoreaction. In each case the experiment was repeated ten times. After the nearly complete disappearance of the starting material (75 hrs) the photolysates were combined and
the solvent was removed by distillation under reduced pressure. The residue dissolved in benzene was repeatedly washed with alkali (2%). The combined alkali washings on acidification yielded an yellow compound in every case. This compound and the residue obtained after evaporating the benzene solution were chromatographed on a column of silica gel and alumina respectively. The results obtained are given in tables 1-5. It was observed that the yield of dibenzo[\(c, f\)][1, 2]diazepin-11-one-5-oxides (7) and 3,6-dihalo-2,7-dimethoxyacridones (8b-d) increased slightly when the irradiation was prolonged for longer periods. On the contrary prolonged irradiation decreased the yield of N,N-dioxide (10a) and benzisoxazoles (5a-d) Table 5.

It was observed that the result of the irradiation with a Philips HPK 125 W high pressure mercury-quartz lamp was almost identical with the irradiation in sunlight. However, the quantity of intractable tarry material formed was very high in the former case and hence the irradiation in sunlight was preferred.
TABLE 1  IRRADIATION OF 5,5'-DIMETHOXY-2,2'-DINITRODIPHENYLMETHANE (3a) IN ISOPROPANOL
(1 gm in 500 ml x 10) Duration of exposure: 75 hours in sunlight
Percentage conversion: 98

<table>
<thead>
<tr>
<th>Nature of the compound</th>
<th>Molecular composition</th>
<th>Name of the compound</th>
<th>Yield</th>
<th>% yield</th>
<th>Melting point°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Light yellow needles</td>
<td>C_{15}H_{14}N_{2}O_{6}</td>
<td>Starting material (3a)</td>
<td>200 mg</td>
<td>2</td>
<td>148</td>
</tr>
<tr>
<td>Colourless needles</td>
<td>C_{15}H_{12}N_{2}O_{7}</td>
<td>5,5'-dimethoxy-2,2'-dinitrobenzophenone (4a)</td>
<td>1.0 g</td>
<td>10</td>
<td>179</td>
</tr>
<tr>
<td>Golden yellow needles</td>
<td>C_{15}H_{12}N_{2}O_{5}</td>
<td>5-methoxy-3-(5'-methoxy-2'-nitrophenyl)-2,1-benzisoxazole (5a)</td>
<td>380 mg</td>
<td>4</td>
<td>161</td>
</tr>
<tr>
<td>Yellow needles</td>
<td>C_{15}H_{12}N_{2}O_{4}</td>
<td>2,9-dimethoxydibenzo[c,f][1,2] diazepin-11-one-5-oxide (7a)</td>
<td>4.64 g</td>
<td>52</td>
<td>182</td>
</tr>
<tr>
<td>Yellow microcrystalline prisms</td>
<td>C_{15}H_{13}NO_{3}</td>
<td>2,7-dimethoxyacridone (8a)</td>
<td>960 mg</td>
<td>12</td>
<td>&gt;300</td>
</tr>
<tr>
<td>Yellow needles</td>
<td>C_{15}H_{12}N_{2}O_{5}</td>
<td>2,9-dimethoxydibenzo[c,f][1,2] diazepin-11-one-5,6-dioxide (10a)</td>
<td>850 mg</td>
<td>9</td>
<td>168 (dec)</td>
</tr>
<tr>
<td>Yellow needles</td>
<td>C_{15}H_{13}NO_{4}</td>
<td>2,7-dimethoxy-N-hydroxyacridone (9a)</td>
<td>800 mg</td>
<td>9</td>
<td>&gt;300</td>
</tr>
<tr>
<td>Nature of the compound</td>
<td>Molecular composition</td>
<td>Name of the compound</td>
<td>Yield</td>
<td>% yield</td>
<td>Melting point °C</td>
</tr>
<tr>
<td>------------------------</td>
<td>-----------------------</td>
<td>----------------------</td>
<td>-------</td>
<td>---------</td>
<td>-----------------</td>
</tr>
<tr>
<td>Light yellow needles</td>
<td>C_{15}H_{12}N_{2}O_{6}Cl_{2}</td>
<td>Starting material</td>
<td>300 mg</td>
<td>3</td>
<td>184</td>
</tr>
<tr>
<td>Colourless needles</td>
<td>C_{15}H_{10}N_{2}O_{7}Cl_{2}</td>
<td>4,4'-dichloro-5,5'-dimethoxy-2,2'-dinitrobenzophenone (4b)</td>
<td>770 mg</td>
<td>7.5</td>
<td>204</td>
</tr>
<tr>
<td>Yellow needles</td>
<td>C_{15}H_{10}N_{2}O_{5}Cl_{2}</td>
<td>6-Chloro-5-methoxy-3-(4'-chloro-5'-methoxy-2'-nitrophenyl)-2,1-benzisoxazole (5b)</td>
<td>330 mg</td>
<td>3.5</td>
<td>226</td>
</tr>
<tr>
<td>Orange red needles</td>
<td>C_{15}H_{10}N_{2}O_{3}Cl_{2}</td>
<td>3,8-dichloro-2,9-dimethoxydibenzo [6,7][1,2]diazepin-11-one (6b)</td>
<td>430 mg</td>
<td>5</td>
<td>256</td>
</tr>
<tr>
<td>Brick red shining flakes</td>
<td>C_{15}H_{12}N_{2}O_{2}Cl_{2}</td>
<td>3,8-dichloro-2,9-dimethoxydibenzo [6,7][1,2]diazepine (11b)</td>
<td>340 mg</td>
<td>4</td>
<td>236</td>
</tr>
<tr>
<td>Yellow needles</td>
<td>C_{15}H_{10}N_{2}O_{4}Cl_{2}</td>
<td>3,8-dichloro-2,9-dimethoxydibenzo [6,7][1,2]diazepin-11-one-5-oxide (7b)</td>
<td>4.4 g</td>
<td>48</td>
<td>245</td>
</tr>
<tr>
<td>Yellow microcrystalline prisms</td>
<td>C_{15}H_{11}NO_{3}Cl_{2}</td>
<td>3,6-dichloro-2,7-dimethoxyacridone (8b)</td>
<td>1.1 g</td>
<td>13</td>
<td>&gt;300</td>
</tr>
<tr>
<td>Yellow solid</td>
<td>*C_{15}H_{10}N_{2}O_{5}Cl_{2}</td>
<td>3,8-dichloro-2,9-dimethoxydibenzo [6,7][1,2]diazepin-11-one-5,6-dioxide (10b)</td>
<td>580 mg</td>
<td>6</td>
<td>-</td>
</tr>
<tr>
<td>Yellow needles</td>
<td>C_{15}H_{11}NO_{4}Cl_{2}</td>
<td>3,6-dichloro-2,7-dimethoxy-N-hydroxyacridone (9b)</td>
<td>1.2 g</td>
<td>14</td>
<td>&gt;300</td>
</tr>
</tbody>
</table>

* The proposed composition is based on ir data and chemical evidences since it could not be obtained in pure form for analysis.
TABLE 3 IRRADIATION CF 4,4'-DIBROMO-5,5'-DIMETHOXY-2,2'-DINITRODIPHENYL METHANE IN ISOPROPANOL (1 g in 500 ml x 10) Duration of exposure: 100 hours in sunlight Percentage conversion: 95

<table>
<thead>
<tr>
<th>Nature of the compound</th>
<th>Molecular composition</th>
<th>Name of the compound</th>
<th>Yield (mg)</th>
<th>% yield</th>
<th>Melting point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Light yellow needles</td>
<td>C₁₅H₁₂N₂O₆Br₂</td>
<td>Starting material</td>
<td>500</td>
<td>5</td>
<td>202</td>
</tr>
<tr>
<td>Colourless needles</td>
<td>C₁₅H₁₀N₂O₇Br₂</td>
<td>4,4'-dibromo-5,5'-dimethoxy-2,2'-dinitrobenzophenone(4c)</td>
<td>930</td>
<td>9</td>
<td>222</td>
</tr>
<tr>
<td>Yellow needles</td>
<td>C₁₅H₁₀N₂O₅Br₂</td>
<td>6-bromo-5-methoxy-3-(4'-chloro-380 mg 5'-methoxy-2'-nitrophenyl)-2,1-benzisoxazole (5c)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Yellow needles</td>
<td>C₁₅H₁₀N₂O₄Br₂</td>
<td>3,8-dibromo-2,9-dimethoxydibenzo [c,f][1,2] diazepin-11-one-5-oxide (7c)</td>
<td>4.6</td>
<td>49</td>
<td>260</td>
</tr>
<tr>
<td>Yellow microcrystalline prisms</td>
<td>C₁₅H₁₁NO₃Br₂</td>
<td>3,6-dibromo-2,7-dimethoxyacridone (8c)</td>
<td>1.2</td>
<td>14</td>
<td>&gt;300</td>
</tr>
<tr>
<td>Yellow solid</td>
<td>*C₁₅H₁₀N₂O₅Br₂</td>
<td>3,8-dibromo-2,9-dimethoxydibenzo [c,f][1,2] diazepin-11-one-5,6-dioxide</td>
<td>570</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>Shining yellow needles</td>
<td>C₁₅H₁₁NO₄Br₂</td>
<td>3,6-dibromo-2,7-dimethoxy-N-hydroxyacridone (9c)</td>
<td>630</td>
<td>7</td>
<td>&gt;300</td>
</tr>
</tbody>
</table>

*The proposed composition is based on ir data and chemical evidences since it could not be obtained in pure form for analysis.
TABLE 4  IRRADIATION OF 4,4'-DIODO-5,5'-DIMETHOXY-2,2'-DINITRODIPHENYL METHANE IN ISOPROPANOL (1 g in 500 ml x 10) Duration of exposure: 150 hours in sunlight Percentage conversion: 85

<table>
<thead>
<tr>
<th>Nature of the compound</th>
<th>Molecular composition</th>
<th>Name of the compound</th>
<th>Yield</th>
<th>% yield</th>
<th>Melting point °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Light yellow needles</td>
<td>C₁₅H₁₂N₂O₆I₂</td>
<td>Starting material</td>
<td>1.5 g</td>
<td>15</td>
<td>188</td>
</tr>
<tr>
<td>Colourless needles</td>
<td>C₁₅H₁₀N₂O₇I₂</td>
<td>4,4'-diiodo-5,5'-dimethoxy-2,2'-dinitrobenzophenone (4d)</td>
<td>1.23 g</td>
<td>12</td>
<td>238</td>
</tr>
<tr>
<td>Yellow needles</td>
<td>C₁₅H₁₀N₂O₅I₂</td>
<td>6-iodo-5-methoxy-3-(4'-iodo-5'-methoxy-2'-nitrophenyl)-2,1-benzisoxazole (5d)</td>
<td>290 mg</td>
<td>3</td>
<td>270</td>
</tr>
<tr>
<td>Brick red shining</td>
<td>C₁₅H₁₂N₂O₂I₂</td>
<td>3,8-diiodo-2,9-dimethoxydibenzo [g,f][1,2] diazepine (11d)</td>
<td>440 mg</td>
<td>5</td>
<td>147</td>
</tr>
<tr>
<td>Yellow needles</td>
<td>C₁₅H₁₀N₂O₄I₂</td>
<td>3,8-diiodo-2,9-dimethoxydibenzo [g,f][1,2] diazepin-11-one-5-oxide (7d)</td>
<td>3.86 g</td>
<td>41</td>
<td>258</td>
</tr>
<tr>
<td>Yellow microcrystalline prisms</td>
<td>C₁₅H₁₁N₀₃I₂</td>
<td>3,6-diiodo-2,7-dimethoxyacridone (8d)</td>
<td>440 mg</td>
<td>5</td>
<td>&gt;300</td>
</tr>
<tr>
<td>Yellow solid</td>
<td>*C₁₅H₁₀N₂O₅I₂</td>
<td>3,8-diiodo-2,9-dimethoxydibenzo [g,f][1,2] diazepin-11-one-5,6-dioxide (10d)</td>
<td>450 mg</td>
<td>5</td>
<td>-</td>
</tr>
<tr>
<td>Yellow needles</td>
<td>C₁₅H₁₁N₁O₄I₂</td>
<td>3,6-diiodo-2,7-dimethoxy-N-hydroxyacridone (9d)</td>
<td>730 mg</td>
<td>8</td>
<td>&gt;300</td>
</tr>
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*The proposed composition is based on IR data and chemical evidences since it could not be obtained in pure form for analysis.
<table>
<thead>
<tr>
<th>Starting material</th>
<th>Duration of irradiation</th>
<th>% Conversion</th>
<th>% yield of products formed</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>4</td>
</tr>
<tr>
<td>3a</td>
<td>75 hrs</td>
<td>98</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>150 hrs</td>
<td>100</td>
<td>10.5</td>
</tr>
<tr>
<td>3b</td>
<td>100 hrs</td>
<td>97</td>
<td>7.5</td>
</tr>
<tr>
<td></td>
<td>200 hrs</td>
<td>100</td>
<td>8.0</td>
</tr>
<tr>
<td>3c</td>
<td>100 hrs</td>
<td>95</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td>200 hrs</td>
<td>100</td>
<td>9</td>
</tr>
<tr>
<td>3d</td>
<td>150 hrs</td>
<td>85</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>250 hrs</td>
<td>92</td>
<td>13</td>
</tr>
</tbody>
</table>
RESULTS OF PHOTOLYSIS IN BENZENE

The photolysis of (3a-d) was also carried out in benzene. The major product in each case was found to be 5,5'-dimethoxy-2,2'-dinitrobenzophenones (4a-d). 3-(2'-Nitrophenyl)-2,1-benzisoxazoles (5a-d) and the related diazepinones (6a-d) were not obtained in this case. Table 6 lists the products obtained in the photolysis.

<table>
<thead>
<tr>
<th>Starting material</th>
<th>Duration of irradiation</th>
<th>% conversion</th>
<th>% yield of products formed</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>4</td>
<td>7</td>
</tr>
<tr>
<td>3a</td>
<td>75</td>
<td>96</td>
<td>43</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>100</td>
<td>45</td>
</tr>
<tr>
<td>3b</td>
<td>100</td>
<td>95</td>
<td>39</td>
</tr>
<tr>
<td></td>
<td>150</td>
<td>98</td>
<td>39</td>
</tr>
<tr>
<td>3c</td>
<td>100</td>
<td>92</td>
<td>34</td>
</tr>
<tr>
<td></td>
<td>150</td>
<td>95</td>
<td>35</td>
</tr>
<tr>
<td>3d</td>
<td>100</td>
<td>70</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>75</td>
<td>42</td>
</tr>
</tbody>
</table>
IDENTIFICATION OF PRODUCTS

1) 2,9-Dimethoxydibenzo [c, f] [1, 2] diazepin-11-one-5-oxides (7a-d)

The structure of the compounds with molecular composition \( C_{15}H_{10}N_2O_4X_2 \) \((X = H \text{ or halogen})\) was arrived at mainly from spectral data and it was supported by satisfactory elemental analyses. The compounds showed absorption maxima in the u.v. spectra around 255 and 340 nm. In the i.r. spectra, the carbonyl stretching vibrations were seen around 1680-1700 cm\(^{-1}\) and the N\(\rightarrow\)O stretching vibrations around 1440-1450 cm\(^{-1}\) and 1300-1310 cm\(^{-1}\). The n.m.r. spectrum of (7a) showed two separate signals at \( \delta \) 3.8 (3H) and 4.0 (3H) which could be attributed to the methoxy protons. Since the methoxy protons appeared as two separate singlets the molecule is asymmetric. The other protons in the compound appeared as two distinct groups, one a multiplet centred between \( \delta \) 7.4-7.65 (5H) and a doublet centered between \( \delta \) 8.15-8.23 (1H). The structure depicted below could satisfactorily account for the above observed pattern of n.m.r. spectrum.

![Structure](image)

The structure assigned to (7a) is further corroborated by the n.m.r. spectra of (7b-d). In the n.m.r. spectrum of (7b)
the methoxy protons were found to appear at $\delta$ 3.98 (3H) and 4.02 (3H). The aromatic protons appeared as four separate singlets at $\delta$ 7.28, 7.38, 7.84 and 8.52. The highly deshielded proton $H_a$ could be assigned to the signal at $\delta$ 8.52 and the singlet at $\delta$ 7.84 to $H_a'$, whereas the ones observed at $\delta$ 7.38 and 7.28 could be attributed to $H_b$ and $H_b'$ protons respectively.

Further support for the assigned structure of 2,9-dimethoxydibenzo[6,7][1,2]diazepin-11-one-5-oxides (7a-d) comes from the mass spectral data of these compounds. The peak due to the molecular ion appeared at m/e 284 as the base peak in the mass spectrum of 2,9-dimethoxydibenzo[6,7][1,2]diazepin-11-one-5-oxide (7a). It was followed by peaks due to subsequent loss of NO, CO and OCH$_3$. Stepwise loss of NO and CO observed in the mass spectra of (7a) lend further support for the structure assigned to it. The fragmentation pattern is depicted in Scheme 1. The mass spectral data of (7b-d) is in support of the assigned N-oxide structure.

Support for the structure assigned to these compounds is obtained by the conversion of these compounds to 2,9-dimethoxydibenzo[6,7][1,2]diazepin-11-one (6a-d) by reduction with Mg in refluxing ethanol solutions.
2) 5-Methoxy-3-(5'-methoxy-2'-nitrophenyl)-2,1-benzisoxazoles (5a-d)

The structure of the benzisoxazoles obtained 5(a-d) were arrived at from spectral analyses as well as from their alternate synthesis. These compounds with molecular composition $\text{C}_{15}\text{H}_{10}\text{N}_2\text{O}_2\text{X}_2$ (X = H or halogen) exhibited $\lambda_{\text{max}}$ around 330 nm
in their u.v. spectrum, which is characteristic of benzisoxazoles. The i.r. spectra showed strong absorption bands around 1540 and 1360 cm\(^{-1}\) which could be assigned to the free nitro group. The absence of any peak in the region 1600-1800 cm\(^{-1}\) indicated the absence of any carbonyl group in these compounds.

The n.m.r. spectrum of (5a) showed two separate signals at \(\delta 3.9\) (3H) and \(\delta 4.02\) (3H) which could only be assigned to the unsymmetrically placed methoxy protons. Since the methoxy protons appeared as two separate signals, the molecule should be asymmetric. The aryl protons in the molecule appeared at two distinct regions, one, a multiplet centered between \(\delta 6.9-7.5\) (5H) and another a doublet centered at \(\delta 8.24\) (1H).

The above data could only be explained by structure (5a) for the compound. The doublet at \(\delta 8.24\) could be assigned to the proton adjacent to the nitro group since it is more deshielded. The signal at \(\delta 3.9\) could be due to the OCH\(_3\) group in the ring which does not carry the nitro group and that at \(\delta 4.02\) may be due to the one in the aromatic ring containing the nitro group.

The above assigned structure for the compound is further supported by the n.m.r. spectra of (5b-d) also. The n.m.r. spectrum of (5b) showed a relatively simple pattern. The methoxy protons appeared at \(\delta 3.98\) (3H) and \(\delta 4.08\) (3H) both as singlets. The aryl protons appeared as four singlets at \(\delta 7.14, \delta 7.20, \delta 7.66\) and \(\delta 8.18\). The signals at \(\delta 8.18\) could be attributed to \(H_a\) (greater deshielding) and at \(\delta 7.66\) due to \(H_d\). Similarly the singlet at \(\delta 7.14\) could be assigned to \(H_b\) and the other signal at \(\delta 7.20\) to \(H_c\).
\[ \text{Scheme 2} \]
The mass spectral data of (5a-d) affords further support for the structure assigned to the compound. In the mass spectrum of (5a) the peak due to the molecular ion appeared at m/e 300 (44%); it was followed by peaks due to the loss of NO at m/e 270 (100%), and NO, CO & O at m/e 226 (68%). This fragmentation pattern depicted in scheme 2 accounts for all the important fragmentation peaks which could be and has been observed in the mass spectrum of (5a).

The assigned structure of (5a-d) was confirmed by its unequivocal synthesis from 5,5'-dimethoxy-2,2'-dinitrodiphenylcarbinols, following the procedure adopted by Silberg and Frenkel. The required diphenylcarbinols were obtained by the NaBH₄ reduction of the corresponding benzophenones (4a-d). The sequence of reactions employed is depicted in the following scheme.

\[
(3a-d) \xrightarrow{i \text{rradiation in benzene and chromatographic separation.}} \xrightarrow{\text{H}_3\text{CO}} \xrightarrow{\text{NaBH}_4} \xrightarrow{\text{cold conc. } \text{H}_2\text{SO}_4} (5a-d)
\]

\[
x = \text{H, Cl, Br or I}
\]
3) 2,9-Dimethoxydibenzo [c,e] [1,2] diazepin-11-ones (6a-d)

All the compounds with molecular composition 
\( \text{C}_{15}\text{H}_{10}\text{N}_{2}\text{O}_{3}\text{X}_2 \) (X = H or halogen) (6a-d) obtained in the photolyis were identified using spectral data. The carbonyl stretching vibration was found to occur around 1680-1700 cm\(^{-1}\) in their i.r. spectra. In the n.m.r. spectrum of (6a) a singlet at \( \delta \) 4.12 (6H) was observed which could be assigned to the protons of the two symmetrically placed methoxy groups in the compound. Since the protons of the two methoxy groups appeared as a singlet and the aryl protons appeared as three distinct groups, one as a singlet at \( \delta \) 6.62 (2H) and the others as two doublets centered at \( \delta \) 6.87(2H) and \( \delta \) 7.38(2H), the following structure (6a) could be assigned to the product. The singlet at \( \delta \) 6.62 could be

\[
6a \quad 6b-d \\
X \text{H}_{a} \text{ Cl,Br,I} \\
X' \text{H}_{a} \text{ Cl,Br,I}
\]

assigned to the protons \( \text{H}_c \) and \( \text{H}_c' \), and of the doublets, the one at \( \delta \) 7.38 to the more deshielded protons \( \text{H}_b \) and \( \text{H}_b' \), and the doublet at \( \delta \) 6.87 to \( \text{H}_a \) and \( \text{H}_a' \). The structure assigned to the product was supported by the n.m.r. spectrum of (6b) also. The methoxy protons appeared as a singlet at \( \delta \) 4.22 (6H). The aryl protons \( \text{H}_b \) and \( \text{H}_b' \) appeared as a singlet at \( \delta \) 8.6 (greater deshielding) and \( \text{H}_c \) and \( \text{H}_c' \), as another singlet at \( \delta \) 7.8. Further evidence for the structures was obtained by their easy conversion to the related diazepinone N-oxides (7a-d) by their
mild oxidation with H$_2$O$_2$ in alcoholic solution. The deoxy­
genated product of (7a-d) did not show any depression in melting
points when mixed with (6a-d).

4) 5,5'-Dimethoxy-2,2'-dinitrobenzophenones (4a-d)

The structure of the products with molecular composition
C$_{19}$H$_{10}$N$_2$O$_7$X$_2$ (where X = H or halogen) were arrived at from their
spectral data and by comparison with samples obtained by the
chromic anhydride oxidation of the corresponding 2,2'-dinitro-
diphenylmethanes (3a-d). The i.r. spectra of these compounds
showed strong absorption around 1680-1700 cm$^{-1}$ and at 1540 and
1340 cm$^{-1}$ indicating the presence of a carbonyl group flanked
between two benzene rings and nitro groups. The n.m.r. spectrum
of (4a) showed a singlet at $\delta$ 3.9 (6H) which could be attributed
to the protons of two methoxy groups. The appearance of methoxy
protons as a singlet adds proof to the symmetry of the molecule.
The aryl protons appeared as two doublets centered at $\delta$ 7.52 (2H)
and $\delta$ 7.04 (2H) and a singlet at $\delta$ 6.98 (2H). The following
structure explains the above mentioned spectral data.

![Chemical Structure](image)

The singlet at $\delta$ 6.98 could be assigned to H$_c$ and H$_c'$, the
doublet at $\delta$ 7.04 to H$_b$ and H$_b'$ and the doublet at $\delta$ 7.52 to
H$_a$ and H$_a'$. The n.m.r. spectra of the dihalo derivatives (4b-d)
showed a much simpler pattern. The methoxy protons appeared as a singlet at $\delta 4.04$ (6H). The aryl protons appeared as two distinct singlets, one at $\delta 7.22$ ($H_2$ & $H_2'$) and the other at $\delta 8.22$ ($H_2$ & $H_2'$). The oxidation of the related 5,5'-dimethoxy-2,2'-dinitrodiphenylmethanes (3a-d) using chromic anhydride in acetic acid afforded products identical with (4a-d).

5) 2,7-Dimethoxyacridones (8a-d)

The i.r. spectra of those compounds with molecular composition $C_{15}H_{11}NO_3X_2$ ($X = \text{H or halogen}$) showed absorption around 3400 cm$^{-1}$ and 1600 cm$^{-1}$. The former absorption indicated the presence of a NH group and the latter, the presence of a C=O group in the molecules. Because of their low solubility in
usual solvents their n.m.r. spectra could not be recorded. The mass spectral data threw much light into the structure of these acridones (8a-d). The peak due to the molecular ion appeared at m/e 255 in the mass spectrum of (8a). It was followed by peaks due to loss of CO & OCH₃ groups. The fragmentation pattern of (8a) is depicted in Scheme 3.

On the basis of the above data, these compounds were assigned a 2,7-dimethoxyacridone structure (8a-d).

![Molecular structure of 2,7-dimethoxyacridone]

6) 2,7-Dimethoxy-N-hydroxyacridones (9a-d)

The structure of those compounds with molecular composition C₁₅H₁₁NO₄X₂ (X = H or halogen) was arrived at mainly from their spectral data and chemical reactions. In their i.r. spectra in addition to the peaks around 3500 cm⁻¹ (OH) and 1600 cm⁻¹ (C=O), peaks around 1360-1300 cm⁻¹ were also seen. These peaks probably are due to the contribution of (N→O) stretching absorption. The n.m.r. spectra of these compounds also could not be recorded due to their low solubility in the usual solvents. In the mass spectrum of (9a) the peak due to the molecular ion appeared at m/e 271. It was followed by peaks due to loss of OH, CO and OCH₃ groups. The scheme depicted in scheme 4 illustrates the fragmentation pattern.
On the basis of the above data the following structure was assigned to compounds (9a-d).

These compounds yielded deep red sodium salts, as observed in the case of other N-hydroxyacridones.\textsuperscript{251}
7) 2,9-Dimethoxydibenzo [c, i] (1, 2) diazepin-11-one-5,6-dioxide

The compound with molecular composition $\text{C}_{15}\text{H}_{12}\text{N}_{2}\text{O}_{5}$ was characterised by spectral analysis. It showed u.v. absorption maximum around 257 nm. The strong peaks appearing around 1680 cm$^{-1}$ in the i.r. spectra of the compound could be attributed to C=O stretching frequency and the two fairly strong peaks at 1380 and 1310 cm$^{-1}$ could be assigned to the N—O stretching frequencies. The n.m.r. spectrum of 10a showed a singlet at $\delta$ 3.98 (6H) which could be attributed to the two symmetrically placed methoxy groups. The aryl protons appeared as three separate groups, one a doublet at $\delta$ 7.98 (2H) and another a doublet at $\delta$ 7.62 (2H) and the third as a singlet at $\delta$ 7.45 (2H). The following structure could account for the above n.m.r. pattern observed for the compound. Further evidence for the above assigned structure for (10a) came from the mass spectral data. In the mass spectrum of (10a) the peak due to molecular ion appeared at m/e 300. It was followed, by peaks due to the loss of NO, NO&O, NO, CO&O etc. The fragmentation pattern is depicted in the following scheme 5. The assigned structure was further confirmed by its conversion to the related diazepinone derivative (6a) by selective reduction with magnesium in refluxing ethanol.227
\[
\begin{align*}
\text{Scheme 5}
\end{align*}
\]
A reasonable mechanism for the formation of various products in the photoreactions of the derivatives of 2,2'-di-nitrodiphenylmethane should account for the following points:-

(a) the nature of the photoexcited state and the various reactions it could perform (b) the various products that could be formed and (c) the variation in the yield of different products in solvents of different characteristics.

A plausible mechanism has been suggested to account for the different products obtained during the irradiation of 2,2'-dinitrodiphenylmethane and some of its derivatives in neutral and acidic media by earlier investigators.\(^{227-230}\) It was assumed that the initial process was an intramolecular hydrogen abstraction from the ortho methylene group by the n-\(\pi^*\) excited triplet state of one of the nitro groups to produce a diradical (12). The diradical was thought to couple internally and produce a cyclic intermediate (13). In neutral media it was assumed that it underwent skeletal rearrangement and yielded 2-nitro-2'-nitrosodiphenylcarbinol (14). Similar hydrogen abstraction by the other excited nitro group and coupling of the diradical and elimination of a molecule of water resulting in the formation of 2,2'-dinitrosobenzophenone (15) which is the precursor of diazepin-11-one-5,6-dioxide (10), 5-oxide (7), acridone (8) and N-hydroxyacridone (9) (Scheme 6 & 7) is known.\(^{227}\)
SCHEME 6

12 13 14 15

(12) (13) (14) (15)

hv

hv

- H_2O
In acidic medium a proton of the cyclic intermediate (13) is known to eliminate a molecule of water and form the benzisoxazole derivative (5).
The formation of dinitrosobenzophenone was also shown to take place without the intervention of a cyclic intermediate (13) following the concept of deMayo and Reid (Scheme 8).

The present study on the photoreactions of methoxy and halogen substituted derivatives of 2,2'-dinitrodiphenylmethane in neutral and acidic media supports the mechanism in which a cyclic intermediate (13) is initially formed. The non-cyclic mechanism based on the concept of deMayo and Reid is untenable as it cannot account for the formation of benzisoxazoles in neutral as well as in acidic medium.

Earlier investigators in this field did not isolate any product with the methylene group intact, during the photolysis of 2,2'-dinitrodiphenylmethane and its derivatives in neutral medium. In their experiments, in all the products isolated and identified, the methylene group was oxidised to a keto function. In the present study the irradiation of 4,4'-dichloro and 4,4'-diiodo derivatives of 5,5'-dimethoxy-2,2'-dinitrodiphenylmethane (compounds 3b & 3d) in isopropanol
Scheme 3
yielded small quantities of dibenzo[σ,ξ][4,2] diazepine derivatives among other products.

Photoexcited nitro groups in 2,2'-dinitrodiphenylmethane derivatives could abstract hydrogen atom either intramolecularly from the σ-methylene group or intermolecularly from another molecule of the starting material or from the solvent. Formation of very small quantity of 2,2'-dinitrobenzophenones and larger quantities of dibenzodiazepin-N-oxides during the irradiation of methoxy and halogen derivatives of 2,2'-dinitrodiphenylmethane in isopropanol suggests that intermolecular reaction has taken place only to a small extent. On the other hand when irradiations were carried out in benzene solution 2,2'-dinitrobenzophenones were formed in about (30-45%) and the yield of dibenzodiazepinone-N-oxides substantially decreased. This suggests that in benzene solution intermolecular hydrogen abstraction occurs to a greater extent. The initial reaction in both benzene and alcoholic solution is predominantly intramolecular hydrogen abstraction and subsequent oxygen insertion, leading to the formation of the cyclic intermediate (13). This intermediate alone could account for the formation of the benzisoxazole derivatives by the elimination of a molecule of water. The formation of this cyclic intermediate (13) is confirmed, by the fact that benzisoxazoles were formed as major products when the irradiations were carried out in acidified alcoholic solutions. The dehydration reaction of the cyclic intermediate (13) leading to benzisoxazoles is facilitated by the protonation of this labile intermediate (13).
It is also possible that 2,2'-dinitrosobenzophenone formed during the photoreaction, abstracted a hydrogen from the unchanged dinitrodiphenylmethane and formed dibenzo[c,f][1,2]diazepin-11-one-5-oxide (7). In such a case the yield of dinitrobenzophenone and dibenzo[c,f][1,2]diazepin-11-one-5-oxide would be in the ratio 1:1. This supposition is found to be true and is supported by the fact that dinitrobenzophenone formed is nearly fifty per cent when the photolysis is carried out in benzene medium.

The yield of dibenzo[c,f][1,2]diazepin-11-one-5-oxides (7a-d) and 3,6-dihalo-2,7-dimethoxyacridone (8a-d) have been found to increase slightly when the irradiation was prolonged for longer periods. On the contrary prolonged irradiation resulted in decreased yield of the N,N-dioxide (10a) and benzisoxazole (5a-d) derivatives. The irradiations of dibenzo-diazepinone-N,N-dioxides as well as benzisoxazoles in protic solvents have been examined and it was found to yield the
N-oxides, acridones and N-hydroxyacridones (vide Section IV). On the other hand, the irradiation of the N-oxides did not result in any change. These observations suggest that 3-(2'-nitrophenyl)-2,1-benzisoxazole and 2,2'-dinitrosobenzophenone (isomeric with 5,6-dioxide) are two probable intermediates in the photolysis of the derivatives of 2,2'-dinitrodiphenylmethane. The N,N-dioxide is the intramolecularly coupled form of the 2,2'-dinitrosobenzophenone. 252

An attempt is made here to correlate the formation of various products isolated and characterised in the present investigation of the photoreactions of methoxy and halogen derivatives of 2,2'-dinitrodiphenylmethane based on mechanism akin to that suggested earlier. 227

(i) 5,5'-Dimethoxy-2,2'-dinitrobenzophenone (4a-d)

Irradiation of 5,5'-dimethoxy-2,2'-dinitrodiphenylmethanes (3a-d) in isopropanol yielded 5,5'-dimethoxy-2,2'-dinitrobenzophenones (4a-d) in small quantities only. The yield was found to increase when the medium of irradiation was changed to benzene.

The interaction of the dinitrosobenzophenone intermediate (15a) with another molecule of 2,2'-dinitrodiphenylmethane could result in hydrogen abstraction from the methylene group and formation of dinitrobenzophenone. The sequence of these reactions is depicted in Scheme 9.
SCHEME 9

H₃CO-NO₂₂₉-NO,OCH₃ + H₃CO-NO₂₂₉-NO₃-OCH₃

H₃CO-NO₂₂₉-NO-OH + H₃CO-NO₂₂₉-NO₃-OCH₃

H₃CO-NO₂₂₉-NO-OH + (15a)

H₃CO-NO₂₂₉-NO-OH + H₃CO-NO₂₂₉-NO₃-OCH₃

SCHEME 9
Alternatively the photoexcited nitro group in (3) by successive hydrogen abstraction of the two benzylic hydrogens from another molecule of dinitrodiphenylmethane (3) and oxygen insertion could lead to dinitrobenzophenone and dinitrosodiphenylmethane derivatives. The fact that the present experiments resulted in the formation of products with methylene group intact suggests the possibility of this pathway also occurring. The low yield of dinitrobenzophenone (4a-d) in protic solvents indicates that the possibility of an intermolecular photoredox reaction of this type occurring is very negligible. In aprotic solvents like benzene, the possibility of hydrogen abstraction from the solvent is very little. Hence the formation of larger quantities of dinitrobenzophenone can easily be accounted for, by the intermolecular photoredox reactions.

(ii) 5-Methoxy-3-(5'-methoxy-2'-nitrophenyl)-2,1-benzisoxazoles (5a-d)

The formation of benzisoxazoles (5a-d) among the
irradiation products in neutral media can be envisaged through the following pathway.

The triplet excited nitro group abstracts a hydrogen from the ortho methylene group and forms a diradical in the first stage of cyclisation of this diradical and subsequent elimination of a molecule of water for the aromatisation of the ring could occur and thus yield a benzisoxazole derivative. The fact that in the presence of acid the yield of benzisoxazole derivatives is considerably increased suggests that the protonation of the OH group in intermediate (13a) has greatly enhanced the removal of water.

(iii) 2,9-Dimethoxydibenzo [c,f][1,2] diazepin-11-one-5-oxide (7a-d)

The formation of dibenzo [c,f][1,2] diazepin-11-one-5-oxide (7a-d) can be accounted for by the photoreduction of one of the nitroso groups of the intermediate (15a) by hydrogen abstraction from the solvent or from the unconverted starting
material and its subsequent intramolecular coupling with the other nitroso group.

Alternatively both the nitroso groups of (15a) could undergo partial photoreduction to form the diradical species (16). Intramolecular coupling of this diradical followed by elimination of a molecular of water could account for the formation of N-oxide. However this possibility is remote as this necessitates the absorption of two photons by the same molecule or the collision of two excited molecules.
Photolysis of diazepin-11-one-5,6-dioxides has resulted in the formation of N-oxides among the other products (vide Section IV). This can be accounted for by assuming that the first step of the photoreaction is the dissociation of N,N-dioxide to the dinitrosobenzophenone intermediate and the second, the conversion of one of the nitroso group to a hydroxylamine function.

(iv) 2,9-Dimethoxydibenzo[c,f][1,2]diazepin-11-ones (6a-d)

The photochemical formation of an amino group from a nitroso function has been reported by Morrison. A similar reaction pathway could explain the photochemical conversion of the dinitrosobenzophenone intermediate (15a) to a nitroso-amino compound (17). The formation of the diazepinone derivatives could then be envisaged to take place by the cyclocondensation of the nitrosoamino compound (17) thus formed during the irradiation.

![Scheme 14](image-url)
The photodeoxygenation of the diazepin-11-one-5-oxides could also result in the formation of diazepinones. However, this alternative route is considered unlikely since diazepinones were not detected among the irradiation products of diazepinone-5-oxides (vide Section IV).

(v) 2,7-Dimethoxyacridones (8a-d)

The formation of the acridone derivatives (8a-d) could be accounted for by the photodissociation of one of the C-nitroso bonds of the intermediate (15a), a coupling of the radical to yield the acridone-N-oxide (18) and subsequent deoxygenation.

\[ \text{Scheme 15} \]
An alternative approach to account for the formation of acridone is from the radical (19) formed by the partial reduction of one of the nitroso groups in dinitrosobenzophenone intermediate (15a). Photodissociation of the C-NO bond in (19) followed by cyclization of the diradical (20) could give N-hydroxyacridone (9a). A homolytic cleavage of the N-OH bond and hydrogen abstraction from solvent could then yield acridone (8a). Formation of acridone (8a) during the photoreaction of N-hydroxyacridone (9a) (vide Section IV) is in support of the mechanism.
(vi) 2,7-Dimethoxy-N-hydroxyacridone (9a-d)

The formation of N-hydroxyacridone derivatives (9a-d) could be envisaged by a partial reduction of one of the nitroso functions in dinitrosobenzophenone intermediate (15a) to a NOH group, photodissociation of the other nitro group and coupling of the diradical as described earlier in the formation of acridone derivatives. The alternate mechanism described by hydrogen abstraction reaction of the nitroxide radical formed by the photodissociation of one of the NO bonds in (15a) and coupling is applicable in the formation of N-hydroxyacridones also.

(vii) 2,9-Dimethoxydibenzo [e,f][1,2]diazepin-11-one-5,6-dioxide (10a-d)

The formation of N,N-dioxides could be accounted by intramolecular dimerisation of photochemically unchanged 2,2'-dinitrosobenzophenones. The intermediate 2,2'-dinitrosobenzophenone (15a) was not isolated from the photolysates of 2,2'-dinitrodiphenylmethanes. It could be due to their rapid conversion to the corresponding 5,6-dioxides. The radical character of the nitroso group makes (15a) possible to undergo internal dimerisation and it is assumed to be a dark reaction.

![Chemical Diagram]
The fact that 5,6-dioxides when heated in solvents produce light green colour which vanishes on cooling is indicative of dissociation and internal dimerisation.

(viii) 2,9-Dimethoxydibenzo [\(\xi,\zeta\)](1,2) diazepines (11b&d)

The formation of dibenzo [\(\xi,\zeta\)](1,2) diazepine derivatives has been observed during the photolysis of certain 2,2'-dinitrodiphenylmethane derivatives (3b&d) in isopropanol although in low yields. The formation of a diazepine derivative indicated an intermolecular photoredox reaction. The pathway for the formation of diazepines cannot be expected to resemble the route for the formation of other photoproducts already discussed. In this case the methylene group is intact unlike in other products where the methylene group has been converted to a keto function.

The formation of diazepines could be rationalised through the following mechanism. Intermolecular hydrogen abstraction between 2,2'-dinitrodiphenylmethane and also solvent could result in the formation of 2-amino-2'-nitrosodiphenylmethane derivatives. Once 2-amino-2'-nitrosodiphenylmethane is formed, by intramolecular condensation it could result in dibenzo [\(\xi,\zeta\)](1,2) diazepine derivative as shown below.

The formation of only very little diazepine derivatives in the photolysis of 2,2'-dinitrodiphenylmethanes show that the major reaction occurred by intramolecular hydrogen abstraction. The preferential hydrogen abstraction from the \(\xi\)-methylene
group, by the photoexcited nitro group could be rationalised on the basis of the following facts.

1. The benzylic hydrogens in 2,2'-dinitrodiphenylmethanes are somewhat acidic due to the presence of two nitro groups in the ortho position of the two aryl rings and their proximity.

2. The radical formed by the intramolecular hydrogen abstraction could be stabilised by delocalisation into both the aryl rings.
PHOTOREACTIONS OF 5,5'-DIMETHOXY-2,2'-DINITRODIPHENYL METHANE AND ITS 4,4'-DIHALO DERIVATIVES IN ACIDIC MEDIA

INTRODUCTION

In a method suggested for the synthesis of 3-aryl-2,1-benzisoxazoles (anthranils) the acid induced condensation of o-nitrobenzaldehyde derivatives with arenes, phenols and arylamines was employed. Conc sulphuric acid and hydrogen halides were generally used for the promotion of the reaction. Zinc chloride has been used as a catalyst in certain cases. Benzisoxazole formation in the presence of sulphuric acid was rationalised on the basis of a benzhydrol intermediate (21) which subsequently got converted into 2-nitrosobenzophenone (22). Reductive cyclisation of the latter into benzisoxazole has been envisaged to occur by the interaction of unchanged benzhydrol, since 2-nitrobenzophenone (23) was isolated in around 50% yield as a side product. It has recently been
reported that $\alpha$-nitrobenzhydrol (21) itself is converted into 3-arylbenzisoxazole in conc. sulphuric acid.\textsuperscript{265}

Photolysis of 5,5'-dimethoxy-2,2'-dinitrodiphenylmethanes (3a-d) in protic solvents (page 50-57) afforded benzisoxazole derivatives (5a-d) in small quantities. It has already been shown that photochemical reaction of 2,2'-dinitrodiphenylmethane in acidic medium results in preferential cyclization of one of the nitro groups with the methylene group forming benzisoxazoles in good yield.\textsuperscript{227}

It was expected that the methoxy derivatives on photolysis in acidic medium also would behave in a similar way and offer an elegant photochemical route to the methoxy substituted derivatives of benzisoxazoles.

RESULTS OF PHOTOLYSIS IN ACIDIC MEDIA

Irradiation of 5,5'-dimethoxy-2,2'-dinitrodiphenylmethanes (3a-d) in weakly acidic alcoholic medium (1 gram of the compound in 600 ml ethanol containing 2 ml of conc. sulphuric acid) was carried out and the photolysate in each case was neutralised with sodium bicarbonate and alcohol removed under reduced pressure. Workup of the residue yielded 5-methoxy-3-(5'-methoxy-2'-nitrophenyl)-2,1-benzisoxazoles (5a-d) as the major product. The results of the irradiations are summarised in Table 7.
TABLE 7

<table>
<thead>
<tr>
<th>Starting material</th>
<th>Duration of irradiation hrs.</th>
<th>% conversion</th>
<th>% yield of products formed</th>
</tr>
</thead>
<tbody>
<tr>
<td>3a</td>
<td>75</td>
<td>80</td>
<td>7 52 5 19 6 8</td>
</tr>
<tr>
<td>3b</td>
<td>100</td>
<td>75</td>
<td>9 46 4 17 7 5</td>
</tr>
<tr>
<td>3c</td>
<td>100</td>
<td>68</td>
<td>12 42 6 16 9 5 6</td>
</tr>
<tr>
<td>3d</td>
<td>100</td>
<td>65</td>
<td>13 40 3 14 6 7</td>
</tr>
</tbody>
</table>

MECHANISM

It has been found that the photolysis of 5,5'-dimethoxy-2,2'-dinitrodiphenylmethane derivatives in a weakly acidic alcoholic medium yields 5-methoxy-3(5'-methoxy-2'-nitrophenyl-2,1-benzisoxazole (5a-d) as the major product. Dibenzo [c,ε][1,2]-diazepin-11-one-5-oxides (7a-d), acridones (8a-d), 2,2'-dinitrobenzophenones (4a-d), N-hydroxyacridones (9a-d) were also obtained in small quantities. It has also been observed that the yield of benzisoxazoles are not dependant on the concentration of the acid. Further when the duration of the irradiation was increased the yield of benzisoxazoles decreased considerably and the yield of dibenzo [c,ε][1,2]diazepin-11-one-5-oxides (7a-d) and acridones (9a-d) increased.

The above results also throw further light into the mechanism of the photoreaction of these compounds. The larger yield of benzisoxazole (5a-d) in the presence of sulphuric acid
gives additional evidence for the intramolecular oxygen insertion process. The dual behaviour of 2,2'-dinitrodiphenylmethanes under these two conditions could be explained as follows; during the photolysis of 2,2'-dinitrodiphenylmethanes in ethanolic sulphuric acid or isopropanol, due to the proximity of the methylene group, one of the nitro groups which is photoexcited abstracts a methylenic hydrogen and forms a diradical which cyclizes spontaneously to the intermediate (13a). In ethanolic sulphuric acid (13a) if formed could undergo easy dehydration and yield 3(2'-nitrophenyl)-2,1-benzisoxazoles (path B). In the absence of the acid it could also rearrange to the nitroso-carbinol. In acid medium aromatisation by elimination of a molecule of water from the intermediate (13a) is made more facile possibly by the protonation of the OH group.

Irradiation of the derivatives of 3-(2'-nitrophenyl)-2,1-benzisoxazole has been shown to result in further reaction and result in dibenzo[3,6]1,2-diazepin-11-one-5-oxides, 5,6-dioxides, acridones and N-hydroxyacridones. Hence it could be envisaged that a part or the whole of dinitrosobenzophenone (15a) is formed through this route. Further this subsequent photo-reaction of benzisoxazoles may be the reason for the observed decrease in their yield and the increased yield of the dibenzo-diazepinone-N-oxides and the acridones when the photolysis of 2,2'-dinitrodiphenylmethane derivative in ethanolic sulphuric acid is prolonged.
EXPERIMENTAL

GENERAL

Melting points were determined using an oil immersion bath and are uncorrected.

U.v. absorption spectra were recorded on a Pye Unicam SP-8-100 Ultraviolet spectrophotometer.

Infrared spectra were run on a Perkin Elmer 397 instrument and the data are given in cm\(^{-1}\).

Nuclear magnetic resonance spectra were measured on a Varian 60 MHz instrument. Chemical shifts reported are relative to tetramethylsilane (\(\delta 0.00\)), used as internal standard.

Mass spectra were recorded on a Varian MAT.CH-7 mass spectrometer operating at 70 ev.

Petroleum ether used in chromatography was the fraction boiling between 60-80°C. Thin layer chromatography was carried out on silica gel Merk GE 254.

Unless otherwise mentioned all reagents used were commercially available samples.

Irradiations were carried out mostly in sunlight. The results of photolyses were found to be identical with the results of irradiation when carried out with a Philips HPK 125W high pressure mercury lamp in a water cooled apparatus, but with less polymeric matter. Hence irradiation in sunlight was preferred, though it took longer time for the completion of the reaction.
Pyrex glass vessels were used for irradiations of the solutions in sunlight.

Removal of the solvent from the photolysate was always carried out under reduced pressure. Similarly the distillations to remove the solvent in chromatographic workup was invariably done at reduced pressure.

PREPARATION OF THE STARTING MATERIALS

4,4'-Diamino-5,5'-dimethoxy-2,2'-dinitrodiphenylmethane (1)

Condensation of o-anisidine with formaldehyde in acidic medium adopting the procedure described by Scanlan250 for the preparation of 4,4'-diaminodiphenylmethane from aniline yielded 4,4'-diamino-3,3'-dimethoxydiphenylmethane (1). To a cold (-5 to 5°C) solution of (1, 25.8g) in concentrated sulphuric acid (36N, 75ml) potassium nitrate (22g) dissolved in twenty five ml concentrated sulphuric acid was added dropwise over a period of 30 minutes with efficient stirring and cooling. Stirring was continued for another three hours keeping the temperature below 5°C. The reaction mixture was then poured on crushed ice (500g) and neutralised with aqueous ammonia. The yellow solid which got precipitated was filtered, washed with water, dried and crystallised from ethanol. Orange yellow plates of 4,4'-diamino-5,5'-dimethoxy-2,2'-dinitrodiphenylmethane was obtained m.p. 166°C (yield 15g; 43%).

(Analysis Found: C,51.5; H,4.6; N,16.1; C_{15}H_{16}N_{4}O_{6} requires: C,51.7; H,4.6; N,16.1). \nu_{\text{max}}(\text{KBr}) 3500, 3400 (\text{NH}_2), 1560,
5,5'-Dimethoxy-2,2'-dinitrodiphenylmethane (3a)

To a solution of 4,4'-diamino-5,5'-dimethoxy-2,2'-dinitrodiphenylmethane (12g) in hypophosphorous acid (50% 180 ml) two grams of freshly prepared cuprous oxide266 was added and the mixture cooled to 0°C. A solution of sodium nitrite (14g) dissolved in 20 ml of water was added to it over a period of two hours with stirring and cooling not allowing the temperature of the reaction mixture to rise above 0°C. Stirring and cooling was continued till the evolution of nitrogen ceased. The mixture was then repeatedly extracted with benzene. The benzene extracts were combined, concentrated and chromatographed on a column of neutral alumina using petroleum ether/benzene (10:1 v/v) as the eluant. Crystallisation of the compound, obtained from the eluate afforded pale yellow flakes of 5,5'-dimethoxy-2,2'-dinitrodiphenylmethane, m.p. 148°C. (Yield 4g, 37%) (Analysis found: C, 56.4; H, 4.3; N, 8.6; C15H14N2O6 requires: C, 56.6; H, 4.4; N, 8.8). λ max(EtOH) 290 nm, μ max(KBr) 1560, 1340 (NO2). 'H nmr (CDCl3) δ 3.95(6H), 4.50(s,2H,CH2), 6.92(s,2H); 7.98 (s,2H).

4,4'-Dichloro-5,5'-dimethoxy-2,2'-dinitrodiphenylmethane (3b)

To an ice cold solution of the diamino compound (2.7g) in 1:1 hydrochloric acid (15 ml) a solution of sodium nitrite (4g) in water (10 ml) was added dropwise (over a period of 1 hr)
with stirring and cooling. The diazotised solution was then poured into a solution of cuprous chloride (5g) in conc. hydrochloric acid (15ml). The resulting mixture was warmed on a boiling waterbath for about five minutes diluted with water and repeatedly extracted with 100 ml lots of benzene. The extracts were combined, washed with 10% aqueous sodium hydroxide solution to remove any phenolic matter, concentrated and chromatographed on a column of alumina. Elution with petroleum ether/benzene (10:1 v/v) yielded a compound which crystallised from CHCl₃/pet. ether (1:5 v/v) as pale yellow flakes identified as 4,4'-di-chloro-5,5'-dimethoxy-2,2'-dinitrodiphenylmethane m.p. 184°C (Analysis found: C,46.5; H,3.1; N,7.2; C₁₅H₁₂N₂O₆Cl₂ requires C,46.6; H,3.1; N,7.3). λ max(EtOH) 278 nm, ν max(KBr) 1560, 1340 (NO₂). ¹H n.m.r.(CDCl₃) δ 4.10 (s,6H,2 OCH₃), 4.65 (s,2H,CH₂), 6.02 (s,2H), 8.04 (s,2H).

4,4'-Dibromo-5,5'-dimethoxy-2,2'-dinitrodiphenylmethane (3c)

The dibromo compound (3c) was prepared by Sandmeyer reaction of the related diazonium bromide of (2) in presence of cuprous bromide. The preparation was carried out under the same conditions, described above for the chloro derivative. Crystallisation of 4,4'-dibromo-5,5'-dimethoxy-2,2'-dinitrodiphenylmethane from chloroform/pet ether (1:4 v/v) afforded pale yellow flakes, m.p 202°C. (Analysis Found: C,37.6; H,2.4; N,5.9; C₁₅H₁₂N₂O₆Br₂ requires: C,37.8; H,2.5; N,5.9). λ max(EtOH) 276 nm, ν max(KBr) 1560, 1340 (NO₂). ¹H n.m.r.(CDCl₃) δ 4.12 (s,6H,2 OCH₃), 4.68 (s,2H,CH₂), 7.14 (s,2H), 8.18 (s,2H).
4,4'-Diiodo-5,5'-dimethoxy-2,2'-dinitrodiphenylmethane (3d)

A solution of 4,4'-diamino-5,5'-dimethoxy-2,2'-dinitrodiphenylmethane (2, 7g) containing concentrated sulphuric acid (20 ml) and water (30 ml) was cooled to 0°C. To this solution an ice cold solution of sodium nitrite (4g) in water (5 ml) was added dropwise over a period of one hour with stirring and cooling. The diazonium sulphate solution obtained was then added to a solution of potassium iodide (7g) in water (15 ml) and warmed on a boiling waterbath. The resulting mixture was then extracted repeatedly with 100 ml lots of benzene. The extracts were combined and washed with 10% aqueous sodium hydroxide solution to remove any phenolic matter. Evaporation of the benzene extracts and chromatography of the residue on a column of neutral alumina using petroleum ether/benzene (5:1 v/v) as eluant yielded 4,4'-diiodo-5,5'-dimethoxy-2,2'-dinitrodiphenylmethane as a pale yellow compound. It crystallised from chloroform/pet· ether (1:2 v/v) as pale yellow needles. m.p. 188°C. (Analysis found: C,31.8; H,2.1; N,5.0; C_{15}H_{12}N_{2}O_{6}I_{2} requires: C,31.6; H,2.1; N,4.9). \( \lambda_{\text{max}} \) (EtOH) 278 nm \( \nu_{\text{max}} \) (KBr) 1560, 1340 (NO₂). 'H n.m.r. (CDCl₃) 4.15 (s,6H, 2 OCH₃), 4.62 (s,2H,CH₂), 7.13 (s,2H), 8.32 (s,2H).

PHOTOLYSIS OF 5,5'-DIMETHOXY-2,2'-DINITRODIPHENYLMETHANES

IN NEUTRAL MEDIA

(i) Irradiation of 5,5'-dimethoxy-2,2'-dinitrodiphenylmethane in isopropanol

A solution of 5,5'-dimethoxy-2,2'-dinitrodiphenylmethane
(3a, 1g) in isopropanol (500 ml) was irradiated in sunlight for 75 hrs by which time most of the starting material disappeared (98%). The experiment was repeated ten times and the solutions were combined. The solvent was then removed by distillation under reduced pressure, the residue dissolved in benzene (600ml) and washed with aqueous sodium hydroxide (2%) solution. Neutralisation of the alkali washings afforded an yellow precipitate which was chromatographed on a column of silica gel. Elution with petroleum ether and benzene (1:1) yielded a compound which crystallised from CHCl₃/pet ether (1:1 v/v) as yellow needles m.p. > 300°C. It was identified as 2,7-dimethoxy-N-hydroxy-acridone (9a, 800 mg, 9%). (Analysis Found: C, 66.5; H, 4.7; N, 5.4; C₁₅H₁₃NO₄ requires: C, 66.4; H, 4.8; N, 5.2). λₑₒₓ(EtOH) 245, 348 nm. Jₑₒₓ(KBr) 3500-3200 (OH), 1600 (C=O). Mass spectrum: m/e 271(M, 100), 254(92), 226(43), 195(64), 164(82).

The solvent from the alkali washed benzene solution was removed by distillation under reduced pressure and the residue chromatographed on a column of neutral alumina. Elution with petroleum ether/benzene (10:1 v/v) yielded unchanged starting material (3a, 200 mg, 2%) as the first fraction. It was followed by a compound which crystallised from benzene/pet ether (1:5 v/v) as colourless needles. It was identified as 5,5'-dimethoxy-2,2'-dinitrobenzophenone (4a, 1g, 10%) m.p. 179°C. This compound was followed by an yellow fraction which crystallised from C₆H₄/pet ether (1:2 v/v) as golden yellow needles identified as 5-methoxy-3-(5'-methoxy-2'-nitrophenyl)-2,1-benzisoxazole (5a, 380 mg, 4%) m.p. 161°C. Further elution of
the column with petroleum ether/benzene (1:1 v/v) resulted in the separation of an yellow band. Removal of the solvent from the eluate and crystallisation of the residue from benzene/pet. ether (1:1 v/v) afforded yellow needles of 2,9-dimethoxy-dibenzo[ɛ,ɛ][1,2]diazepin-11-one-5-oxide (7a, 4.64g, 52%) m.p. 182°C. (Analysis found: C, 63.3; H, 4.3; N, 10.0; \( \text{C}_{15}\text{H}_{12}\text{N}_{2}\text{O}_{4} \) requires C, 63.4; H, 4.2; N, 9.9). \( \lambda_{\text{max}}(\text{EtOH}) 340, 255 \text{ nm.} \) \( \mu_{\text{max}}(\text{KBr}) 1670 (\text{C=O}), 1440, 1310 (\text{N-O}). \) \( ^{1}H \text{n.m.r. (CDCl}_{3} \} 3.8 \text{ (s, 3H, CH}_{3} \}; 4.0 \text{ (s, 3H, CH}_{3} \}; 7.4-7.65 \text{ (m, 5H), 8.15-8.23 (d, 1H). Mass spectrum: m/e 284(M,100), 254(38), 226(28), 195(64), 164(72). \)

Continued elution of the column with benzene/chloroform (1:1 v/v) yielded an yellow compound which crystallised from isopropanol as yellow microcrystalline prisms. It was identified as 2,7-dimethoxyacridone (8a, 960mg, 12%) m.p. > 300°C. (Analysis found: C, 70.4; H, 5.0; N, 5.5; \( \text{C}_{15}\text{H}_{13}\text{NO}_{3} \) requires C, 70.6; H, 5.1; N, 5.5). \( \mu_{\text{max}}(\text{KBr}) 3400 (\text{NH}), 1600 (\text{C=O}). \) The n.m.r. spectrum of 8a could not be taken due to its insolubility in most of the usual solvents. Mass spectrum: m/e 255(M,100), 227(79), 196(62), 165(78).

Elution of the column when continued with benzene/chloroform (1:2 v/v) afforded an yellow material which crystallised from isopropanol as yellow needles. It was identified as 2,9-dimethoxydibenzo[ɛ,ɛ][1,2]diazepin-11-one-5,6-dioxide (10a, 850mg, 9%) m.p. 168° (dec). (Analysis found: C, 60; H, 3.9; N, 9.5; \( \text{C}_{15}\text{H}_{12}\text{N}_{2}\text{O}_{5} \) requires C, 60, H, 4.0; N, 9.5).
$\lambda_{\text{max}}$(EtOH) 257 nm. $\nu_{\text{max}}$(KBr) 1680 (C=O) 1380, 1310 (N-O).

$^1$H n.m.r. (CDCl$_3$) $\delta$ 3.98 (s, 6H), 7.45 (s, 2H), 7.62 (d, 2H), 7.98 (d, 2H). Mass spectrum: m/e 300 (M, 25), 270(100), 254(78), 242(12), 226(85), 195(74), 164(86).

Final elution of the column with chloroform yielded only some darkish resinous material (900 mg) which could not be characterised.

(ii) Irradiation of 4,4'-dichloro-5,5'-dimethoxy-2,2'-dinitrodiphenylmethane in isopropanol

A solution of 4,4'-dichloro-5,5'-dimethoxy-2,2'-dinitrodiphenylmethane (3b, 1g) in isopropanol (500 ml) was irradiated for 100 hrs in sunlight. The experiment was repeated ten times and the irradiated solutions were combined. The solvent was then removed by distillation under reduced pressure and the residue dissolved in benzene (300 ml). The benzene solution when washed with aqueous sodium hydroxide solution (2%) and the extract acidified yielded an yellow compound which on crystallisation from acetic acid afforded yellow needles of 3,6-dichloro-2,7-dimethoxy-N-hydroxyacridone (9b, 1.2g, 14%) m.p. $\geq$ 300°C. (Analysis found: C, 52.9; H, 3.1; N, 4.2; $C_{15}H_{11}NO_4Cl_2$ requires: C, 53.1; H, 3.2; N, 4.1). $\nu_{\text{max}}$(KBr) 3500-3200 (OH), 1600 (C=O). Mass spectrum: m/e 339(M,100), 322(90), 294(47), 263(65), 232(85). It formed a deep red sodio derivative when treated with aqueous sodium hydroxide (40%) a reaction characteristic of N-hydroxyacridones.
The solvent from the alkali washed benzene solution was then removed by distillation under reduced pressure and the residue obtained chromatographed on a column of alumina. Elution with petroleum ether/benzene (5:1 v/v) yielded unchanged starting material (300 mg, 3%) as the first fraction. It was followed by a colourless compound which when crystallised from C₆H₆/pet ether (1:2 v/v) yielded colourless needles of 4,4'-dichloro-5,5'-dimethoxy-2,2'-dinitrobenzophenone (4b, 770 mg, 7.5%) m.p. and mixed m.p. with authentic sample (vide p 111) 204°C. Further elution with petroleum ether/benzene (2:1 v/v) yielded an orange red material which when crystallised from benzene/pet ether (1:1 v/v) afforded orange red needles of 3,8-dichloro-2,9-dimethoxydibenzo [c, f] (1,2) diazepin-11-one (6b, 430 mg, 5%) m.p. and mixed m.p. with the sample obtained by the reduction of the related N-oxide with Mg in ethanol (vide p.111) 256°C. (Found: C, 53.5; H, 3.0; N, 8.2; C₁₅H₁₀N₂O₃Cl₂ requires: C, 53.6; H, 3.0; N, 8.3). λ max (KBr) 1680 (C=O). Continued elution with petroleum ether/benzene, (1:1 v/v) yielded 3,8-dichloro-2,9-dimethoxydibenzo [c, f] (1,2) diazepine (11b). It crystallised from C₆H₆/pet ether (2:1 v/v) as brick red flakes (340 mg, 4%) m.p. and mixed m.p. with authentic sample prepared (vide p.114a) 236°C. The elution of the column when continued with petroleum ether/benzene (1:2 v/v) resulted in the separation of an yellow band. Removal of the solvent under reduced pressure and crystallisation of the residue from benzene/pet ether (1:1 v/v) afforded yellow needles of 3,8-dichloro-2,9-dimethoxydibenzo [c, f] (1,2)-diazepin-11-one-5-oxide (7b, 4.4 g, 48%) m.p. 245°C. (Found:
Further elution of the column with benzene yielded an yellow compound which when crystallised from chloroform afforded microcrystalline yellow prisms of 3,6-dichloro-2,7-dimethoxy-acridone (8b, 1.1g,13%). m.p. > 300°C. (Analysis found: C,55.8; H, 3.3; N, 4.5; C_{15}H_{11}NO_{3}Cl_{2} requires: C,55.7; H, 3.4; N,4.3). Mass spectrum: m/e 323(M,100), 295(81), 264(58), 233(74).

Final elution of the column with chloroform yielded only some resinous darkish matter which could not be identified.

The solid which precipitated during the photolysis was chromatographed on a column of alumina. Diazepinone-N-oxide (7b) m.p. 245°C acridone (8b) m.p. > 300°C and an yellow solid which was found to decompose when crystallisation was attempted from boiling solvents, were obtained. The ir spectra of the unstable compound showed that it could be 3,8-dichloro-2,9-dimethoxydibenzo [c,f][1,2]diazepin-11-one-5,6-dioxide (10b). $\nu_{\text{max}}$(KBr) 1670 (C=O), 1460, 1310 (N-O).

(iii) **Irradiation of 4,4'-dibromo-5,5'-dimethoxy-2,2'-dinitrodiphenylmethane in isopropanol**

A solution of 4,4'-dibromo-5,5'-dimethoxy-2,2'-dinitrodiphenylmethane (1g) in isopropanol (500 ml) was exposed
to sunlight for 100 hrs, when the conversion of the starting material appeared complete. The experiment was repeated 10 times and the photolysates were combined. The solid which separated during photolysis was removed by filtration and the solvent from the filtrate distilled off at reduced pressure. The residue was dissolved in benzene (200 ml) and the benzene solution was repeatedly washed with sodium hydroxide solution (2%). Acidification of the alkali washings yielded an yellow solid which was chromatographed on a silica gel column. Elution with pet. ether/C₆H₆ (1:1 v/v) afforded a solid which on crystallisation from CHCl₃/pet ether (1:1 v/v) yielded shining yellow needles of 3,6-dibromo-2,7-dimethoxy-N-hydroxyacridone (9c, 630 mg, 7%) m.p. > 300°C. (Analysis found: C,42.2; H,2.5; N,3.1; C₁₅H₁₁NₒBr₂ requires: C,42.0; H,2.6; N,3.3). λ max(EtOH) 230, 280, 400 nm. μ max(KBr) 3500-3200 (OH), 1600 (C=O), 1310 (N-O). Mass spectrum* m/e: 429(M,100), 412(94), 384(45), 353(60), 322(83). The benzene solution was then concentrated and chromatographed on a column of alumina. Elution with petroleum ether/benzene mixture (5:1 v/v) afforded unchanged starting material (500 mg, 5%). It was followed by a compound which crystallised from C₆H₆/pet ether (1:4 v/v) as colourless needles and was identified as 4,4'-dibromo-5,5'-dimethoxy-2,2'-dinitrobenzophenone (4c, 930 mg, 9%), m.p. and mixed m.p. with authentic sample (vide p.111) 222°C. Further elution with petroleum ether/benzene (2:1 v/v) yielded an yellow compound which crystallised from C₆H₆/pet ether (1:2 v/v) as yellow needles. It

*The m/e values given are the mean value of the isotopic peaks.
was identified as 6-bromo-5-methoxy-3(4'-bromo-5'-methoxy-2' nitrophenyl)-2,1-benzisoxazole (5c, 380 mg, 4%) m.p. and mixed m.p. with its authentic sample 195°C (vide p.112). When the elution of the column was continued with petroleum ether/ benzene (1:2 v/v) an yellow band got separated. Removal of the solvent and crystallisation of the residue from benzene/pet ether (1:1 v/v) yielded yellow needles of 3,8-dibromo-2,9-dimethoxydibenzo [c,e][1,2] diazepin-11-one-5-oxide (7c, 4.6g, 49%) m.p. 160°C (Analysis found: C, 40.7; H, 2.3; N, 6.3). \( \lambda_{\text{max}}(\text{EtOH}) \) 230, 250 and 340 nm. \( \nu_{\text{max}}(\text{KBr}) \) 1670 (C=O), 1440, 1300 (N–O). \(^1\)H n.m.r. (CDCl\(_3\)) \( \delta \) 3.95 (s, 3H, OCH\(_3\)); 4.03 (s, 3H, OCH\(_3\)); 7.30 (s, 1H), 7.39 (s, 1H); 7.87 (s, 1H), 8.57 (s, 1H). Mass spectrum: m/e 442(M, 100), 412(32), 384(26), 353(62), 322(73). Continued elution of the column with benzene yielded a compound which when crystallised from isopropanol afforded yellow microcrystalline prisms of 3,6-dibromo-2,7- dimethoxyacridone (8c, 1.2g, 14%), m.p. > 300°C. (Analysis found: C, 43.5; H, 2.8; N, 3.5). \( \lambda_{\text{max}}(\text{EtOH}) \) 340 and 230 nm, \( \nu_{\text{max}}(\text{KBr}) \) 3400 (NH), 1620 (C=O). Mass spectrum: m/e 413(M, 100), 385(77), 354(65), 323(72).

Final elution of the column with chloroform yielded only dark resinous material, which could not be identified. The solid which precipitated during the photolysis was chromatographed separately on a column of alumina. Diazepin-N-oxide (7c) m.p. 260°C, acridone (8c) m.p. > 300°C and
diazepinone-5,6-dioxide were obtained from the column. Diaze-
pinone-5,6-dioxide could not be purified since it was found to
decompose on dissolution in warm solvents.

(iv) **Irradiation of 4,4'-diiodo-5,5'-dimethoxy-2,2'-dinitro-
diphenylmethane in isopropanol.**

A solution of 4,4'-diiodo-5,5'-dimethoxy-2,2'-dinitro-
diphenylmethane (1g) in isopropanol (500 ml) was irradiated
for 150 hrs in sunlight when the starting material almost dis-
appeared. The experiment was repeated ten times and the photo-
lysates were combined. The solvent was then removed by disti-
llation under reduced pressure and the residue dissolved in
benzene (600 ml) and washed repeatedly with an aqueous solution
of sodium hydroxide (2%). The combined alkali washings when
neutralised with acid afforded an yellow precipitate. The
precipitate was chromatographed on a column of silica gel.
The product obtained on elution when crystallised from CHCl₃/
pet ether (1:1 v/v) afforded 3,6-diiodo-2,7-dimethoxy-N-
hydroxyacridone (9d, 730mg, 8%) as yellow needles m.p. > 300°C.
(Analysis found: C, 34.2; H, 2.0; N, 2.8; \( \text{C}_{15}\text{H}_{11}\text{NO}_{4}\text{I}_2 \) requires
C, 34.4; H, 2.1; N, 2.7). \( \nu_{\text{max}} \) (KBr) 3500-3200 (OH) 1600 (C=O).
Mass spectrum: m/e 523(M,100), 506(88), 478(41), 447(62),
416(81). It formed a deep red sodio derivative when treated
with aqueous sodium hydroxide solution, (40%), a reaction
characteristic of N-hydroxyacridones.

The alkali washed benzene solution was then distilled
under reduced pressure to remove the solvent and the residue chromatographed on a column of neutral alumina. Elution with petroleum ether/benzene (2:1 v/v) afforded unreacted starting material as the first fraction (1.5g). It was followed by compound which crystallised from benzene/pet.ether (1:2 v/v) as colourless needles. It was identified as 4,4'-diiodo-5,5'-dimethoxy-2,2'-dinitrobenzophenone (4d,1.23g,12%), m.p. and mixed m.p. with authentic sample (vide p.111) 238°C. Further elution with petroleum ether/benzene (1:1 v/v) yielded compound which crystallised from benzene/petroleum ether as yellow needles. It was identified as 6-iodo-5-methoxy-3(4'-iodo-5'-methoxy-2'-nitrophenyl)-2,1-benzisoxazole (5d,290mg,3%) m.p. and mixed m.p. with authentic sample (vide p.113) 270°C. It was followed by a compound which crystallised from benzene/pet. ether (1:1 v/v) as brick red shining flakes, and was identified as 3,8-diiodo-2,9-dimethoxydibenzo [c, f][1,2] diazepine (11d,440mg,5%) m.p. and mixed m.p. with authentic sample (vide p.114a) 147°C. When the elution was continued with petroleum ether/benzene (1:2 v/v) an yellow band separated. Removal of the solvent and crystallisation of the residue from chloroform/pet.ether (1:1 v/v) yielded yellow needles of 3,8-diiodo-2,9-dimethoxydibenzo [c, f][1,2] diazepin-11-one-5-oxide (7d,3.86g,41%) m.p. 258°C. (Analysis found: C,33.5; H,2.0; N,5.3; C_{15}H_{10}N_{2}O_{4}I_{2} requires C,33.6; H,1.9; N,5.2). λ_{max}(EtOH) 240, 250 nm. V_{max}(KBr) 1670 (C=O), 1450, 1310 (N- O). ^1H n.m.r. (CDCl₃) δ 3.98 (s,3H,OCH₃); 4.03 (s,3H,OCH₃); 7.32 (s,1H); 7.45 (s,1H); 7.85 (s,1H), 8.56 (s,1H).
Mass spectrum: m/e 536(M,100), 506(28), 478(25), 447(59), 416(68). Further elution of the column with benzene/chloroform (1:1 v/v) yielded a compound, which when crystallised from isopropanol afforded yellow microcrystalline prisms of 3,6-diodo-2,7-dimethoxyacridone (8d, 440mg, 5%) m.p. $>300^\circ$C. (Analysis found: C,35.6; H,2.2; N,2.8; $\text{C}_{15}\text{H}_{11}\text{NO}_3\text{I}_2$ requires C,35.5; H,2.2; N,2.8). $\lambda_{\text{max}}$(EtOH) 340, 230 nm. Mass spectrum: m/e 507(M,100), 479(78), 448(60), 417(75).

IRRADIATIONS IN BENZENE

Irradiation of a solution of (3a–d, 1g) in dry benzene (160 ml) for 75 hrs effected almost complete conversion of the starting material. The photolysate was then washed repeatedly with aqueous sodium hydroxide solution (2%). Neutralisation of the alkali washings afforded N-hydroxyacridones (9a–d). The solvent was then removed from the alkali washed benzene solution and the residue chromatographed on a column of alumina. The products listed in table 6, were obtained in the photolyses. Each compound was identified by comparison of their ir spectra and melting points with samples obtained in the photolyses of (3a–d) in isopropanol.

IRRADIATIONS IN ACIDIFIED ETHANOL

A solution of 5,5'-dimethoxy-2,2'-dinitrodiphenylmethane (3a, 1g) in ethanol (600 ml) containing concentrated sulphuric acid (2 ml) was irradiated in sunlight for 75 hrs when almost all starting material disappeared. The experiment was repeated.
6 times and the photolysates combined. The resulting solution was then neutralised with NaHCO₃ and the precipitated sodium sulphate filtered off. The solvent from the filtrate was then removed by distillation under reduced pressure. The residue obtained, was dissolved in benzene (200 ml) and washed with an aqueous solution of alkali (2%). Neutralisation of the alkali washings yielded 2,7-dimethoxy-N-hydroxyacridone (9a, 410mg, 8%) m.p. >300°C. The solvent from the alkali washed benzene solution was removed under reduced pressure and the residue chromatographed on a column of alumina. Elution with petroleum ether/benzene (10:1 v/v) yielded unchanged starting material (3a, 2g) as the first fraction. It was followed by dinitrobenzophenone (4a, 440mg, 7%) mp.179°C. Further elution with petroleum ether/benzene (5:1 v/v) afforded 5-methoxy-3-(5'-methoxy-2'-nitrophenyl)-2,1-benzisoxazole (5a, 2.94g, 52%) m.p. 161°C. Continued elution with petroleum ether/benzene (1:1 v/v) afforded 2,9-dimethoxydibenz[c,f][1,2]diazepin-11-one-5-oxide (7a, 1.02g, 19%) m.p. 182°C. Continued elution with benzene yielded 2,7-dimethoxyacridone (8a, 290mg, 6%). Final elution with chloroform yielded only some dark resinous product which could not be identified.

Irradiation of 4,4'-dihalo-5,5'-dimethoxy-2,2'-dinitrodiphenylmethanes (3b-d) in acidified ethanol and workup were carried out as described above. The products obtained and isolated are listed in table 7.
Reduction of dibenzo [c, f][1, 2] diazepin-11-one-5-oxides (7a-d) to dibenzo [c, f][1, 2] diazepin-11-one (6a-d)

Dibenzo [c, f][1, 2] diazepin-11-one-5-oxides (7a-d, 500mg) were refluxed with ethanol (50 ml) containing finely divided magnesium ribbon (1g) for 2½ hrs and filtered to remove the suspended solids. The solvent was then evaporated and the residue chromatographed on a column of neutral alumina. Elution with petroleum ether/benzene (2:1 v/v) afforded a compound which crystallised from C₆H₆/pet ether (1:1 v/v) as orange red needles. It was identified as 2,9-dimethoxydibenzo [c, f][1, 2] diazepin-11-one (6a-d). This reduction afforded almost quantitative yield of the product.

Preparation of 5,5'-dimethoxy-2,2'-dinitrobenzophenones (4a-d)

A solution of 5, 5'-dimethoxy-2, 2'-dinitrodiphenylmethane (3a, 2g) in glacial acetic acid (40 ml) was refluxed for 2 hrs with 6 g of chromic anhydride. After cooling, the reaction mixture was poured into crushed ice. A white compound which got precipitated was collected and crystallised from benzene/pet ether (1:2 v/v). Colourless needles of 5,5'-dimethoxy-2,2'-dinitrobenzophenone (8a, 15mg, 1%) were obtained. Oxidation of the dihaloderivatives of (3a) were also carried out in a similar manner with chromic anhydride. The related benzo-phenone (4b-d) were obtained in about 1-2% yield only. The m.p., analysis, spectral data etc. are detailed below.
5,5'-Dimethoxy-2,2'-dinitrobenzophenone (4a)

Colourless needles m.p. 179°C. (Analysis found: C, 54.4; H, 3.8; N, 8.2; C_{15}H_{12}N_2O_7 requires C, 54.2; H, 3.6; N, 8.4). \( \lambda_{\text{max}} \) (EtOH) 210 nm \( \nu_{\text{max}} \) (KBr) 1700 (C=O), 1540, 1340 (NO_2). 'H n.m.r. (CDCl_3) \( \delta \) 3.9 (s, 6H, 2 OCH_3), 6.98 (s, 2H), 7.04 (s, 2H), 7.52 (d, 2H).

4,4'-Dichloro-5,5'-dimethoxy-2,2'-dinitrobenzophenone (4b)

Colourless needles m.p. 201°C. (Found: C, 44.8; H, 2.6; N, 7.4; C_{15}H_{10}N_2O_7Cl_2 requires C, 45.0; H, 2.5; N, 7.7). \( \lambda_{\text{max}} \) (EtOH) 220 nm. \( \nu_{\text{max}} \) (KBr) 1700 (C=O), 1570, 1360 (NO_2). 'H n.m.r. (CDCl_3) \( \delta \) 4.04 (s, 6H, 2 OCH_3), 7.22 (s, 2H), 8.22 (s, 2H).

4,4'-Dibromo-5,5'-dimethoxy-2,2'-dinitrobenzophenone (4c)

Colourless needles, m.p. 222°C. (Found: C, 36.5; H, 1.8; N, 5.8; C_{15}H_{10}N_2O_7Br_2 requires C, 36.7; H, 2.0; N, 5.7). \( \lambda_{\text{max}} \) (EtOH) 220 nm. \( \nu_{\text{max}} \) (KBr) 1700 (C=O), 1560, 1370 (NO_2). 'H n.m.r. (CDCl_3) \( \delta \) 4.02 (s, 6H, 2 OCH_3), 7.20 (s, 2H), 8.18 (s, 2H).

4,4'-Diiodo-5,5'-dimethoxy-2,2'-dinitrobenzophenone (4d)

Colourless needles, m.p. 238°C. (Found: C, 30.6; H, 1.9; N, 5.0; C_{15}H_{10}N_2O_7I_2 requires: C, 30.8; H, 1.7; N, 4.8). \( \lambda_{\text{max}} \) (EtOH) 215 nm. \( \nu_{\text{max}} \) (KBr) 1690 (C=O), 1570, 1370 (NO_2). 'H n.m.r. (CDCl_3) \( \delta \) 4.04 (s, 6H, 2 OCH_3); 7.24 (s, 2H); 8.20 (s, 2H).

Synthesis of 5-methoxy-3-(5'-methoxy-2'-nitrophenyl)-2,1-benzisoxazoles (5a-d)

Photolysis of a concentrated solution of 5,5'-dimethoxy-
2,2'-dinitrodiphenylmethane (3a) in benzene medium yielded 5,5'-dimethoxy-2,2'-dinitrobenzophenone (4a) in good yield (43%). It was isolated by chromatography on a column of alumina using petroleum ether/benzene (5:1 v/v) as the eluant. 5,5'-Dimethoxy-2,2'-dinitrobenzophenone (4a, 800mg) was reduced with sodium borohydride in isopropyl alcohol when 5,5'-dimethoxy-2,2'-dinitrodiphenylcarbinol (500 mg) was obtained. It was dissolved in cold concentrated sulphuric acid and kept aside for 10 min. A deep red solution which was formed, was then poured into crushed ice and extracted with benzene. The benzene extract when concentrated, chromatographed on a column of alumina, and eluted with petroleum ether/benzene (10:1 v/v) afforded an yellow product. It crystallised from benzene/pet. ether (1:2 v/v) as bright yellow needles and it was identified as 5-methoxy-3-(5'-methoxy-2'-nitrophenyl-2,1-benzisoxazole (5a, 50mg), m.p. 161°C.

Similar NaBH₄ reduction of 4,4'-dihalo-5,5'-dimethoxy-2,2'-dinitrobenzophenones (4b-d) and cyclodehydration with conc. H₂SO₄ and chromatographic work up yielded the respective benzisoxazole derivative (5b-d). The m.p., analysis, spectral data etc. are detailed below.

5-Methoxy-3-(5'-methoxy-2'-nitrophenyl)2,1-benzisoxazole (5a)

M.p. 161°C. (Found: C, 59.8; H, 4.2; N, 9.4; C₁₅H₁₂N₂O₅ requires: C, 60.0; H, 4.0; N, 9.3). λ_max (EtOH), 330 nm. ν_max (KBr) 1540, 1360 (NO₂). 'H n.m.r. (CDCl₃) δ 3.9 (s, 3H, OCH₃),
4.02 (s, 3H, -OCH₃), 6.9-7.5 (m, 5H), 8.24 (d, 1H). Mass spectrum: m/e 300(M, 44), 270(100), 226(68), 195(59), 164(64).

6-Chloro-5-methoxy-3-(4'-chloro-5'-methoxy-2'-nitrophenyl)-2,1-benzisoxazole (5b)

M.p. 226°C. (Found: C, 50.1; H, 2.6; N, 7.7; C₁₅H₁₀N₂O₅Cl₂ requires: C, 48.9; H, 2.7; N, 7.6). λ max (EtOH) 330 nm. λ max (KBr) 1520, 1350 (NO₂). 'H n.m.r. (CDCl₃) δ 3.98 (s, 3H, OCH₃), 4.08 (s, 3H, OCH₃), 7.14 (s, 1H), 7.20 (s, 1H), 7.66 (s, 1H), 8.18 (s, 1H). Mass spectrum: m/e 368(M, 49), 338(100), 294(70), 263(62), 232(69).

6-Bromo-5-methoxy-3-(4'-bromo-5'-methoxy-2'-nitrophenyl)-2,1-benzisoxazole (5c)

M.p. 195°C. (Found: C, 39.1; H, 2.3; N, 6.1; C₁₅H₁₀N₂O₅Br₂ requires: C, 39.3; H, 2.2; N, 6.1). λ max (EtOH) 325 nm. λ max (KBr) 1520, 1360 (NO₂). 'H n.m.r. (CDCl₃) δ 3.70 (s, 3H, OCH₃), 4.01 (s, 3H, OCH₃), 7.16 (s, 1H), 7.22 (s, 1H), 7.70 (s, 1H), 8.20 (s, 1H). Mass spectrum: m/e 458(M, 38), 428(100), 384(67), 353(60), 322(60).

6-Iodo-5-methoxy-3-(4'-iodo-5'-methoxy-2'-nitrophenyl)-2,1-benzisoxazole (5d)

M.p. 270°C (Found: C, 32.5; H, 1.8; N, 5.0; C₁₅H₁₀N₂O₅I₂ requires: C, 32.6; H, 1.8; N, 5.1). λ max (EtOH) 325 nm. λ max (KBr) 1520, 1360 (NO₂). 'H n.m.r. (CDCl₃) δ 3.68 (s, 3H, OCH₃), 4.0 (s, 3H, OCH₃), 7.14 (s, 1H), 7.24 (s, 1H), 7.72 (s, 1H0; 8.28 (s, 1H). Mass spectrum: m/e 552(M, 42), 522(100), 478(65), 447(58), 416(66).
Synthesis of 3,8-dihalo derivatives of 2,9-dimethoxydibenzo-\(\varepsilon,\gamma\)1,2 diazepines (11b&d)

The dibenzo \(\varepsilon,\gamma\)1,2 diazepines (11b&d) were prepared by the LiAlH\(_4\) reduction of the corresponding 2,2'-dinitrodiphenylmethanes (3b&d). To a solution of (3b, 500 mg) in dry diethyl ether (500 ml), LiAlH\(_4\) (500 mg) was added in small lots with vigorous shaking. The reaction mixture was kept at room temperature for 30 minutes. The excess LiAlH\(_4\) was destroyed by adding water in small quantities. The ether layer which contained the diazepine was filtered and the filtrate concentrated and chromatographed on a column of alumina. Elution with petroleum ether/benzene (1:1 v/v) yielded brick red shining flakes of 3,8-dichloro-2,9-dimethoxydibenzo-\(\varepsilon,\gamma\)1,2 diazepine (11b, 450 mg). 3,8-Diiodo-2,9-dimethoxydibenzo-\(\varepsilon,\gamma\)1,2 diazepine (11d) was also obtained adopting similar procedure. The results of analyses are listed below.

3,8-Dichloro-2,9-dimethoxydibenzo-\(\varepsilon,\gamma\)1,2 diazepine (11b). m.p. 236°C. (Analysis found: C, 60.0; H, 3.5; N, 8.8; \(\text{C}_{15}\text{H}_{12}\text{N}_{2}\text{O}_{2}\text{Cl}_{2}\) requires C, 55.9; H, 3.7; N, 8.7). 'H n.m.r. (CDCl\(_3\)) \(\delta\) 4.12 (s, 6H, 20CH\(_3\)), 4.58 (s, 2H, CH\(_2\)), 7.45 (s, 2H), 7.84 (s, 2H).

3,8-Diiodo-2,9-dimethoxydibenzo-\(\varepsilon,\gamma\)1,2 diazepine (11d) m.p. 147°C. (Analysis found: C, 35.8; H, 2.4; N, 5.3; \(\text{C}_{15}\text{H}_{12}\text{N}_{2}\text{O}_{2}\text{I}_{2}\) requires C, 85.6; H, 2.4; N, 5.5). 'H n.m.r. (CDCl\(_3\)) \(\delta\) 4.14 (s, 6H, 20CH\(_3\)), 4.56 (s, 2H, CH\(_2\)), 7.48 (s, 2H), 7.9 (s, 2H).
SECTION II

SYNTHESIS AND PHOTOREACTIONS OF 5,5'-DICHLORO-2,2'-DINITRODI-PHENYLMETHANE AND ITS 4,4'-DIHALO DERIVATIVES

INTRODUCTION

Results of the irradiation of 5,5'-dimethoxy-2,2'-dinitrodiphenylmethane in neutral and acidic media detailed in Section I, show that the major product in each case of the irradiation was found to be dibenzo [e, f][1, 2] diazepin-11-one-5-oxides in isopropanol, 2,2'-dinitrobenzophenone in benzene and benzisoxazole in acidified ethanol. The halogen substituents at 4,4'-positions were found to have little influence on the reaction pathway and in the nature and yield of the products formed. To confirm the generality of this behaviour it was decided to examine the photochemistry of a few more halogen substituted 2,2'-dinitrodiphenylmethanes. Hence the photoreactions of 5,5'-dichloro-2,2'-dinitrodiphenylmethane and its 4,4'-dihalo derivatives were examined and the results are outlined in this section.

PREPARATION OF THE STARTING MATERIALS

Condensation of formaldehyde with o-chloroaniline in acidic medium following the procedure of Scanlan, yielded a white crystalline compound, mp 111°C, with molecular formula C_{13}H_{12}N_{2}Cl_{2}. This compound was identified as 4,4'-diamino-3,3'-dichlorodiphenylmethane (24) from elemental analysis and
spectral data.

Diazotisation of the diamino compound (24) in hypophosphorous acid containing cuprous oxide afforded 3,3'-dichlorodiphenylmethane (25a) in reasonable yield. The tetrahalo derivatives (25b&c) were prepared by Sandmeyer reaction of (24).
A t.l.c. examination of the product obtained in nitration of (25a) using a mixture of conc. sulphuric acid and conc. nitric acid (1:1 v/v) showed the presence of three products. These three compounds were separated by chromatography on a column of neutral alumina using petroleum ether/benzene (1:2 v/v) as eluant. The first fraction yielded a pale yellow product mp 126°C (22%) having the molecular composition $\text{C}_{13}\text{H}_8\text{N}_2\text{O}_4\text{Cl}_2$ indicating that it contains two nitro groups. This compound was identified as 5,5'-dichloro-2,2'-dinitrodiphenylmethane (26a) based on its elemental analysis, chemical behaviour and spectral data.

![Structure of 26a](image)

The compound (26a) was found to be photoactive, suggesting that at least one of the nitro groups is ortho to the methylene group. When treated with LiAlH$_4$ in ethereal solution it gave an yellow compound which was characterised as 2,9-dichlorodibenzo [e,f][1,2] diazepine. The formation of a diazepine ring requires the presence of two 2,2'-dinitro groups in the system. The structure which could account for the above observations can be represented as shown below.
The n.m.r. spectrum of the compound showed a simple pattern in the aromatic region. There were two doublets (2 protons each) and a singlet (2 protons), confirming that the compound is 5,5'-dichloro-2,2'-dinitrodiphenylmethane (26a).

The second fraction yielded a pale yellow compound melting at 110°C (42%). This compound was also found to be photoactive and when treated with LiAlH₄ in ethereal solution formed a dibenzo[c,f][1,2]diazepine derivative. The n.m.r. spectrum of the compound showed a singlet (1H) and two multiplets (3H & 2H) in the aromatic region. Structure (36) accounts for the above mentioned chemical and spectral data.

The third fraction afforded a light yellow compound melting at 161°C (38%). This compound was not photoactive and did not form a diazepine derivative when treated with LiAlH₄ in ethereal solution. The n.m.r. spectrum of the
compound showed a singlet (2H) and two doublets (2 protons each). The only structure which could account for the above data is (44).

![Structure 44]

Similar nitration of compounds (25b-c) resulted in the formation of only one nitro derivative in each case. These compounds were found to have molecular formula \( \text{C}_{13}\text{H}_6\text{N}_2\text{O}_4\text{Cl}_2\text{X}_2 \) (X = Cl or Br) and were identified as the related 4,4',5,5'-tetrahalo-2,2'-dinitrodiphenylmethane (26b&c) from their elemental analysis, chemical reactions and spectral data.

![Structure 26b-c]

The compounds (26b-c) were found to be photoactive and their ethereal solution with LiAlH\(_4\) yielded diazepine derivatives. The n.m.r. spectra of these showed only two singlets (2H each) in the aryl proton region. This type of pattern and chemical behaviour can be rationalised only by assigning structure (26b-c) to these compounds.

RESULTS OF THE PHOTOLYSIS IN ISOPROPANOL

Solutions of 5,5'-dichloro-2,2'-dinitrodiphenylmethane and its 4,4'-dihalo derivatives (26a-c) in isopropanol
(1 gm in 500 ml) were irradiated in sunlight till the starting material disappeared completely. The solvent in each case was then removed by distillation under reduced pressure. The residue was dissolved in minimum quantity of benzene and extracted with aqueous alkali. The alkali soluble fraction on acidification yielded an orange yellow compound in each case, having the molecular composition $C_{13}H_5NO_2Cl_2X_2$ ($X = H, Cl, Br$). These compounds were characterised as the corresponding N-hydroxyacridones from their elemental, chemical and spectral analysis (vide experimental). The alkali washed benzene solution was then concentrated and chromatographed on a column of alumina. The products obtained in each case are detailed in Tables 8-10.

It has been observed that the photoreactions of 5,5'-dichloro-2,2'-dinitrodiphenylmethane and 4,4',5,5'-tetrahalo derivatives are similar to that of 5,5'-dimethoxy-2,2'-dinitrodiphenylmethane and its 4,4'-dihalo derivatives. The major product of irradiation in each case was found to be the dibenzo [e,f][1,2]diazepin-11-one-5-oxide derivative. In these photoreactions also prolonged irradiation resulted in a decrease in the yield of benzisoxazoles and N,N-dioxide, whereas the yield of N-oxides increased (Table 11).
<table>
<thead>
<tr>
<th>Nature of the compound</th>
<th>Molecular composition</th>
<th>Name of the compound</th>
<th>Yield</th>
<th>% Yield</th>
<th>Melting point °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pale yellow needles</td>
<td>C_{13}H_{8}N_{2}O_{4}Cl_{2}</td>
<td>Starting material (26a)</td>
<td>400 mg</td>
<td>4</td>
<td>126</td>
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<tr>
<td>Yellowish green needles</td>
<td>C_{13}H_{6}N_{2}O_{3}Cl_{2}</td>
<td>5-Chloro-3-(5'-chloro-2'-nitrophenyl)-2,1-benzisoxazole (29a)</td>
<td>380 mg</td>
<td>4</td>
<td>188</td>
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<tr>
<td>Colourless needles</td>
<td>C_{13}H_{6}N_{2}O_{5}Cl_{2}</td>
<td>5,5'-Dichloro-2,2'-dinitrobenezophenone (30a)</td>
<td>940 mg</td>
<td>9</td>
<td>134</td>
</tr>
<tr>
<td>Yellow needles</td>
<td>C_{13}H_{6}N_{2}O_{2}Cl_{2}</td>
<td>2,9-Dichlorodibenzo [c,f][1,2] diazepin-11-one-5-oxide (27a)</td>
<td>4.03 g</td>
<td>45</td>
<td>268</td>
</tr>
<tr>
<td>Yellow microcrystalline prisms</td>
<td>C_{13}H_{7}N O Cl_{2}</td>
<td>2,7-Dichloroacridone (31a)</td>
<td>810 mg</td>
<td>10</td>
<td>&gt;300</td>
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<tr>
<td>Yellow solid</td>
<td>C_{13}H_{6}N_{2}O_{3}Cl_{2}</td>
<td>2,9-Dichlorodibenzo [c,f][1,2] diazepin-11-one-5,6-dioxide (33a)</td>
<td>850 mg</td>
<td>9</td>
<td>187</td>
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<tr>
<td>Yellow needles</td>
<td>C_{13}H_{7}NO_{2}Cl_{2}</td>
<td>2,7-Dichloro-N-hydroxyacridone (32a)</td>
<td>1.28 g</td>
<td>15</td>
<td>&gt;300</td>
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TABLE 9  IRRADIATION OF 4,4',5,5'-TETRACHLORO-2,2'-DINITRODIPHENYL METHANE (26b) IN ISOPROPANOL (1 gm in 500 ml x 10) DURATION OF EXPOSURE: 150 HRS  PERCENTAGE CONVERSION: 95

<table>
<thead>
<tr>
<th>Nature of the compound</th>
<th>Molecular composition</th>
<th>Name of the compound</th>
<th>Yield</th>
<th>% Yield</th>
<th>Melting point °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pale yellow needles</td>
<td>C_{13}H_{6}N_{2}O_{4}Cl_{4}</td>
<td>Starting material (26b)</td>
<td>500 mg</td>
<td>5</td>
<td>140</td>
</tr>
<tr>
<td>Yellowish green needles</td>
<td>C_{13}H_{4}N_{2}O_{3}Cl_{4}</td>
<td>5,6-Dichloro-3-(4',5'-dichloro-2'-nitrophenyl)-2,1-benzisoxazole (29b)</td>
<td>290 mg</td>
<td>3</td>
<td>183</td>
</tr>
<tr>
<td>Orange red needles</td>
<td>C_{13}H_{4}N_{2}Cl_{4}</td>
<td>2,3,8,9-Tetrachlorodibenzo [c,f] [1,2] diazepin-11-one (28b)</td>
<td>610 mg</td>
<td>7</td>
<td>255</td>
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<tr>
<td>Lemon yellow shining flakes</td>
<td>C_{13}H_{6}N_{2}Cl_{4}</td>
<td>2,3,8,9-Tetrachlorodibenzo [c,f] [1,2] diazepine (35b)</td>
<td>420 mg</td>
<td>5</td>
<td>144</td>
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<tr>
<td>Colourless needles</td>
<td>C_{13}H_{6}N_{2}O_{5}Cl_{4}</td>
<td>4,4',5,5'-Tetrachloro-2,2'-dinitrobenzophenone (30b)</td>
<td>930 mg</td>
<td>9</td>
<td>176</td>
</tr>
<tr>
<td>Yellow needles</td>
<td>C_{13}H_{6}N_{2}O_{3}Cl_{4}</td>
<td>4,4',5,5'-Tetrachloro-2-amino-2'-nitrobenzophenone (34)</td>
<td>770 mg</td>
<td>8</td>
<td>198-199</td>
</tr>
<tr>
<td>Yellow needles</td>
<td>C_{13}H_{6}N_{2}O_{2}Cl_{4}</td>
<td>2,3,8,9-Tetrachlorodibenzo-[c,f] [1,2] diazepin-11-one-5-oxide (27b)</td>
<td>3.93 g</td>
<td>43</td>
<td>264</td>
</tr>
<tr>
<td>Yellow microcrystalline prisms</td>
<td>C_{13}H_{5}NOCl_{4}</td>
<td>2,3,6,7-Tetrachloroacridone (31b)</td>
<td>920 mg</td>
<td>11</td>
<td>&gt;300</td>
</tr>
<tr>
<td>Yellow solid</td>
<td>*C_{13}H_{4}N_{2}O_{3}Cl_{4}</td>
<td>2,3,8,9-Tetrachlorodibenzo-[c,f] [1,2] diazepin-11-one-5,6-dioxide (33b)</td>
<td>550 mg</td>
<td>6</td>
<td>-</td>
</tr>
<tr>
<td>Yellow needles</td>
<td>C_{13}H_{5}NO_{2}Cl_{4}</td>
<td>2,3,6,7-Tetrachloro-N-hydroxyacridone (32b)</td>
<td>790 mg</td>
<td>9</td>
<td>&gt;300</td>
</tr>
</tbody>
</table>

* The proposed composition is based on ir data and chemical evidences. Since it could not be isolated in pure form for analysis.
<table>
<thead>
<tr>
<th>Nature of the compound</th>
<th>Molecular composition</th>
<th>Name of the compound</th>
<th>Yield</th>
<th>Yield %</th>
<th>Melting point °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pale yellow needles</td>
<td>C_{13}H_{6}N_{2}O_{4}Cl_{2}Br_{2}</td>
<td>Starting material (26c)</td>
<td>800 mg</td>
<td>8</td>
<td>121</td>
</tr>
<tr>
<td>Yellow needles</td>
<td>C_{13}H_{4}N_{2}O_{3}Cl_{2}Br_{2}</td>
<td>6-Bromo-5-chloro-3-(4'-bromo-5'-chloro-2'-nitrophenyl)-2,1-benzisoxazole (29c)</td>
<td>580 mg</td>
<td>6</td>
<td>218</td>
</tr>
<tr>
<td>Orange red needles</td>
<td>C_{13}H_{4}N_{2}OCl_{2}Br_{2}</td>
<td>3,8-Dibromo-2,9-dichlorobenzo-[c,g][1,2]diazepin-11-one (28c)</td>
<td>720 mg</td>
<td>8</td>
<td>246</td>
</tr>
<tr>
<td>Colourless needles</td>
<td>C_{13}H_{4}N_{2}O_{5}Cl_{2}Br_{2}</td>
<td>4,4'-Dibromo-5,5'-dichloro-2,2'-dinitrobenzophenone (30c)</td>
<td>1.13 g</td>
<td>11</td>
<td>199</td>
</tr>
<tr>
<td>Yellow needles</td>
<td>C_{13}H_{4}N_{2}O_{3}Cl_{2}Br_{2}</td>
<td>3,8-Dibromo-2,9-dichlorodibenzo-[c,g][1,2]diazepin-11-one-5-oxide (27c)</td>
<td>4.28 g</td>
<td>46</td>
<td>277</td>
</tr>
<tr>
<td>Yellow prisms</td>
<td>C_{13}H_{5}NOCl_{2}Br_{2}</td>
<td>3,6-Dibromo-2,7-dichloroacridone (31c)</td>
<td>780 mg</td>
<td>9</td>
<td>&gt;300</td>
</tr>
<tr>
<td>Yellow solid</td>
<td>*C_{13}H_{4}N_{2}O_{3}Cl_{2}Br_{2}</td>
<td>3,8-Dibromo-2,9-dichlorodibenzo-[c,g][1,2]diazepin-11-one-5,6-dioxide (33c)</td>
<td>670 mg</td>
<td>7</td>
<td>-</td>
</tr>
<tr>
<td>Yellow needles</td>
<td>C_{13}H_{5}NO_{2}Cl_{2}Br_{2}</td>
<td>3,6-Dibromo-2,7-dichloro-N-hydroxyacridone (32c)</td>
<td>900 mg</td>
<td>10</td>
<td>&gt;300</td>
</tr>
</tbody>
</table>

*The proposed composition is based on i.r. data and chemical evidences since it could not be isolated in pure form for analysis.
TABLE 11

<table>
<thead>
<tr>
<th>Starting material</th>
<th>Duration of irradiation</th>
<th>% conversion</th>
<th>% yield of products</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>27</td>
<td>29</td>
</tr>
<tr>
<td>26a</td>
<td>100 hrs</td>
<td>96</td>
<td>45</td>
</tr>
<tr>
<td></td>
<td>175 hrs</td>
<td></td>
<td>50</td>
</tr>
<tr>
<td>26b</td>
<td>150 hrs</td>
<td>95</td>
<td>43</td>
</tr>
<tr>
<td></td>
<td>250 hrs</td>
<td>100</td>
<td>45</td>
</tr>
<tr>
<td>26c</td>
<td>150 hrs</td>
<td>92</td>
<td>46</td>
</tr>
<tr>
<td></td>
<td>250 hrs</td>
<td>100</td>
<td>53</td>
</tr>
</tbody>
</table>
RESULTS OF PHOTOLYSIS IN BENZENE

Irradiation of (26a–c) was carried out in benzene also. Chromatographic separation of the various products isolated and characterised were carried out on neutral alumina, using eluants with successive increasing polarity. The results are detailed in Table 12.

TABLE 12

<table>
<thead>
<tr>
<th>Compound</th>
<th>Duration of exposure</th>
<th>% Conversion 27</th>
<th>30</th>
<th>31</th>
<th>32</th>
<th>33</th>
</tr>
</thead>
<tbody>
<tr>
<td>26a</td>
<td>100 hrs</td>
<td>98</td>
<td>25</td>
<td>39</td>
<td>8</td>
<td>12</td>
</tr>
<tr>
<td>26b</td>
<td>150 hrs</td>
<td>95</td>
<td>24</td>
<td>36</td>
<td>10</td>
<td>11</td>
</tr>
<tr>
<td>26c</td>
<td>150 hrs</td>
<td>92</td>
<td>26</td>
<td>35</td>
<td>9</td>
<td>8</td>
</tr>
</tbody>
</table>

RESULTS OF PHOTOLYSIS IN ACIDIFIED ETHANOL

Since the irradiation of (3a–d) in ethanol containing sulphuric acid led to the formation of benzisoxazoles in larger quantities, it was expected that (26a–c) also in acidified ethanol would yield the related benzisoxazoles as the major products. The irradiation of (26a–c) in acidified ethanol and workup of the photolysate afforded unchanged starting material, diazepinone-N-oxides (27a–c), acridones (31a–c), dinitrobenzophenones (30a–c), benzisoxazoles (29a–c), diazepinones (28a–c) and alkali soluble compounds identified as M-hydroxyacridones (32a–c). The results are listed in Table 13.
TABLE 13

<table>
<thead>
<tr>
<th>Compound</th>
<th>Duration of exposure</th>
<th>% conversion</th>
<th>% yield of products</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>27</td>
<td>28</td>
</tr>
<tr>
<td>26a</td>
<td>100 hrs</td>
<td>93</td>
<td>14</td>
</tr>
<tr>
<td>26b</td>
<td>150 hrs</td>
<td>92</td>
<td>13</td>
</tr>
<tr>
<td>26c</td>
<td>150 hrs</td>
<td>90</td>
<td>14</td>
</tr>
</tbody>
</table>

The results derived from the photoreactions of (26a-c) in neutral and acidic media reveal that the pattern of reactions are similar to that of the photoreactions of (3a-d) described in Section I.

IDENTIFICATION OF PRODUCTS

(i) 2,9-Dichlorodibenzo [c,f][1,2]diazepin-11-one-5-oxide and its dihalo derivatives (27a-c)

The structure of the N-oxides (27a-c) was arrived at mainly from the spectral data and was supported by satisfactory elemental analyses. These compounds with molecular composition $\text{C}_{13}\text{H}_{4}\text{N}_2\text{O}_2\text{Cl}_2\text{X}_2$ ($\text{X} = \text{H}$ or halogens) showed u.v. absorption maxima around 260 and 340 nm. The carbonyl stretching vibration in the i.r. spectra were seen around 1670-1700 cm$^{-1}$ and the N-O stretching vibrations around 1440-1450 cm$^{-1}$ and 1300-1310 cm$^{-1}$. The n.m.r. spectrum of (27a) showed a doublet centered at $\delta 8.40$ (1H) and another multiplet between $\delta 7.44-8.12$ (5H). The above data could be
explained by assigning the following structure to (27a). The doublet at $\delta 8.40$ could be attributed to the proton Ha near the

\[
\begin{align*}
\text{N} & \rightarrow \text{O} \text{ linkage since it will be more deshielded. The n.m.r.} \\
\text{spectra of the tetrahalo derivatives (27b&c) further support} \\
\text{the structure assigned to (27a). The n.m.r. spectrum of 27c} \\
\text{showed a singlet at $\delta 8.76$ (Ha) and a multiplet between} \\
\delta 7.92-8.20 \ (H_c H_d \text{ and } H_f).
\end{align*}
\]

The assigned structure was supported by the mass spectral fragmentation pattern of (27a-c) also. The fragmentation pattern is depicted in Scheme 18. The stepwise loss of O, N$_2$ and CO observed in the mass spectra is fully explained by structure (27) for these compounds. As observed in the case of (7a-d) the compounds (27a-c) were also readily converted to the corresponding dibenzo [c,f][1,2]diazepin-11-ones (28a-c) by refluxing them with finely divided magnesium in ethanol.

(ii) 5-Chloro-3-(5'-chloro-2'-nitrophenyl)-2,1-benzisoxazole and its dihalo derivatives (29a-c)

All the compounds with molecular composition $\text{C}_{13}\text{H}_4\text{N}_2\text{O}_3\text{Cl}_2X_2$ showed peaks around 1540 and 1360 cm$^{-1}$ in the i.r. spectra, indicating the presence of a nitro group. These
Scheme 18

Cl
N
O
Cl
m/e - 292 (100%)

Cl
N
O
Cl
m/e - 276 (14%)

Cl
N
O
Cl
m/e - 248 (9%)

m/e - 262 (42%)

m/e - 234 (24%)

m/e - 220 (18%)
compounds showed $\lambda_{\text{max}}$ near 330-335 nm in their u.v. spectrum.

The n.m.r. spectrum of (29a) had a complex multiplet of 5 aromatic protons centered between $\delta$7.44-7.84 and doublet of one aromatic proton at $\delta$8.20, which appears to be the proton adjacent to the nitro group (due to greater deshielding). On the basis of the above mentioned data and elemental analysis, the following structure could be assigned for (29a).

![Structure of 29a](image)

The aromatic protons of the tetra chloro derivative 29b appeared as four singlets at $\delta$ 7.2 (1H), $\delta$ 7.85 (1H), $\delta$ 7.96 (1H) and $\delta$ 8.20 (1H) which may be assigned to $H_c$, $H_b$, $H_d$ and $H_a$ respectively.

The structures of (29a-c) were further confirmed by the mass spectral data. In the mass spectrum of (29a) the peak due to molecular ion appeared at m/e 308 followed by peaks due to subsequent loss of NO, CO and O. The important modes of fragmentation observed for (29a-c) in the electron impact studies are represented in Scheme 19.

Conclusive evidence for the assigned structures was obtained when these compounds were synthesised from the related diphenylcarbinols as represented in the case of compounds (5a-d) (Section I identification of compounds).
SCHEME 19

\[ \text{Scheme Diagram} \]
(iii) 2,9-Dichlorodibenzo[c,f][1,2]diazepin-11-one and its dihalo derivatives (28a-c)

The compounds with molecular composition $C_{13}H_4N_2OCl_2X_2$ ($X = H$ or halogen) were identified from their spectral data. Strong absorption around 1690-1670 cm$^{-1}$ in the i.r. spectra of these compounds indicated the presence of a carbonyl group. The n.m.r. spectrum of (28a) showed three signals in the aromatic region, one as a singlet at $\delta 7.30$ (2H) and the others as two doublets centred at $\delta 7.74$ (2H) and $\delta 8.0$ (2H). The following structure fits in with the above mentioned data.

![Structure of 2,9-Dichlorodibenzo[c,f][1,2]diazepin-11-one]

The n.m.r. spectrum of the tetrahalo derivatives 28b&c showed two singlets, one around $\delta 7.65$ (2H) and the other at $\delta 8.52$ (2H). The signal at $\delta 7.65$ is assigned to protons $H_b$ and $H_b'$, and $\delta 8.52$ to $H_a$ and $H_a'$. 

![Structure of tetrahalo derivatives]
The oxidation of (28b-c) using \( \text{H}_2\text{O}_2 \) in alkaline alcoholic solution yielded the related diazepinone-5-oxides (27a-c). The deoxygenation of these (vide p.155) resulted in the formation of (28a-c). These results lend additional proof for the assigned structures (28a-c).

(iv) 5,5'-Dichloro-2,2'-dinitrobenzophenone and its dihalo derivatives (30a-c)

The dihalo and tetrahalo derivatives of 2,2'-dinitrobenzophenone were confirmed by comparison with samples obtained from the chromic anhydride oxidation of the corresponding 2,2'-dinitrodiphenylmethane derivatives (26a-c) and was supported by satisfactory spectral and elemental analyses.

All these compounds having molecular composition \( \text{C}_{13}\text{H}_4\text{N}_2\text{O}_5\text{Cl}_2\text{X}_2 \) showed strong absorption around 1700-1670 \( \text{cm}^{-1} \) in the i.r. spectra, indicating the presence of a \( \text{C} = \text{O} \) group. Absorption around 1560 \( \text{cm}^{-1} \) and 1350 \( \text{cm}^{-1} \) indicated the presence of nitro groups. The n.m.r. spectrum of 30a (\( \text{X} = \text{H} \)) showed a singlet at \( \delta 7.35(2\text{H}) \) and two doublets centred at \( \delta 7.7 \) (2H) and \( \delta 8.10 \) (2H) confirming the structure of (30a). In the n.m.r. spectra of (30b&c), the protons appeared as two singlets, one at \( \delta 8.35 \) due to \( \text{H}_a \) and \( \text{H}_a' \), protons and the other
67.6 due to $H_C$ and $H_{C'}$ protons (greater deshielding due to halogen and nitro functions).

(v) 2,7-Dichloroacridone and its dihalo derivatives (31a-c)

The structures of compounds with molecular composition $C_{13}H_{5}NO\cdot Cl_2X_2$ were arrived at mainly from spectral data. They showed carbonyl absorption around 1600 cm$^{-1}$ and absorption due to N-H group around 3290 cm$^{-1}$ in the i.r. spectra. These compounds were insoluble in usual solvents and hence their n.m.r. spectra could not be recorded. In the mass spectrum of (31a) the peak due to molecular ion was observed at m/e 263 as the base peak. This was followed by peaks due to the loss of CO, Cl etc. The fragmentation pattern depicted in Scheme 20 provided additional evidence for assigning an acridone structure to these compounds (31a-c).

(vi) 2,7-Dichloro-N-hydroxyacridone and its dihalo derivatives (32a-c)

The structure of these acidic compounds with molecular composition $C_{13}H_{5}NO_2Cl_2X_2$ was arrived at from their spectral data and was supported by their chemical behaviour. The OH stretching frequency in the i.r. spectrum appeared as a broad
peak around 3500 cm\(^{-1}\). The carbonyl absorption, was around 1600 cm\(^{-1}\) which is characteristic of acridone derivatives. Further, the spectra had peaks at 1300 and 1360 cm\(^{-1}\), which was probably due to the contribution of N-0 absorption since tautomeric forms involving these species are also possible.\(^{251}\) The n.m.r. spectra of these compounds could not be recorded, due to their low solubility in usual solvents. Further evidence for assigning a N-hydroxyacridone structure to the compounds was obtained from the mass spectral data. In the mass spectrum of (32a) the peak due to molecular ion appeared at m/e 279. It was followed by ions at 262 and 251 due to stepwise loss of OH and CO. The major fragmentation pattern observed for (32a) is depicted in Scheme 21. The tetrahalo derivatives also behaved in a similar manner in the mass spectral analysis. The compounds (32a-c) gave deep red sodium salts as observed with other N-hydroxyacridones.

(vii) 2,9-Dichlorodibenzo [c,f] [1,2] diazepin-11-one-5,6-dioxide (33a)

The compound with molecular composition C\(_{13}\)H\(_6\)N\(_2\)O\(_3\)Cl\(_2\) (X=H-or-halogen) was assigned a dibenzo [c,f] [1,2] diazepin-11-one-5,6-dioxide structure from the following spectral and chemical evidences. In the i.r. spectra, strong absorption at 1680 cm\(^{-1}\), and at 1310 cm\(^{-1}\) indicated the presence of a keto group and a N-0 linkage respectively. The n.m.r. spectra of (33a) showed a singlet at 67.8 (2H) which could be assigned to (H\(_C\) and H\(_C'\)) and two doublets, one centred at
$\delta$7.95 (2H) assigned to ($H_b$ and $H_{b'}$) and the other centred at $\delta$8.55 (2H) assigned to ($H_a$ and $H_{a'}$) (greater deshielding). The mass spectral fragmentation pattern of the (33a) gave further support to the structure assigned to the compound. The peak due to the molecular ion appeared at m/e 308. The major fragmentation pattern is depicted in Scheme 22. Reduction of (33a) with Mg in ethanol afforded (28a).

(viii) 2-Amino-4,4',5,5'-tetrachloro-2'-nitrobenzophenone (34)

The spectral data detailed below provided evidence for assigning an aminonitrobenzophenone structure to the compound with molecular composition $C_{13}H_{6}N_2O_3Cl_4$. In the i.r. spectrum absorptions were observed at 3470 and 3380 cm$^{-1}$ due to NH$_2$ group and at 1660 cm$^{-1}$ due to a keto group and at 1580 cm$^{-1}$ and 1350 cm$^{-1}$ due to the presence of a nitro group. The broad singlet at $\delta$3.6 (2H) observed in the n.m.r. spectrum could be attributed to the NH$_2$ protons. The aromatic protons appeared as four singlets at $\delta$7.40 ($H_c$), $\delta$7.52 ($H_d$), $\delta$8.12 ($H_a$) and $\delta$8.76 ($H_b$).

In the mass spectrum of the compound peak due to the molecular ion appeared at m/e 378 followed by peaks due to loss of O, NO and CO. The fragmentation pattern is depicted in Scheme 23.
The mechanism which has been postulated to describe the various photoreactions of 5,5'-dimethoxy-2,2'-dinitrodiphenylmethanes (3a-d) (vide Section I) could be applied to these compounds (26a-c) also. In the following paragraph an attempt has been made to account for the formation of 2-amino-4,4',5,5'-tetrachloro-2'-nitrobenzophenone (34) from the photolysis of 4,4',5,5'-tetrachloro-2,2'-dinitrodiphenylmethane in isopropanol. Aminonitrobenzophenones were not isolated in the photolysis of other derivatives of 2,2'-dinitrodiphenylmethane.

The formation of 2-amino-4,4',5,5'-tetrachloro-2'-nitrobenzophenone (34) during the photolysis of 4,4',5,5'-tetrachloro-2,2'-dinitrodiphenylmethane
2,2'-dinitrodiphenylmethane (26b) could be envisaged to take place as follows: One of the nitro groups in (26b) after excitation, if it successively abstracted hydrogen from the methylene group then it could form 2-hydroxylamino-2'-nitrobenzophenone derivative (45). A homolytic cleavage of the N-OH bond in (45) and subsequent hydrogen abstraction by the radical from the solvent or another molecule of (26b) could then yield 4,4',5,5'-tetrachloro-2'-nitrobenzophenone (34).
EXPERIMENTAL

PREPARATION OF STARTING MATERIALS

4,4'-Diamino-3,3'-dichlorodiphenylmethane (24)

4,4'-Diamino-3,3'-dichlorodiphenylmethane was prepared by the condensation of o-chloroaniline with formaldehyde in acidic medium following the procedure adopted by Scanlan for the preparation of 4,4'-diaminodiphenylmethane from aniline. Crystallisation of the product from ethanol afforded colourless shining flakes of 4,4'-diamino-3,3'-dichlorodiphenylmethane (24) m.p. 111°C. (Analysis: found C, 58.6; H, 4.7; N, 10.4; \(C_{13}H_{12}N_2Cl_2\) requires; C, 58.6; H, 4.5; N, 10.5).

3,3'-Dichlorodiphenylmethane (25a)

To a solution of 4,4'-diamino-3,3'-dichlorodiphenylmethane (12 g) in hypophosphorous acid (50%, 175 ml) cuprous oxide (2 g) was added and the mixture cooled to 0°C. A solution of sodium nitrite (14.5 g) dissolved in water (20 ml) was added dropwise over a period of thirty minutes with stirring and cooling, not allowing the temperature of the reaction mixture to rise above 0°C. The solution was stirred for another 3 hrs, when the evolution of nitrogen ceased. The mixture was then extracted repeatedly with benzene. The benzene extracts were combined, the solvent removed by distillation and the residue chromatographed on a column of alumina, using petroleum ether as the eluant. 3,3'-Dichlorodiphenylmethane obtained from the eluate was crystallised from benzene/petroleum ether (1:10 v/v) as colourless flakes (yield: 8 g, 75%) m.p. 41°C.
3,3',4,4'-Tetrachlorodiphenylmethane (25b)

4,4'-Diamino-3,3'-dichlorodiphenylmethane (12 g) dissolved in 1:1 HCl (30 ml) and cooled to 0°C was diazotised with sodium nitrite (14.5g). The diazonium chloride solution was then added with stirring to an ice cold solution of Cu₂Cl₂ (10g) in concentrated HCl (30 ml). The mixture was kept at room temperature for about 2 hrs by which time the evolution of nitrogen gas ceased. It was then extracted repeatedly with benzene. Benzene extracts were combined and the solvent was removed by distillation. The residue obtained was chromatographed on a column of alumina using petroleum ether/benzene (5:1 v/v) as eluant. 3,3',4,4'-Tetrachlorodiphenylmethane obtained from the eluate was crystallised from benzene/petroleum ether (1:10 v/v) as colourless flakes (yield: 7.5g, 54%) m.p. 113°C. (Analysis found: C,51.5; H,2.7; C₁₃H₈Cl₄ requires: C,51.3; H,2.63).

4,4'-Dibromo-3,3'-dichlorodiphenylmethane (25c)

Diazonium bromide solution prepared from 4,4'-diamino-3,3'-dichlorodiphenylmethane (12g) and sodium nitrite (14.5g) and hydrobromic acid (48%,35 ml) was added with stirring to an ice cold solution of Cu₂Br₂ (15 g) in hydrobromic acid (48%, 35 ml). The mixture was then heated on a water bath for about 30 minutes, by which time the evolution of nitrogen
gas ceased. The reaction mixture was then cooled and extracted repeatedly with benzene. The benzene extracts were combined, the solvent removed by distillation and the residue chromatographed on a column of neutral alumina using pet ether/benzene (10:1 v/v) as the eluant. The eluate yielded 4,4'-dibromo-3,3'-dichlorodiphenylmethane (yield 10g, 56%). Its crystallization from benzene/petroleum ether (1:10 v/v) afforded colourless flakes of 4,4'-dibromo-3,3'-dichlorodiphenylmethane (25c) m.p. 139°C. (Analysis found: C,39.7; H,1.9; C_{13}H_8Cl_2Br_2 requires C,39.6; H,2.0).

**Nitration of 3,3'-dichlorodiphenylmethane (25a)**

To a mixture of concentrated nitric acid (40 ml) and concentrated sulphuric acid (40 ml) taken in a round bottomed flask (250 ml) 3,3'-dichlorodiphenylmethane (22.5g) was added in portions of 2g at a time with efficient stirring and not allowing the reaction temperature to rise above 50-60°C. When it was found that the temperature no longer increased owing to the heat of the reaction, the solution was heated on a boiling water bath for 15 min. The reaction mixture was then allowed to cool to room temperature and was poured on to crushed ice (200 gm). The yellow solid formed was filtered washed with cold water and dried. A t.l.c. examination of the nitratred material showed three distinct spots, indicating the presence of three different products.

The mixture of nitro derivatives of (25a) was separated by chromatography on a column of alumina. Elution with
petroleum ether/benzene (5:1 v/v) yielded an yellow compound as the first fraction, which when crystallised from CHCl₃/pet.
ether (1:4 v/v) yielded pale yellow prisms m.p. 126°C (6.8g,22%). It was identified as 5,5'-dichloro-2,2'-dinitrodiphenylmethane (26a) based on spectral and chemical data. (Analysis found: C,48.0; H,2.4; N,8.5; C₁₃H₈N₂O₄Cl₂ requires: C,47.9; H,2.5; N,8.6). λ_max(EtOH) 278 nm, μ_max(KBr) 1360 (N-O). 'H n.m.r. (CDCl₃) δ 4.72 (s,2H), 7.23 (s,2H), 7.54-7.62 (d,2H), 8.12-8.24 (d,2H).

Continued elution of the column with benzene/petroleum ether (1:1 v/v) yielded another pale yellow compound which crystallised from chloroform/pet ether (1:2 v/v) as pale yellow needles having m.p. 110°C (13g, 42%). This compound was assigned 5,3'-dichloro-2,2'-dinitrodiphenylmethane structure (36) based on spectral and chemical evidences. (Analysis found: C,47.9; H,2.7; N,8.7; C₁₃H₈N₂O₄Cl₂ requires: C,47.9; H,2.5; N,8.6). λ_max(EtOH) 276 nm, μ_max(KBr) 1560, 1370 (N-O). 'H n.m.r. (CDCl₃) δ 4.48 (s,2H), 7.35 (s,1H), 7.4-7.65 (m,3H), 7.84-8.22 (m,2H).

Final elution of the column with benzene afforded another pale yellow compound which when crystallised from chloroform/petroleum ether yielded pale yellow needles. It was identified as 5,5'-dichloro-4,4'-dinitrodiphenylmethane (44, 11.8g, 38%) m.p. 161°C. (Analysis found: C,48.1; H,2.4; N,8.6; C₁₃H₈N₂O₄Cl₂ requires: C,47.9; H,2.5; N,8.6). λ_max(EtOH) 275nm, μ_max(KBr) 1540, 1350 (N-O) 'H n.m.r. (CDCl₃) δ 4.18(s,2H), 7.37 (d,2H), 7.59(s,2H), 8.0-8.18(d,2H).
4,4',5,5'-Tetrachloro-2,2'-dinitrodiphenylmethane

Nitration of 3,3',4,4'-tetrachlorodiphenylmethane (25b, 29g) as described in the nitration of the compound (25a, p.144) yielded 4,4',5,5'-tetrachloro-2,2'-dinitrodiphenylmethane. It crystallised from chloroform/petroleum ether (1:2 v/v) as pale yellow needles. m.p. 140°C. (yield 30g, 80%). (Analysis found: C,39.6; H,1.6; N,7.2; $\text{C}_{13}\text{H}_6\text{N}_2\text{O}_4\text{Cl}_4$ requires: C,39.6; H,1.5; N,7.1). $\lambda_{\text{max}}$(EtOH) 280 nm. $\nu_{\text{max}}$(KBr) 1560, 1360 (N-O). $^1\text{H}$ n.m.r. (CDCl$_3$) $\delta$ 4.5 (s,2H), 7.38 (s,2H), 8.45 (s,2H).

4,4'-Dibromo-5,5'-dichloro-2,2'-dinitrodiphenylmethane

4,4'-Dibromo-3,3'-dichlorodiphenylmethane (38g) was nitrated following the procedure described for 3,3'-dichlorodiphenylmethane (p.144). The yellow compound obtained on crystallisation from chloroform/petroleum ether (2:1 v/v) yielded yellow needles of 4,4'-dibromo-5,5'-dichloro-2,2'-dinitrodiphenylmethane (40 g, 86%) m.p. 121°C. (Analysis found: C,32.1; H,1.1; N,5.9; $\text{C}_{13}\text{H}_6\text{N}_2\text{O}_4\text{Cl}_2\text{Br}_2$ requires: C,32.2; H,1.2; N,5.8). $\nu_{\text{max}}$(KBr), 1560, 1350 (N-O). $^1\text{H}$ n.m.r. (CDCl$_3$): $\delta$ 4.55 (s,2H), 7.40 (s,2H), 8.44 (s,2H).

Irradiation of 5,5'-dichloro-2,2'-dinitrodiphenylmethane in isopropanol (26a)

A solution of 5,5'-dichloro-2,2'-dinitrodiphenylmethane (26a, 1g) was irradiated for 100 hrs in sunlight by which time the starting material almost disappeared (Tlc).
The experiment was repeated ten times and the solutions were combined. The solvent was then removed by distillation under reduced pressure and the residue dissolved in benzene (600 ml). The benzene solution was repeatedly washed with sodium hydroxide (2%) solution. Neutralisation of the combined alkali washings afforded an yellow precipitate, which was collected and chromatographed on a column of silica gel, using petroleum ether/benzene (1:1 v/v) as the eluant. Crystallisation of the product obtained from acetic acid yielded yellow needles of 2,7-dichloro-N-hydroxyacridone (32a, 1.28g, 15%) m.p. $>300^\circ$C.

(Analysis found: C, 55.7; H, 2.6; N, 4.9; $C_{13}H_{7}NO_2Cl_2$ requires: C, 55.9; H, 2.5; N, 5.0). $\lambda_{max}(\text{EtOH}) 250, 345 \text{ nm}$. $\nu_{max}(\text{KBr})$ 3500-3200 (OH), 1600 (C=O), 1360, 1300 (N-O). Mass spectrum: m/e 279 (M,100), 262(92), 251(42), 234(34).

The sodium hydroxide washed benzene solution was then distilled under reduced pressure and the residue obtained chromatographed on a column of neutral alumina. Elution with petroleum ether/benzene (10:1 v/v) yielded unchanged starting material (26a, 400 mg, 4%) as the first fraction. It was followed by an yellow compound which crystallised from benzene/petroleum ether (1:5 v/v) as yellowish green needles of 5-chloro-3(5'-chloro-2'-nitrophenyl)-2,1-benzisoxazole (29a, 380mg, 4%), m.p. and mixed m.p. with authentic sample (vide p.156) 188°C.

Further elution of the column with petroleum ether/benzene (2:1 v/v) yielded a colourless compound which crystallised from benzene/petroleum ether (1:2 v/v) as colourless needles.
It was identified as 5,5'-dichloro-2,2'-dinitrobenzophenone (30a, 940mg, 9%) m.p. and mixed m.p. with authentic sample (vide p.159 134°C. Further elution of the column with petroleum ether/benzene (1:1 v/v) resulted in the separation of an yellow band. Removal of the solvent from the eluate and recrystallisation of the residue from chloroform/petroleum ether (1:1 v/v) yielded yellow needles of 2,9-dichlorodibenzo [g,f] [1,2] diazepin-11-one-5-oxide (27a, 4.03g, 45%). m.p. 268°C. (Analysis found: C, 53.6; H, 2.1; N, 9.5; \( C_{13}H_6N_2O_2Cl_2 \) requires: C, 53.4; H, 2.1; N, 9.6). \( \lambda_{\text{max}} \) (EtOH) 340, 260 nm, \( \nu_{\text{max}} \) (KBr) 1670 (C=O), 1300 (N-O). \( \delta \) (KBr) 1670 (C=O), 1310 (N-O). \( \delta \) (CDCl3) 8.40 (d, 1H), 7.44-8.12 (m, 5H). Mass spectrum: 292(M, 100), 276(14), 262(42), 248(9), 234(24), 220(18).

Continued elution of the column with benzene alone afforded an yellow compound which crystallised from isopropanol as yellow microcrystalline prisms. It was identified as 2,7-dichloroacridone (31a, 810mg, 10%) m.p. >300°C. (Analysis found: C, 59.4; H, 2.6; N, 5.2; \( C_{13}H_7NOC\) requires: C, 59.3; H, 2.7; N, 2.3). \( \lambda_{\text{max}} \) (EtOH) 355, 250 nm, \( \nu_{\text{max}} \) (KBr) 3290 (N-H), 1600 (C=O). Mass spectrum: m/e 263(M, 100), 235(85).

Elution of the column when continued with benzene/chloroform (1:1 v/v) yielded 2,9-dichlorodibenzo [g,f][1,2] diazepin-11-one-5,6-dioxide (33a, 850mg, 9%) m.p. 187°C (dec). (Analysis found: C, 50.5; H, 1.8; N, 9.2; \( C_{13}H_6N_2O_3Cl_2 \) requires C, 50.7; H, 1.9; N, 9.1). \( \nu_{\text{max}} \) (KBr) 1680 (C=O), 1310 (N-O). \( \delta \) (CDCl3) 7.8 (s, 2H), 7.95 (d, 2H), 8.55 (d, 2H). Mass spectrum: m/e 308(M, 34), 278(100), 262(81), 250(18), 234(92).
Photolysis of 4,4',5,5'-tetrachloro-2,2'-dinitrodi phenylmethane (26b) in isopropanol

A solution of 4,4',5,5'-tetrachloro-2,2'-dinitrodi phenylmethane (1g) in isopropanol (500 ml) was irradiated for 150 hrs in sunlight when the starting material almost disappeared. The experiment was repeated ten times and the solutions were combined. The solvent was then distilled off under reduced pressure and the residue dissolved in benzene (500 ml). The benzene solution was then repeatedly washed with sodium hydroxide solution (2%). Acidification of the alkali extract yielded an yellow solid which when chromatographed on a column of silica gel using petroleum ether/benzene (2:1 v/v) as the eluant and crystallization of the residue obtained from the eluate from acetic acid yielded yellow needles of 2,3,6,7-tetrachloro-N-hydroxyacridone (32b,790mg,9%) m.p. > 300°C. (Analysis found: C,44.9; H,1.4; N,4.1; C_{13}H_{5}NO_{2}Cl_{4} requires C,45.0; H,1.4; N,4.0). λ_{max}(EtOH) 230, 270, 290 nm, υ_{max}(KBr) 3500-3200 (OH), 1600 (C=O), 1310 (N-O). N.m.r. spectra of (32b) could not be taken due to its low solubility in most of the usual solvents. Mass spectrum: m/e 347(M,100), 330(94), 319(43), 302(32).

The alkali washed benzene solution was then distilled under reduced pressure and the residue chromatographed on a column of neutral alumina. Elution with petroleum ether/benzene (5:1 v/v) yielded unreacted material (26b,500mg,5%) as the first fraction. It was followed by an yellow compound
which crystallised from benzene/petroleum ether (1:5 v/v) as yellowish green needles. It was identified as 5,6-dichloro-3(4',5'-dichloro-2'-nitrophenyl)-2,1-benzisoxazole (29b, 290mg, 3%) m.p. and mixed m.p. with authentic sample (vide p.156) 183°C. Continued elution of the column with petroleum ether/benzene (2:1 v/v) yielded an orange-red material. It crystallised from benzene/petroleum ether (1:2 v/v) as orange red needles and was identified as 2,3,8,9-tetrachlorodibenzo-[c,f][1,2]diazepin-11-one (27b, 610mg, 7%) m.p. and mixed m.p. with the sample obtained by the magnesium reduction of the related N-oxide (vide p.155) 255°C. Further elution of the column yielded another compound which crystallised from benzene/petroleum ether (1:2 v/v) as lemon yellow shining flakes. This compound was identified as 2,3,8,9-tetrachlorodibenzo-[c,f][1,2]diazepine (35b, 420mg, 5%), m.p. and mixed m.p. with the sample prepared by the LiAlH₄ reduction of 4,4',5,5'-tetrachloro-2,2'-dinitrodiphenylmethane (26a) in diethylether solution 144°C. Continued elution of the column with petroleum ether/benzene (1:1 v/v) yielded a colourless compound. It crystallised from benzene/petroleum ether (1:1 v/v) as colourless needles and was identified as 4,4',5,5'-tetrachloro-2,2'-dinitrobenzophenone (30b, 930mg, 9%) m.p. and mixed m.p. with authentic sample (vide p.155) 176°C. It was followed by an yellow compound which crystallised from benzene/petroleum ether (1:1 v/v) as yellow needles. This compound was identified as 2-amino-4,4',5,5'-tetrachloro-2'-nitrobenzophenone (34, 770mg, 8%) m.p. 198-199°C. (Analysis found: C,41.0; H,1.5; N,7.5;
C\textsubscript{13}H\textsubscript{6}N\textsubscript{2}O\textsubscript{3}Cl\textsubscript{4} requires: C, 41.3; H, 1.6; N, 7.4. \(\lambda\)\textsubscript{max}(EtOH) 385, 230 nm, \(\nu\)\textsubscript{max}(KBr) 3470, 3350 (NH\textsubscript{2}), 1640 (C=O), 1340 (N-O).'H n.m.r. (CDCl\textsubscript{3}) \delta 8.35 (s, 2H); 7.6 (s, 2H); 3.6 (bs, 2H), Mass spectrum: m/e 378(M,100), 333(34), 332(28).

Then the column was eluted with benzene, when 2,3,8,9-tetrachlorodibenzo [g,f][1,2] diazepin-11-one-5-oxide (27b, 3.93g, 43%) was obtained. It crystallised from chloroform/petroleum ether (1:1 v/v) as yellow needles m.p. 164°C. (Analysis found: C, 43.2; H, 1.1; N, 7.9; C\textsubscript{13}H\textsubscript{4}N\textsubscript{2}O\textsubscript{2}Cl\textsubscript{4} requires: C, 43.3; H, 1.1; N, 7.8). \(\lambda\)\textsubscript{max}(EtOH) 235, 250, 330 nm, \(\nu\)\textsubscript{max}(KBr) 1680 (C=O), 1300 (N-O). 'H n.m.r. (CDCl\textsubscript{3}) \delta 7.9-8.18 (m, 3H), 8.72 (s, 1H). Mass spectrum: m/e 360(M,100), 344(12), 330(38), 316(16), 302(26), 288(20).

Further elution of the column with benzene/chloroform (1:1 v/v) afforded an yellow compound which crystallised from isopropanol as yellow microcrystalline prisms. It was identified as 2,3,6,7-tetrachloroacridone (31b, 920mg, 11%) m.p. >300°C. (Analysis found: C, 47.0; H, 1.6; N, 4.0; C\textsubscript{13}H\textsubscript{5}NOCl\textsubscript{4} requires: C, 47.1; H, 1.5; N, 4.2). \(\lambda\)\textsubscript{max}(EtOH) 360, 250 nm; \(\nu\)\textsubscript{max}(KBr) 3350 (N-H), 1630, 1600 (C=O), 1310 (N-O). The n.m.r. spectrum of the compound (31b) could not be taken due to its insolubility in usual solvents. Mass spectrum: m/e 331(M,100), 303(82).

The column when eluted further with chloroform alone yielded an yellow solid, which was found to gradually decompose when crystallisation was attempted from boiling solvents.
The i.r. spectrum of the compound obtained by cold crystallisation (dissolution in a cold isopropanol and gradual evaporation of the solvent in a current of air or by addition of diethyl ether) indicated that the compound is probably 2,3,8,9-tetrachlorodibenzo[\(\gamma,\delta\)][1,2]diazepin-11-one-5,6-dioxide (33b, 550mg, 6%). \(\nu_{\text{max}}\) (KBr) 1680 (C=O), 1310 (N=O).

**Photolysis of 4,4'-dibromo-5,5'-dichloro-2,2'-dinitrodiphenylmethane (26c)**

A solution of 4,4'-dibromo-5,5'-dichloro-2,2'-dinitrodiphenylmethane (26c, 1g) in 500 ml of isopropanol was irradiated in sunlight for 150 hrs, when the reaction appeared complete. The experiment was repeated ten times and the photolysates were combined. The solvent was then removed by distillation under reduced pressure and the residue dissolved in benzene (750 ml). The benzene solution was repeatedly washed with sodium hydroxide solution (2%) and the washings were combined and acidified. An yellow precipitate which was obtained on crystallisation from acetic acid yielded yellow needles of 3,6-dibromo-2,7-dichloro-N-hydroxyacridone (32c, 900mg, 10%) m.p. >300°C. (Analysis found: C, 35.5; H, 1.0; N, 3.3; \(\text{C}_{13}\text{H}_{5}\text{NO}_2\text{Cl}_2\text{Br}_2\), requires: C, 35.7; H, 1.1; N, 3.2). \(\nu_{\text{max}}\) (KBr) 3500 (OH), 1600(C=O), 1320 (N=O). The n.m.r spectrum of the compound could not be taken due to its insolvability in common solvents. Mass spectrum: m/e 437(M,100), 420(90), 409(38), 393(36).

The alkali washed benzene solution was then distilled under reduced pressure and the residue chromatographed on a
column of alumina. Elution with petroleum ether/benzene (5:1 v/v) yielded unchanged starting material (26c, 800mg, 8%). It was followed by an yellow compound which crystallised from benzene/petroleum ether (1:5 v/v) as yellow needles. It was identified as 6-bromo-5-chloro-3(4'-bromo-5'-chloro-2'-nitro-phenyl)-2,1-benzisoxazole (29c, 580mg, 6%) m.p. and mixed m.p. with authentic sample (vide p.156) 218°C. Further elution of the column with petroleum ether/benzene (2:1 v/v) yielded an orange red compound (28c, 720mg, 8%) which crystallised from benzene/petroleum ether (1:2 v/v) as orange red needles. It was identified as 3,8-dibromo-2,9-dichlorodibenzo [ε, ε][1,2] diazepin-11-one (28c) m.p. and mixed m.p. with the sample obtained by the reduction of the related N-oxide (vide p.155) 246°C. (Analysis found: C, 36.0; H, 1.0; N, 6.5; \( \text{C}_{13}\text{H}_4\text{N}_2\text{OCl}_2\text{Br}_2 \) requires: C, 35.9; H, 0.92; N, 6.5). \( \nu_{\text{max}}(\text{KBr}) \) 1680 (C=O), \( \text{'H n.m.r. (CDCl}_3) \) 7.65 (s, 2H), 8.52 (s, 2H).

Further elution of the column with petroleum ether/benzene (1:1 v/v) yielded a colourless compound (30c, 1.13g, 11%). It crystallised from benzene/petroleum ether (1:2 v/v) as colourless needles and was identified as 4,4'-dibromo-5,5'-dichloro-2,2'-dinitrobenzophenone (30c) m.p. and mixed m.p. with authentic sample (vide p.155) 199°C. When the elution of the column was continued with petroleum ether/benzene (1:2 v/v) separate a yellow band. Removal of the solvent and crystallisation of the residue from benzene/petroleum ether (1:1 v/v) yielded yellow needles of 3,8-dibromo-2,9-dichlorodibenzo [ε, ε][1,2] diazepin-11-one-5-oxide (27c, 4.28g, 46%) m.p. 277°C.
(Analysis found: C, 34.8; H, 0.9; N, 6.3; \(\text{C}_{13}\text{H}_4\text{N}_2\text{O}_2\text{Cl}_2\text{Br}_2\);
requires: C, 34.7; H, 0.89; N, 6.2). \(\nu_{\text{max}}\) (KBr) 1680 (C=O),
1310 (N-O). \(^1\text{H} \text{n.m.r.} \delta 8.76 (S, 1H), 7.92-8.20 (m, 3H). \text{Mass}
\) spectrum: m/e 450 (M, 100), 434 (11), 420 (40), 406 (8), 392 (25),
378 (16).

Continued elution of the column with benzene alone
yielded an yellow compound which when crystallised from isopropanol afforded yellow microcrystalline prisms of 3,6-di-
bromo-2,7-dichloroacridone (31c, 780mg, 9%) m.p. > 300°C.
(Analysis found: C, 37.0; H, 1.2; N, 3.2; \(\text{C}_{13}\text{H}_5\text{NOCl}_2\text{Br}_2\);
requires: C, 37.1; H, 1.2; N, 3.3). \(\lambda_{\text{max}}\) (EtOH) 340, 230 nm. \(\nu_{\text{max}}\) (KBr)
3350 (N-H) 1610, 1580 (C=O). \text{Mass spectrum: m/e 421 (M, 100),
393 (84).}

Final elution of the column with chloroform yielded an
yellow compound whose i.r. spectrum indicated that it is 3,8-
dibromo-2,9-dichlorodibenzo\([g,f]\)1,2]diazepin-11-one-5,6-dioxide
(33c, 670mg, 7%). Due to its gradual decomposition during
crystallisation it could not be obtained in pure form.
\(\nu_{\text{max}}\) (KBr) 1690 (C=O), 1300 (N-O).

IRRADIATIONS IN BENZENE

Irradiation of a solution of (26a-c) in dry benzene
(200 ml) in sunlight was carried out till almost complete
conversion of the starting material was effected. The experi-
ment was repeated six times and the photolysates were combined
and washed repeatedly with sodium hydroxide solution (2%).
Neutralisation of the alkali washings afforded an yellow
precipitate which when crystallised from acetic acid afforded N-hydroxyacridones as bright yellow needles (32a-c). The alkali washed benzene solution was then distilled under reduced pressure and the residue chromatographed on a column of neutral alumina. The products listed in Table 11 were thus obtained. Each compound was identified by comparison with the i.r. spectra and mixed melting points of the related samples obtained in the photolysis of (26a-c) in isopropanol.

**IRRADIATIONS IN ACIDIC ETHANOL**

Irradiation of a solution of (26a-c, 1g) in ethanol (600 ml) containing concentrated sulphuric acid (2 ml) carried out in sunlight resulted in almost complete conversion of the starting material in about hundred hours. The experiment was repeated six times and the photolysates were combined. The combined solution was neutralised with sodium bicarbonate and the precipitated sodium sulphate filtered off. The solvent from the filtrate was then removed by distillation under reduced pressure. The residue obtained was then dissolved in benzene (200 ml) and was repeatedly extracted with a solution of sodium hydroxide (2%). Neutralisation of the alkali washings yielded an yellow precipitate which when crystallised from acetic acid afforded N-hydroxyacridones as yellow needles (32a-c). The alkali washed benzene solution was then distilled under reduced pressure to remove the solvent and the residue chromatographed, on a column of neutral alumina. The products isolated and characterised are listed in Table 12.
Reduction of dibenzo \([c,f][1,2]\) diazepin-11-one-5-oxides (27b&c) to dibenzo \([c,f][1,2]\) diazepin-11-ones (28b&c)

Reduction of compounds (27b&c) was carried out as described in the case of the reduction of compounds (7a-d) on page 111. The dibenzo \([c,f][1,2]\) diazepin-11-ones obtained were crystallised from benzene/petroleum ether (1:2 v/v) as orange red needles. The yield in each case was found to be almost quantitative.

Synthesis of 2,2'-dinitrobenzophenone derivatives (30a-c)

Oxidation of compounds (26a-c) using chromic anhydride in glacial acetic acid, as described in the oxidation of compounds (3a-d), yielded the related benzophenones (30a-c) in almost quantitative yield. The m.p., analysis and spectral data are detailed below.

5,5'-Dichloro-2,2'-dinitrobenzophenone (30a) crystallised from benzene/petroleum ether (1:2 v/v) m.p. 134°C. (Found: C, 46.0; H, 1.7; N, 8.4; \(\text{C}_{13}\text{H}_6\text{N}_2\text{O}_5\text{Cl}_2\) requires: C, 45.9; H, 1.8; N, 8.2).

\(\lambda_{\text{max}}\) (EtOH) 210 nm. \(\nu_{\text{max}}\) (KBr) 1700 (C=O), 1560, 1330 (N=O).

'\(H\) n.m.r. (CDCl\(_3\)) \(\delta\) 7.35 (s, 2H), 7.7 (d, 2H), 8.10 (d, 2H).

4,4',5,5'-Tetrachloro-2,2'-dinitrobenzophenone (30b). Colourless needles from benzene/petroleum ether (1:2 v/v) m.p. 176°C. (Found: C, 38.3; H, 1.0; N, 7.0; \(\text{C}_{13}\text{H}_4\text{N}_2\text{O}_5\text{Cl}_4\) requires: C, 38.2; H, 0.98; N, 6.9).

\(\lambda_{\text{max}}\) (EtOH) 210 nm. \(\nu_{\text{max}}\) (KBr) 1700 (C=O), 1550, 1360 (N=O). '\(H\) n.m.r. (CDCl\(_3\)) \(\delta\) 8.35 (s, 2H), 7.6 (s, 2H).
4,4'-Dibromo-5,5'-dichloro-2,2'-dinitrobenzophenone (30c).

Colourless needles from chloroform/petroleum ether (1:1 v/v)
m.p. 199°C. (Found: C, 31.2; H, 0.80; N, 5.4; \( \text{C}_{13}\text{H}_4\text{N}_2\text{O}_5\text{Cl}_2\text{Br}_2 \);
requires: C, 31.3; H, 0.80; N, 5.6). \( \lambda_{\text{max}}(\text{EtOH}) \) 220 nm. \( \nu_{\text{max}}(\text{KBr}) \)
1700 (C=O), 1560, 1370 (N-O). \( ^1\text{H} \text{n.m.r. (CDCl}_3 \) \( \delta \) 8.37 (s, 2H),
7.6 (s, 2H).

\textit{Synthesis of 3-(2'-nitrophenyl)-2,1-benzisoxazoles (29a-c)}

5,5'-Dichloro-2,2'-dinitrobenzophenone (30a, 1g)
prepared by the oxidation of 5,5'-dichloro-2,2'-dinitrodiphenylmethane with chromic anhydride in glacial acetic acid, was
reduced with sodium borohydride in isopropyl alcohol to afford crude 5,5'-dichloro-2,2'-dinitrodiphenylmethanol. It was
dissolved in cold concentrated sulphuric acid (50 ml) and the
solution so obtained turned dark red when it was kept for ten
minutes at room temperature. The solution so obtained was
poured into crushed ice and was extracted with benzene. The
benzene extract was concentrated and chromatographed on a
column of neutral alumina. Elution with petroleum ether/
benzene (5:1 v/v) afforded 3-(2'-nitrophenyl)-2,1-benzisoxazole
(29a) as yellow needles m.p. 188°C.

Similar reduction of 4,4',5,5'-tetrachloro-2,2'-di-
nitrobenzophenone (30b) and 4,4'-dibromo-5,5'-dichloro-2,2'-
dinitrobenzophenone (30c) with NaBH\(_4\) and cyclodehydration of
the related benzhydrols with concentrated sulphuric acid and
work up yielded the respective benzisoxazole derivatives
(29b&c). The results obtained are listed below.
5-Chloro-3-(5'-chloro-2'-nitrophenyl)-2,1-benzisoxazole (29a)
yellow green needles from benzene/petroleum ether (1:1 v/v)
m.p. 188°C. (Analysis found: C, 50.9; H, 2.0; N, 9.2; 
\( \text{C}_{13}\text{H}_6\text{N}_2\text{O}_3\text{Cl}_2 \) requires: C, 50.7; H, 1.9; N, 9.1. 
\( \lambda_{\text{max}}\text{(EtOH)} \) 330 nm. \( \nu_{\text{max}}\text{(KBr)} \) 1350 (N-O). 'H n.m.r. (CDCl\(_3\)) \( \delta \) 7.44-7.84 6
(m, 5H), 8.20 (d, 1H). Mass spectrum: m/e 308(M, 34), 278(100), 262(18), 234(75).

5,6-Dichloro-3(4',5'-dichloro-2'-nitrophenyl)-2,1-benzisoxazole (29b): Yellowish green needles from chloroform/petroleum ether (1:2 v/v) m.p. 183°C. (Analysis found: C, 41.3; H, 1.0; N, 7.6; \( \text{C}_{13}\text{H}_4\text{N}_2\text{O}_3\text{Cl}_4 \) requires: C, 41.5; H, 1.1; N, 7.4). 
\( \lambda_{\text{max}}\text{(EtOH)} \) 330 nm. \( \nu_{\text{max}}\text{(KBr)} \) 1360 (N-O). 'H n.m.r. (CDCl\(_3\)) \( \delta \) 7.2 (1H), 7.85 (1H), 7.96 (1H) and 8.20 (1H). Mass spectrum: m/e 376(M, 36), 346(100), 330(20), 302(74).

6-Bromo-5-chloro-3(4'-bromo-5'-chloro-2'-nitrophenyl)-2,1-benzisoxazole (29c): Yellowish green needles from chloroform/petroleum ether (1:1 v/v) m.p. 218°C. (Analysis found: C, 33.6; H, 0.90; N, 6.2; \( \text{C}_{13}\text{H}_4\text{N}_2\text{O}_3\text{Cl}_2\text{Br}_2 \) requires: C, 33.5; H, 0.85; N, 6.0). \( \lambda_{\text{max}}\text{(EtOH)} \) 330 nm. \( \nu_{\text{max}}\text{(KBr)} \) 1360 (N-O). 'H n.m.r. (CDCl\(_3\)) \( \delta \) 7.25(H), 7.98 (1H), 8.24(1H). Mass spectrum: m/e 466(M, 33), 436(100), 420(21), 392(76).

Preparation of 2,3,8,9-tetrachlorodibenzo[c,f][1,2]diazepine (35b)

2,3,8,9-Tetrachlorodibenzo[c,f][1,2]diazepine (35b) was prepared adopting the procedure used for the related
diazepines (1a-d, vide p.114). It crystallised from benzene/petroleum ether (1:1 v/v) as lemon yellow shining flakes, m.p. 144°C. (Analysis found: C, 47.5; H, 1.9; N, 8.4; C₁₃H₆N₂Cl₄ requires: C, 47.3; H, 1.8; N, 8.5). 'H n.m.r. (CDCl₃) δ 4.55 (s, 2H), 7.60 (d, 2H), 8.50 (d, 2H).
SECTION III

PHOTOREACTIONS OF 5,3'-DICHLOORO-2,2'-DINITRO-DIPHENYL METHANE

INTRODUCTION

The photoreactions of 5,5'-dimethoxy-2,2'-dinitrodiphenylmethanes and 5,5'-dichlorodiphenylmethanes in neutral and acidic media, dealt with in the previous two sections show that the major product is the related diazepinone-N-oxide in neutral medium and benzisoxazole in acidic medium. The photoreactions of these were not much influenced by the electronic effect of substituents in the aryl ring.

The photoreactions of 2,2'-dinitrodiphenylmethanes examined in sections I & II possessed symmetrically placed substituents at 5,5' and 4,4' positions of 2,2'-dinitrodiphenylmethane. It was of interest to examine the photoreactions of 5,3'-dichloro-2,2'-dinitrodiphenylmethane wherein chlorine atoms are ortho and para with respect to each of the nitro groups. The compound as such has an unsymmetrical structure and hence could form more than one benzisoxazole and diazepin-N-oxide derivatives.

The results of the irradiation of 5,3'-dichloro-2,2'-dinitrodiphenylmethane (36) in protic and aprotic media are discussed in this section.
RESULTS OF PHOTOLYSIS IN ISOPROPANOL

Irradiation of a solution of (36) in isopropanol for 100 hrs resulted in almost complete disappearance of the starting material. Workup of the photolysate as described in the earlier cases yielded the following compounds: starting material (4%) an yellow compound with molecular composition C₁₃H₆N₂O₃Cl₂ (7%) which was identified as 5/7-chloro-3-(3/5'-chboro-2'-nitrophenyl)-2,1-benzisoxazole (37), an orange red compound with molecular composition C₁₃H₆N₂OCl₂ and identified as 2,7-dichlorodibenzo [c,f] [1,2] diazepin-11-one (38), a colourless compound with molecular composition C₁₃H₆N₂O₂Cl₂ identified as 5,3'-dichloro-2,2'-dinitrobenzophenone (39) an yellow compound with molecular composition C₁₃H₆N₂O₂Cl₂ identified as 2,7-dichlorodibenzo [c,f] [1,2] diazepin-11-one-5 or 6-oxide (40) an yellow fluorescent compound with molecular composition C₁₃H₇NOCl₂ identified as 2,5-dichloroacridone (41) and an yellow compound which was found to decompose when crystallisation was attempted from warm solvents. The products obtained in the irradiations are presented in Table 14.

It has been observed that as in the case of irradiation of (3a-d) and (26a-c) the major product in isopropanol is dibenzo [c,f] [1,2] diazepin-11-one-5 or 6-oxide.

RESULTS OF PHOTOLYSIS IN BENZENE

Photolysis of 5,3'-dichloro-2,2'-dinitrodiphenylmethane
in benzene yielded 5,3'-dichloro-2,2'-dinitrobenzophenone as the major product, akin to the irradiation of (3a-d) and (26a-c). In benzene medium, benzisoxazoles and diazepinones were not obtained. The results of irradiation are listed in Table 15.

RESULTS OF PHOTOLYSIS IN ACIDIFIED ETHANOL

Since the irradiation of (3a-d) and (26a-c) in ethanol containing sulphuric acid led to preferential formation of benzisoxazoles, it was expected that (36) also in acidified ethanol would yield benzisoxazole as the major product.

Irradiation of a solution of 5,3'-dichloro-2,2'-dinitrodiphenylmethane in ethanol containing concentrated sulphuric acid was therefore experimented. Almost complete conversion of the starting material resulted in about 100 hrs. Workup of the photolysate afforded unchanged starting material (8%) benzisoxazole (37, 32%), diazepinone (38, 7%) dinitrobenzophenone (39, 8%), diazepinone-N-oxide (40, 14%) acridone (41, 11%) and N-hydroxyacridone (43, 8%). As expected the major product of irradiation was found to be benzisoxazole (37).

Since the dinitro compound (36) is asymmetric and has only one chlorine ortho to one of the nitro group, theoretically two isomers of benzisoxazole and N-oxide are possible. It has been noted that only one isomer of the benzisoxazole and N-oxide derivative viz. 5-chloro-3(3'-chloro-2'-nitrophenyl)-2,1-benzisoxazole (37a) or 7-chloro-3-(5'-chloro-2'-nitrophenyl)-2,1-benzisoxazole (37b) and 2,7-dichlоро-
TABLE 14  IRRADIATION OF 5,3'-DICHLORO-2,2'-DINITRODIPHENYL METHANE IN ISOPROPANOL
(1 gm in 500 ml. x 10) Duration of exposure: 100 Hrs
Percentage conversion: 9%

<table>
<thead>
<tr>
<th>Nature of the compound</th>
<th>Molecular composition</th>
<th>Name of the compound</th>
<th>Yield</th>
<th>% yield</th>
<th>Melting point</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pale yellow crystalline</td>
<td>C\textsubscript{13}H\textsubscript{8}N\textsubscript{2}O\textsubscript{4}Cl\textsubscript{2}</td>
<td>Starting material (36)</td>
<td>400 mg</td>
<td>4</td>
<td>110</td>
</tr>
<tr>
<td>Yellow needles</td>
<td>C\textsubscript{13}H\textsubscript{6}N\textsubscript{2}O\textsubscript{3}Cl\textsubscript{2}</td>
<td>5\textsubscript{7}-Chloro-3\textsubscript{G}/\textsubscript{S}-chloro-2'-nitrophenyl)-2,1-benzisoxazole (37)</td>
<td>670 mg</td>
<td>7</td>
<td>191</td>
</tr>
<tr>
<td>Orange red needles</td>
<td>C\textsubscript{13}H\textsubscript{6}N\textsubscript{2}OCl\textsubscript{2}</td>
<td>2,7-Dichlorodibenzo[c,f][1,2]diazepin-11-one (38)</td>
<td>1 g</td>
<td>11</td>
<td>204</td>
</tr>
<tr>
<td>Colourless needles</td>
<td>C\textsubscript{13}H\textsubscript{6}N\textsubscript{2}O\textsubscript{5}Cl\textsubscript{2}</td>
<td>5,3'-Dichloro-2,2'-dinitrobenzophenone (39)</td>
<td>930 mg</td>
<td>9</td>
<td>145</td>
</tr>
<tr>
<td>Yellow needles</td>
<td>C\textsubscript{13}H\textsubscript{6}N\textsubscript{2}O\textsubscript{2}Cl\textsubscript{2}</td>
<td>2,7-Dichlorodibenzo[c,f][1,2]diazepin-11-one-5or6-oxide (40)</td>
<td>4.2 g</td>
<td>45</td>
<td>225</td>
</tr>
<tr>
<td>Yellow prismons</td>
<td>C\textsubscript{13}H\textsubscript{7}NOCl\textsubscript{2}</td>
<td>2,5-Dichloroacridone (41)</td>
<td>350 mg</td>
<td>4</td>
<td>&gt;300</td>
</tr>
<tr>
<td>Yellow solid</td>
<td>*C\textsubscript{13}H\textsubscript{6}N\textsubscript{2}O\textsubscript{3}Cl\textsubscript{2}</td>
<td>2,7-Dichlorodibenzo[c,f][1,2]diazepin-11-one-5,6-dioxide (42)</td>
<td>480 mg</td>
<td>5</td>
<td>-</td>
</tr>
<tr>
<td>Yellow needles</td>
<td>C\textsubscript{13}H\textsubscript{7}NO\textsubscript{2}Cl\textsubscript{2}</td>
<td>2,5-Dichloro-N-hydroxyacridone (43)</td>
<td>540 mg</td>
<td>6</td>
<td>&gt;300</td>
</tr>
</tbody>
</table>

*The proposed composition is based on i.r. data and chemical evidences since it could not be isolated in pure form for analysis.
### TABLE 15 IRRADIATION OF 5,3'-DICHLORO-2,2'-DINITRO-DIPHENYL METHANE

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Duration of irradiation</th>
<th>% conversion</th>
<th>% yield of products formed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isopropanol</td>
<td>100 hrs</td>
<td>96</td>
<td>7, 11, 9, 45, 4, 5, 6</td>
</tr>
<tr>
<td>Benzene</td>
<td>150 hrs</td>
<td>94</td>
<td>34, 22, 6, 4, 3</td>
</tr>
<tr>
<td>Acidified ethanol</td>
<td>150 hrs</td>
<td>92</td>
<td>32, 7, 8, 14, 11, 8</td>
</tr>
</tbody>
</table>

Dibenzo [c, e][1, 2] diazepin-11-one-5-oxide (40a) or 2,7-dichlorodibenzo [c, e][1, 2] diazepin-11-one-5-oxide (40b) were formed in the photo reaction. It is difficult to choose the correct structure of isoxazole and N-oxide from the available spectral data.

### IDENTIFICATION OF PRODUCTS

**2,7-Dichlorodibenzo [c, e][1, 2] diazepin-11-one-5 or 6 oxide (40)**

The compound with molecular composition $C_{13}H_{6}N_{2}O_{2}Cl_{2}$ (40) was assigned 2,7-dichlorodibenzo [c, e][1, 2] diazepin-11-one-5 or 6-oxide structure based on spectral data, elemental analysis and chemical reactions. In the i.r. spectrum, the compound showed strong absorption peaks at 1670 cm$^{-1}$ (C=O stretching vibration) and at 1320 cm$^{-1}$ (due to N-O stretching vibration). Reduction of (40) with Mg in ethanol afforded
2,7-dichlorodibenzo [g, f][1, 2] diazepin-11-one as observed in the case of compounds (7a-d) and (27(a-c)) discussed in Sections I and II respectively. The unsymmetric structure of (26) shows that the formation of two isomers of diazepin-N-oxide (40a) and (40b) is possible. In the n.m.r. spectrum the aromatic protons appeared as three distinct signals. The first appeared as a singlet at $\delta 7.52 (1H)$, the second as a doublet centered between $\delta 7.6-7.7 (1H)$ and the third a multiplet centered between $\delta 7.72-8.10 (4H)$. From these data it is difficult to assign the position of the oxygen in the structure.

Further proof for a N-oxide structure for the compound came from the mass spectral data. In the mass spectrum of (40) the base peak due to the molecular ion should appear at $m/e$ 292 followed by peaks due to the loss of NO and CO. The major fragmentation pattern depicted in scheme 25 confirms to the expected pattern. The spectral data of 40 was found to be very much akin to those of dibenzodiazepinone-N-oxides (27a-c) thus confirming the proposed N-oxide structure for the compound.

5/7-Chloro-3(3'/5'-chloro-2'-nitrophenyl)-2,1-benzisoxazole (37)

The compound with the molecular composition
Scheme 25

Cl\[\text{m/e 262 (54\%)}\]

\[\text{-NO}\]

\[\text{Cl}\text{m/e 292 (100\%)}\]

\[\text{-CO}\]

Cl\[\text{m/e 264 (34\%)}\]

\[\text{-CO}\]

\[\text{-NO}\]

\[\text{Cl}\text{m/e 234 (12\%)}\]
\( \text{C}_13\text{H}_6\text{N}_2\text{O}_3\text{Cl}_2 \) was assigned a 2,1-benzisoxazole structure based on spectral data, elemental analysis and alternative synthesis. Strong bands at 1540 cm\(^{-1}\) and 1330 cm\(^{-1}\) observed in the i.r. spectra indicated the presence of a free nitro group. In the n.m.r. spectrum two signals were observed one as a doublet (1H) centred at 6.8.15 and the other as a multiplet centred between 6.7.2-7.8 (5H). The n.m.r. spectral data suggests that the structure of the compound could either be 5-chloro-3(3'-chloro-2'-nitrophenyl)-2,1-benzisoxazole (37a) or 7-chloro-3(5'-chloro-2'-nitrophenyl)-2,1-benzisoxazole (37b) (one of the two theoretically possible isomers vide page 163). From the available spectral data it is difficult to choose the correct structure of the compound. In the mass spectrum of (37), the
SCHEME 26

\[
\begin{align*}
Cl\text{-}NO_2 \rightarrow e^- & \rightarrow Cl\text{-}N=\text{O} \\
m/e 308 (35\%) \\
\text{m/e 278 (64\%)} & \rightarrow \text{CO} \\
\text{m/e 250 (28\%)} & \rightarrow \text{Cl} \text{-N}^+ \text{O} \\
\text{m/e 234 (100\%)} & \rightarrow CL \text{-N}^+ \text{O}
\end{align*}
\]
peak due to the molecular ion appeared at m/e 308. It was followed by peaks due to the loss of NO, NO and O3NO and CO. The fragmentation pattern is depicted in Scheme 26.

The spectral data of (37) is found to have close similarities with the benzisoxazoles (29a) obtained during the photolysis of (26a-c). The benzisoxazole was synthesised by cold conc. sulphuric acid treatment of the diphenyl carbinal (obtained by the NaBH4 reduction of (39). In this acid catalysed cyclo-condensation also only one isomer (37a or b) was formed.

2,7-Dichlorodibenzo[c,f][1,2]diazepin-11-one (38)

The structure of the compound (38) with the molecular composition C13H6N2OCl2 was arrived at from its spectral data and chemical reactions. The u.v. absorption maxima of (38) was observed at 340 and 270 nm. In its i.r. spectrum the carbonyl stretching vibration appeared at 1680 cm⁻¹. The aromatic protons appeared as a doublet centered between δ 8.05-8.10 (1H) and a multiplet centered in the region δ 7.4-8.0 (5H). The following structure (38) which could account for the above data has been suggested for the compound.
The doublet centered between $\delta$ 8.50-8.10 could be assigned to proton $H_a$ (due to greater deshielding effect) and the multiplet centered between $\delta$ 7.4-8.0 is due to the overlapping of remaining aryl protons. The assigned structure was further confirmed by obtaining the compound (38) by reducing 2,7-dichlorodibenzof[f][1,2]diazepin-11-one-5 or 6-oxide (41) with Mg in ethanol.

5,3'-Dichloro-2,2'-dinitrobenzophenone (39)

The colourless needles with molecular composition $C_{13}H_{6}N_2O_5Cl_2$ was identified as 5,3'-dichloro-2,2'-dinitrobenzophenone from spectral data and alternative synthesis. Strong absorption at 1680 cm$^{-1}$ indicated the presence of C=O group. The presence of free nitro group was indicated by absorptions at 1550 cm$^{-1}$ and 1330 cm$^{-1}$. In the n.m.r. spectrum the protons appeared as a doublet centered between $\delta$ 8.10 ($1H_a$, 8.18 and a multiplet in the region $\delta$ 7.30-7.85 ($5H$). The following structure could explain all the above data. The doublet observed between $\delta$ 8.10-8.18 could be due to the proton $H_a$ and the multiplet due to the overlapping of the remaining five aromatic protons. The structure assigned to (39) has been confirmed by its synthesis from (36) by oxidation with chromic anhydride in glacial acetic acid.
2,5-Dichloroacridone (41)

The compound with molecular composition $C_{13}H_7NO_2Cl_2$ was identified as 2,5-dichloroacridone, from its spectral data and chemical behaviour. Similar to other derivatives of acridones (8a-d) and (31a-c) the compound (41) also showed blue fluorescence in isopropanol. In the i.r. spectra the absorption due to the NH group was observed at 3280 cm$^{-1}$. The carbonyl absorption peak appeared at 1620 cm$^{-1}$. The n.m.r. spectra of these compounds could not be taken due to their very low solubility in usual solvents. Further evidence for the suggested structure came from the mass spectral fragmentation pattern. In the mass spectrum of (41) the peak due to the molecular ion appeared at m/e 263, as the base peak, followed by peaks due to the loss of CO, CO and H and N. The fragmentation pattern is depicted in Scheme 27.

2,5-Dichloro-N-hydroxyacridone (43)

The alkali soluble compound obtained in the photolysis of (36), was identified from the spectral data and chemical behaviour and was supported by satisfactory elemental analysis. The molecular composition of (43) was found to be $C_{13}H_7NO_2Cl_2$ from elemental analysis. In the ir spectrum in addition to peaks at 3500 cm$^{-1}$ (OH) and 1600 cm$^{-1}$ (C=O), peak at 1300 cm$^{-1}$ characteristic of N- O absorption was observed. Clean n.m.r. spectrum of (32) could not be obtained due to its low solubility in usual solvents. In the mass spectrum of (43), the peak due to the molecular ion appeared at m/e 279 followed by
a peak due to loss of OH at m/e 262 and CO at m/e 251. A peak due to loss of OH and CO appeared at m/e 234. The major fragmentation pattern observed is depicted in Scheme 28 and it corresponds to a N-hydroxyacridone structure. The structure is supported by the observation that this compound formed deep red sodium salt with sodium hydroxide, an observation made with the other N-hydroxyacridones also.
Scheme 28
EXPERIMENTAL

PREPARATION OF STARTING MATERIALS

5,3'-Dichloro-2,2'-dinitrodiphenylmethane

Separation of the fraction with m.p. 110°C from the mixture of nitro compounds obtained in the nitration of 3,3'-dichlorodiphenylmethane adopting chromatographic techniques yielded 5,3'-dichloro-2,2'-dinitrodiphenylmethane (36) (p.143). It crystallised from C₆H₆/pet ether (1:1 v/v) as pale yellow needles m.p. 110°C.

IRRADIATION IN ISOPROPANOL

A solution of 5,3'-dichloro-2,2'-dinitrodiphenylmethane (36, 1g) in isopropanol (500 ml) was irradiated for 100 hrs in sunlight when the conversion appeared complete. The experiment was repeated ten times and the photolysates were combined. The solvent from the reaction mixture was then removed under reduced pressure and the residue dissolved in benzene (600 ml). The benzene solution when repeatedly washed with sodium hydroxide solution, (2%) and the washings when acidified yielded an yellow compound. It was chromatographed on a column of silica gel. Elution with petroleum ether/benzene (1:1 v/v) afforded an yellow solid. Its crystallisation from acetic acid yielded yellow needles of 2,5-dichloro-N-hydroxyacridone (43,540mg,6%), m.p. >300°C. (Analysis found: C,56.1; H,2.4; N,4.9; C₁₃H₇NO₂Cl₂ requires: C,55.9; H,2.5; N,5.0). \( \nu_{\text{max}}^{(\text{KBr})} \) 3500 (OH), 1600 (C=O), 1300 (N-O). The n.m.r. spectrum of
the compound was not recorded due to its low solubility in usual solvents. Mass spectrum: m/e 279(M,100), 262(84), 251(54), 234(29).

The alkali washed benzene solution was then distilled under reduced pressure and the residue chromatographed on a column of neutral alumina. Elution of the column with petroleum ether/benzene (10:1 v/v) yielded unchanged starting material (36, 400mg,4%) as the first fraction. It was followed by an yellow compound which crystallised from benzene/petroleum ether (1:5 v/v) as yellow needles. From spectral data & elemental analyses it was identified as 5/7-chloro-3(3\'5\'chloro-2'-nitrophenyl)-2,1-benzisoxazole (37, 670mg,7%) m.p. and mixed m.p. with authentic sample (vide p.179), 191°C. Further elution of the column with petroleum ether/benzene (5:1 v/v) afforded a compound which when crystallised from benzene/petroleum ether (1:4 v/v) yielded orange red needles of 2,7-dichlorodibenzo [c,e]1,2]diazepin-11-one (38, 1g,11%) m.p. and mixed m.p. with sample obtained by the reduction of the related N-oxide with Mg in ethanol (vide p.178) 204°C. (Analysis found: C,56.7; H,2.2; N,9.9; C_{13}H_{6}N_{2}OCl_{2} requires: C,56.5; H,2.2; N,10.1). 

\[ \lambda_{\text{max}}(\text{EtOH}) 340 \text{ nm, 270 nm. } \nu_{\text{max}}(\text{KBr}) 1680 \text{ (C=O). } \]

'H n.m.r. (CDCl₃) δ 8.05-8.10 (d,1H) 7.4-8.0 (m,5H). When the elution was continued with petroleum ether/benzene (2:1 v/v) a colourless compound was obtained. It crystallised from benzene/petroleum ether (1: 2 v/v) as colourless needles and was identified as 5,3'-dichloro-2,2'-dinitrobenzophenone (39, 930mg, 9%) m.p. and mixed m.p. with authentic sample, (vide p.178)
Continued elution of the column with petroleum ether/benzene (1:1 v/v) afforded a compound which crystallised from benzene/petroleum ether as yellow needles. It was identified as 2,7-dichlorodibenzoc[δ,ε][1,2]diazepin-11-one-5 or 6-oxide (40.42g, 45%), mp. 225°C. (Analysis found: C, 53.2; H, 2.2; N, 9.5; \( \text{C}_{13}\text{H}_{6}\text{N}_{2}\text{O}_{2}\text{Cl}_{2} \) requires: C, 53.4; H, 2.1; N, 9.6). \( \lambda_{\text{max}} \) (EtOH) 340, 250 nm. \( \nu_{\text{max}} \) (KBr) 1670 (C=O), 1320 (N-O). 1H n.m.r. (CDCl\(_3\)) \( \delta \) 7.52 (s, 1H), 7.6-7.7 (d, 1H), 7.72-8.10 (m, 4H). Mass spectrum: m/e 292(M, 100), 264(34), 262(54), 234(12).

Further elution of the column with benzene yielded a compound which crystallised as yellow microcrystalline prisms from isopropanol and was identified as 2,5-dichloroacrindione (41.350mg, 4%) m.p. \( \triangleright \) 300°C. (Analysis found: C, 59.5; H, 2.8; N, 5.1; \( \text{C}_{13}\text{H}_{7}\text{NOCl}_{2} \) requires: C, 59.3; H, 2.7; N, 5.3). \( \lambda_{\text{max}} \) (EtOH) 400, 380, 260, 220 nm. \( \nu_{\text{max}} \) (KBr) 1620 (C=O), 3280 (NH). Mass spectrum: m/e 263(M, 100), 235(8), 234(18), 220(12). Final elution of the column with chloroform yielded an yellow compound which is assumed to be 2,7-dichlorodibenzoc[δ,ε][1,2]diazepin-11-one-5,6-dioxide (42.480mg, 5%) from its i.r. spectrum. \( \nu_{\text{max}} \) (KBr) 1680 (C=O), 1310(N=O). It was found to decompose when crystallisation was attempted from warm solvents.

IRRADIATION IN BENZENE

Irradiation of a solution of (36.5g) in benzene (1500 ml) for 150 hrs in sunlight and workup of the resulting solution as in the above case yielded the products listed in Table 15.
IRRADIATION IN ACIDIFIED ETHANOL

A solution of 5,3'-dichloro-2,2'-dinitrodiphenylmethane (36,1g) in ethanol (600 ml) containing conc. sulphuric acid (2 ml) was irradiated in sunlight for 150 hrs. The experiment was repeated 5 times and the resultant solutions were then combined and neutralised with sodium bicarbonate. The precipitated sodium sulphate was filtered off and the solvent from the filtrate removed by distillation under reduced pressure. Workup of the resulting solution as in the case of the irradiation in isopropanol yielded the products listed in Table 15.

Reduction of 2,7-dichlorodibenzo [c,f][1,2]diazepin-11-one-5 or 6 oxide (40): Formation of 2,7-dichlorodibenzo [c,f][1,2]diazepin-11-one (38)

A solution of (40,100mg) in ethanol was refluxed with finely divided magnesium (100mg) for two hours when the reduction appeared complete (t.l.c.). The experiment was repeated five times. The resultant solutions were then combined and filtered, the solvent evaporated off and the residue chromatographed on a column of alumina. Elution with petroleum ether/benzene (2:1 v/v) yielded an orange red compound. It crystallised from benzene/petroleum ether (1:1 v/v) as orange red needles and was identified as 2,7-dichlorodibenzo [c,f][1,2]diazepin-11-one (38,350mg) m.p. 204°C.

Preparation of 5,3'-dichloro-2,2'-dinitrobenzophenone (39)

A solution of (36,1g) and chromic anhydride (3g) in
glacial acetic acid (20 ml) was refluxed for 2 hrs. The reaction mixture was then poured on to crushed ice and the precipitate formed collected and dried. 5,3'-Dichloro-2,2'-dinitrobenzophenone, crystallised from benzene/petroleum ether (1:2 v/v) as colourless needles (39, 95mg) m.p. 145°C. (Analysis found: C,45.9; H,1.9; N,8.3; C₁₃H₆N₂O₅Cl₂ requires: C,45.9; H,1.8; N,8.2). \( \lambda_{\text{max}}(\text{EtOH}) \) 220 nm, \( \nu_{\text{max}}(\text{KBr}) \) 1680 (C=O), 1550, 1330 (N-O). 'H n.m.r. (CDCl₃) \( \delta 8.10-8.18 \) (d,1H), 7.30-7.85 (m,5H).

**Synthesis of 5/7-chloro-3(3'/5'-chloro-2'-nitrophenyl)-2,1-benzisoxazole (37)**

5/7-Chloro-3(3'/5'-chloro-2'-nitrophenyl)-2,1-benzisoxazole (37) was synthesised from 5,3'-dichloro-2,2'-dinitrobenzophenone (39) using the method adopted for the synthesis of benzisoxazoles (29a-c) (vide p.156) m.p. 191°C. (Analysis found: C,50.6; H,1.8; N,9.0; C₁₃H₆N₂O₃Cl₂ requires: C,50.7; H,1.9; N,9.1). \( \lambda_{\text{max}}(\text{EtOH}) \) 330 nm, \( \nu_{\text{max}}(\text{KBr}) \) 1540, 1370(N-O). 'H n.m.r. (CDCl₃) \( \delta 8.15 \) (d,1H), 7.2-7.8 (m,5H).
PHOTOREACTIONS OF CERTAIN PHOTOPRODUCTS OBTAINED DURING THE IRRADIATION OF 2,2'-DINITRODIPHENYL METHANE DERIVATIVES

In the previous sections the photoreactions of methoxy and halogen derivatives of 2,2'-dinitrodiphenylmethanes in neutral and acidic media were discussed. It has been observed that prolonged irradiation of (3a-d), (26a-c) and (36) resulted in decreased yield of benzisoxazoles and N,N-dioxides and increased yield of N-oxides and acridones. It is obvious that the benzisoxazoles and N,N-dioxides underwent further photoreactions. This observation, therefore, necessitated an examination of the photobehaviour of benzisoxazoles, N-oxides and N,N-dioxides.

PHOTOREACTIONS OF METHOXY AND HALOGEN DERIVATIVES OF 3-(2'-NITROPHENYL)-2,1-BENZISOXAZOLES

A literature survey revealed that the photo-chemistry of 2,1-benzisoxazoles has attracted considerable interest in recent years, because of the involvement of a potential aryl nitrene intermediate in these reactions.

\[ R_1 = H, \text{Me or Ph} \quad R_2 = H \text{ or Cl} \quad R_3 = H \text{ or Cl} \]
Ogata and coworkers\textsuperscript{267,268} reported that the photolysis of 2,1-benzisoxazoles in methanol resulted in ring \textit{expansion} to 3-H azepines (48).

\begin{equation}
\begin{array}{c}
(46) \\
\end{array} \rightarrow \begin{array}{c}
(48) \\
(49)
\end{array}
\end{equation}

The authors assumed that the reaction proceeded via an initial N-O bond \textit{cleavage} in (46) followed by the ring closure of the resonance stabilized aziridine intermediate (49). This aziridine intermediate underwent ring expansion by \textit{cleavage} of the bridging bond and addition of a molecule of methanol to afford the azepine (48). Berwick\textsuperscript{269} who examined the photo-reaction of several other related compounds also proposed a similar mechanism for the formation of 3H-azepine, in which a photochemically produced aryl nitrene intermediate was involved. His conclusion was based on the observation that photolytic decomposition of 2-\textit{azido}acetophenone as well as 3-methyl-2,1-benzisoxazole yielded the same product. His finding that 3-methyl-2,1-benzisoxazole when irradiated in piperidine yielded 3-acetyl-2-piperidino-3H-azepine (50) (almost quantitatively) supported fully the intermediacy of the nitrene in these reactions.

Anthranils have also been reported\textsuperscript{209-211} to undergo
photoconversion to 5-substituted-2-aminophenylketones (51) in strongly acidic medium.

A study of the photoreactions of 3-(2'-nitrophenyl)-2,1-benzisoxazoles was, therefore, of great interest since in these compounds, in addition to the presence of a photolabile isoxazole ring, a photoactive nitro group is also present. A study of the photoreactions of these compounds were of further interest because it could throw further light into the pathway of the photoreactions of (3a-d), (26a-c) and (36).

RESULTS OF THE PHOTOLYSIS

Irradiation of 5-methoxy-3-(5'-methoxy-2'-nitrophenyl)-2,1-benzisoxazole (5a) in weakly acidic alcoholic medium (1g in 500 ml of ethanol containing 2 ml of conc. sulphuric acid) for 75 hrs in sunlight brought about 75% disappearance of the starting material. The photolysate was neutralised with
sodium bicarbonate, alcohol removed under reduced pressure and the residue chromatographed on a column of alumina. It afforded 2,9-dimethoxydibenzo \([c,f]\)[1,2]diazepin-11-one-5-oxide (7a, 45%), 2,7-dimethoxy-N-hydroxyacridone (9a, 20%), 2,7-dimethoxyacridone (8a, 12%) and traces of 2,9-dimethoxydibenzo \([c,f]\)[1,2]diazepin-11-one-5,6-dioxide (10a).

The generality of this photoreaction was verified by carrying out the irradiation of (5b-d), (29a-c) and (37) in acidified ethanol. The results of the photolysis are given in Table 16.

The isolation of diazepinone-N,N-dioxide in small quantities in the photoreaction shows that it is likely that 2,2'-dinitrosobenzophenones were formed as intermediates and they underwent rapid hydrogen abstraction and coupling to yield the related diazepinone-N-oxide. The hydrogen abstraction reaction of the intermediate could be made minimum if the irradiation of the benzisoxazoles was carried out in a non-protonic medium like benzene. Thus the yield of diazepinone-N-oxide could be reduced and the N,N-dioxides could be enhanced. To assert this, the irradiation of (5a) was carried out in dry benzene also. Irradiation of 500 mg of (5a) in 160 ml of benzene for 100 hrs in sunlight led to hardly 40% disappearance of the starting material. Concentration of the photolysate under reduced pressure and chromatography afforded 2,9-dimethoxydibenzo \([c,f]\)[1,2]diazepin-11-one-5,6-dioxide (10a) in 7% yield along with the diazepinone-N-oxide (7a, 25%),
<table>
<thead>
<tr>
<th>Starting material</th>
<th>Duration of exposure</th>
<th>% conversion</th>
<th>% yield of products</th>
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<tr>
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<td>N-oxides</td>
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acridone (8a,15%) and N-hydroxyacridone (9a,16%). Similar photolysis of the other benzisoxazoles (5b-d) (29a-c) and (37) also was carried out in order to confirm the generality of the reaction. It was observed that in these cases also the yield of N,N-dioxides increased while that of N-oxides decreased. The duration needed for a reasonable conversion of the starting material was also found to be longer. Results are summarised in Table 17.
MECHANISM OF THE PHOTOREACTION

A plausible mechanism which could account for the observed photoproducts of 3-(2'-nitrophenyl)-2,1-benzisoxazoles is given below. The N-O bond in 2,1-benzisoxazole which has been shown to undergo cleavage resulting in a nitrene intermediate would occur in the present cases examined also. If a similar initial rupture of the N-O bond in 3-(2'-nitrophenyl)-2,1-benzisoxazoles occurred it could yield a nitrene intermediate (52). The electron deficient nitrogen in (52) then could undergo intramolecular coupling with the proximal photoexcited nitro group and subsequently rearrange to form (15a). The formation of diazepinone-N-oxides acridones and N-hydroxyacridones from 2,2'-dinitrosobenzophenones (15a) could then occur as discussed in the earlier sections of this chapter.

The electron deficient nitrogen in the nitrene intermediate could also undergo intramolecular coupling with the
vacant 2-position of the phenyl substituent and yield a 1-nitroacridone (54).

Since 1-nitroacridone (54) was not obtained in the photoreactions of these benzisoxazoles an alternative mechanism would have to be thought of. The attack of an excited nitro group at the 3-position of the benzisoxazole could also be envisaged to occur. If it occurs the intermediate thus formed could rearrange and yield 2,2'-dinitrosobenzophenone (15a) as shown below.
It is hard to decide which of these processes is taking place in the photoreactions of these 3-(2'-nitrophenyl)-2,1-benzisoxazoles, unless studies with isotopically labelled compounds are performed.

It was observed that 3-(2'-nitrophenyl)-2,1-benzisoxazoles on photolysis failed to yield any azepine derivatives by ring expansion, as observed in the case of 3-arylbenzisoxazoles. This could be explained by assuming that in these cases the photoexcited nitro group interacted with the 3-position of the benzisoxazole ring resulting in the exclusive formation of 2,2'-dinitrosobenzophenone rather than in the rupture of the isoxazole ring to a nitrene intermediate and subsequent ring expansion.
PHOTOREACTIONS OF METHOXY AND HALOGEN DERIVATIVES OF DIBENZO (g, f) [1, 2] DIAZEPIN-11-ONE-5, 6-DIOXIDE

Dibenzo (g, f) [1, 2] diazepin-11-one-5, 6-dioxides could be considered as the intramolecularly dimerized form of 2,2'-dinitrosobenzophenones, the proposed key intermediate in the photochemical transformations of 2,2'-dinitrodiphenylmethanes to various products described earlier. In order to study the role of the dibenzo (g, f) [1, 2] diazepin-11-one-5, 6-dioxide in the formation of the final products viz. dibenzodiazepinone-N-oxide, acridone and N-hydroxyacridone in the photoreactions of 2,2'-dinitrodiphenylmethane derivatives, it was necessary to examine its photoreactions also.

Irradiation of a solution of 2,9-dimethoxydibenzo (g, f) [1, 2] diazepin-11-one-5, 6-dioxide (10a) in ethanol (200 mg in 200 ml) for 50 hrs resulted in almost complete disappearance of the starting material. Work up of the photolysate afforded 2,9-dimethoxydibenzo (g, f) [1, 2] diazepin-11-one-5-oxide (7a) N-hydroxyacridone (9a) and acridone (8a) in 52, 28 and 18% respectively. The results of the irradiation of remaining derivatives of N,N-dioxides were found to give comparable results.

PHOTOREACTIONS OF OTHER PHOTOPRODUCTS OBTAINED IN THE IRRADIATION OF 2,2'-DINITRODIPHENYL METHANES

The other photo products viz. dibenzodiazepinone-N-oxides, acridones, etc. were found to be photostable, in neutral medium. But irradiation of the derivatives of N-hydroxyacridones in isopropanol for 200 hrs in sunlight resulted in about 10% disappearance of the starting material and afforded the res-
pective acridones in about $\frac{3}{4}$ yield.

It has already been observed that when azoxy compounds are irradiated in acidic solutions, the oxygen migrated to the ring forming an isomeric hydroxyazo compound familiarly known as the Wallach rearrangement. The diazepinone-N-oxides also could undergo Wallach rearrangement when they are subjected to photolysis in acidic solutions. Irradiation of (7a) in ethanol containing conc. sulphuric acid for 200 hrs in sunlight and work up of the photolysate yielded only the unchanged starting material. Similar observations were made in the photolysis of the remaining derivatives of diazepinone-N-oxide also.

The results derived from the experiments on photolysis of the photoproducts obtained during the irradiation of 2,2'-dinitrodiphenylmethane derivatives provided additional support for the mechanism suggested for these reactions (p. 72). The photolysis of benzisoxazoles and diazepinone-N,N-dioxides has been found to yield all the other products formed in the photolysis of 2,2'-dinitrodiphenylmethanes (3a-d) (26a-c) and (36). Therefore it is possible that both benzisoxazoles and N,N-dioxides are intermediates in these photoreactions. As envisaged in the mechanism, benzisoxazole derivatives could be a precursor to diazepinone-N,N-dioxide also as it is formed in the photoreactions of benzisoxazoles but not vice-versa.
Photolysis of 3-(2'-nitrophenyl)-2,1-benzisoxazoles (5a-d, 29a-c & 37) in ethanolic sulphuric acid

A solution of 5-methoxy-3-(5'-methoxy-2'-nitrophenyl)-2,1-benzisoxazole (5a, 1g) in ethanol (500 ml) containing concentrated sulphuric acid (2 ml) was irradiated in sunlight for 75 hrs, when almost all the starting material disappeared. The resultant solution was then neutralised with NaHCO₃ and the precipitated sodium sulphate filtered off. The solvent from the filtrate was then distilled off under reduced pressure and the residue obtained dissolved in benzene (200 ml) and repeatedly washed with aqueous solution of sodium hydroxide (2%). Neutralisation of the alkali washings afforded an yellow precipitate which when filtered, dried and crystallised from acetic acid afforded yellow needles of 2,7-dimethoxy-N-hydroxyacridone (9a, 20%). The alkali washed benzene solution was then distilled under reduced pressure and the residue chromatographed on a column of neutral alumina. Elution with petroleum ether/benzene (10:1 v/v) afforded unchanged starting material (5a, 25%) as the first fraction. Further elution with petroleum ether/benzene (2:1 v/v) yielded 2,9-dimethoxy-dibenzo [g,f]1,2]diazepin-11-one-5-oxide (7a, 45%) m.p. 182°C (alone or when admixed with authentic sample). Continued elution of the column with benzene/chloroform (1:1 v/v) afforded 2,7-dimethoxyacridone (8a, 12%). Final elution of the column with chloroform yielded a compound in very low
yield (3%) which was identified as 2,9-dimethoxydibenzo[c,f]1,2 diazepin-11-one-5,6-dioxide (10a, 3%).

Similar irradiations of compounds (5b-d, 29a-c & 37) were also carried out and results are listed in Table 16.

Irradiation of 3-(2'-nitrophenyl)-2,1-benzisoxazoles (5a-d, 29a-c & 37) in benzene

A solution of (5a, 500 mg) in dry benzene (160 ml) was irradiated for 100 hrs in sunlight. The solvent was then removed, from the photolysate under reduced pressure and the residue chromatographed on a column of alumina, after separating the acidic fraction by repeated washing with aqueous sodium hydroxide (2%). Elution of the column with petroleum ether/benzene yielded unreacted starting material (5a, 300 mg). Further elution of the column with petroleum ether/benzene mixture (1:1 v/v) yielded 2,9-dimethoxydibenzo[c,f]1,2 diazepin-11-one-5-oxide (7a, 25%). The column when eluted further with benzene/chloroform (1:1 v/v) yielded 2,7-dimethoxyacridone (8a, 15%). Final elution of the column with chloroform afforded 2,9-dimethoxydibenzo[c,f]1,2 diazepin-11-one-5,6-dioxide (10a, 7%).

Irradiation of the benzene solutions of (5b-d, 29a-c & 37) and work up of the photolysates afforded the related products. They are listed in Table 17.

Irradiation of 2,9-dimethoxydibenzo[c,f]1,2 diazepin-11-one-5,6-dioxide (10a) in isopropanol

A solution of (10a, 200 mg) in isopropanol (200 ml)
was irradiated in sunlight till no further change in u.v. absorption was observed (50 hrs). The solvent was then removed under reduced pressure and the residue dissolved in benzene (50 ml) and washed with sodium hydroxide (2%). Neutralisation of the alkali washing afforded a precipitate which when crystallised from acetic acid yielded yellow needles of 2,7-dimethoxy-N-hydroxyacridone (9a, 28%).

The alkali washed benzene solution was distilled under reduced pressure to remove the solvent and the residue chromatographed on a column of neutral alumina. Work up of the column yielded 2,9-dimethoxydibenzo [c,f][1,2] diazepin-11-one-5-oxide (7a, 52%) and 2,7-dimethoxyacridone (8a, 18%).

**Irradiation of 2,7-dimethoxy-N-hydroxyacridones (9a-d, 32a-c & 43) in isopropanol**

A solution of 2,7-dimethoxy-N-hydroxyacridone (9a, 200mg) in isopropanol (500 ml) was irradiated in sunlight for 200 hrs. The solvent was then removed from the photolysate under reduced pressure and the residue dissolved in benzene (750 ml). The benzene solution was repeatedly washed with aqueous solution of sodium hydroxide (2%). Neutralisation of the alkali washings afforded an yellow precipitate which when filtered dried and crystallised from acetic acid yielded yellow needles of 2,7-dimethoxy-N-hydroxyacridone (9a, 90%). The alkali washed benzene solution was distilled under reduced pressure and the residue chromatographed on a column of neutral alumina. Elution of the column with benzene afforded 2,7-dimethoxy-
acridone (8a,6%3%). Final elution of the column with chloroform yielded only some resinous darkish matter which could not be characterised.

The results of irradiations of the remaining derivatives of N-hydroxyacridones (9b-d, 32a-c & 43) were comparable.