Synthesis and spectral studies of (E)-7a-[2-(arylsulphonyl)ethenyl]-1a,7a-dihydro-1-arylcyclopropa[el]pyran-7(1H)-ones
CHAPTER I
INTRODUCTION

The studies on sulphonyl derivatives of cyclopropanes and other related compounds have received considerable interest during the last two decades even though investigation of cyclopropane compounds had actually began long ago when Freund\(^1\) synthesised the parent hydrocarbon in 1882.

A number of products containing cyclopropane ring system exhibited marked biological activity. Some examples which stimulated research in the development of synthetic strategies to cyclopropanes are Chrysanthamic acid \((1)^2\), a natural insecticide; Sirelin \((2)^3\), a potent sperm attractant; Ildudin-S \((3)^4\), an effective antibacterial agent and derivatives of 3-azabicyclohexane carboxylic acid \((4)^5\), which are used in the treatment of Schizophrenia, Huntington's, Chorea, Cerebra insufficiency and epilepsy.
A number of methods\textsuperscript{6-13} were developed in the past for the preparation of cyclopropanes, but most of them suffered from a lack of generality. The reaction of carbenes, derivatives of bivalent carbon, with carbon–carbon multiple bonds provides one of the important methods for the preparation of cyclopropane compounds. The addition of a divalent carbon intermediate to carbon-carbon double bond, especially when stereo specific, presents a highly general approach from the standpoint of the organic chemist. The utility of sulphur ylides with Michael acceptors seem to be more important and of very good synthetic value. Sulphur ylides are nucleophilic alkylidene transfer agents in contrast to carbenes which are electrophilic alkylidene transfer agents and they react with electron deficient functional groups. These reagents allow generation of new carbon-carbon bonds in a variety of fashions making them invaluable synthetic intermediates.

The carbene which was often called methylene was formed\textsuperscript{14} by gas or liquid phase photolysis of diazomethane or ketene. Transfer of carbene to the Ti–bond is responsible for the cyclopropanation. The carbene carbon is linked to the non-bonding electrons which may have antiparallel spins (single state) or parallel spins (triple state). The nature of the ground state depends on the relative energies of the non-bonding orbitals. The majority of the carbenes are produced in the singlet state irrespective of the nature of the ground state and they are electron deficient species. Therefore the carbene reactions are enhanced by electron donating groups and retarded by electron withdrawing groups. The singlet carbenes react stereospecifically cis with
olefinic double bonds\textsuperscript{15,16}. For example, Van Leusen et al.\textsuperscript{17} synthesised cyclopropyl sulphones by the addition of a sulphonyl carbene (5) to alkenes.

\[
\begin{align*}
\text{H}_3\text{CO}_2\text{C} & \xrightarrow{\text{CH}_2\text{N}_2} \text{H}_3\text{CO}_2\text{C} \\
\text{Et} & \text{th} & \text{h} & \text{v} & \text{v}
\end{align*}
\]

Synthesis utilizing the concept of addition of a divalent carbon have been realised in the classical reactions of aliphatic diazo compounds with olefins\textsuperscript{18} and in the addition of halocarbenes to olefins\textsuperscript{19}. Diazomethane adds to the olefinic bond of \(\alpha,\beta\) unsaturated esters\textsuperscript{20-22} or ketones\textsuperscript{23} and sulphones\textsuperscript{24} giving pyrazolines which lose nitrogen on heating, usually forming the cyclopropane derivatives. Methyl cyclobutene-1-carboxylate undergoes smooth cyclo addition with diazomethane followed by photochemical loss of nitrogen to give methyl bicyclo (2-1-0) pentane-1-carboxylate (6)\textsuperscript{25}.

\[
\begin{align*}
\text{H}_3\text{CO}_2\text{C} & \xrightarrow{\text{CH}_2\text{N}_2} \text{H}_3\text{CO}_2\text{C} \\
\text{Et} & \text{h} & \text{v} & \text{v}
\end{align*}
\]

Takeo Saegusa and his co-workers\textsuperscript{26} prepared a number of 1,2-trans-cyclopropanes using copper isonitrile complex through the copper(I) carbenoid intermediate. Schoeillkopf et al.\textsuperscript{27-29} obtained cyclopropanes by treating olefins with chloromethylphenylether (PhOCH\textsubscript{2}Cl) in the presence of
butyllithium. Similarly, chloromethylphenylthioether in the presence of potassium-t-butoxide or butyllithium yielded phenylthiocyclopropanes, through phenylthiocarbene intermediate\textsuperscript{29}. These reactions were considered to proceed stereospecifically cis.

\[
\text{PhCH}=\text{CH}_2 + \text{ArSCH}_2\text{Cl} \xrightarrow{\text{t-BuOK} \ 20\% \ Excess} \begin{array}{c}
\text{Ph} \\
\text{SPh}
\end{array}
\]

Simmons and Smith\textsuperscript{30} described the stereospecific reaction of unsaturated compounds with carbenoids generated by the reaction of methylene iodide and zinc-copper couple. The reactive intermediate (7) is believed to be an iodomethylenezinc iodide complex which reacts with the olefin in a bimolecular process to give a cyclopropane and zinc iodide\textsuperscript{31}.

\[
\begin{array}{c}
\text{CH}_2 \\
\text{I}
\end{array} \xrightarrow{\text{Zn-I}} \begin{array}{c}
\text{CH}_2 \\
\text{Zn-I}
\end{array} \rightarrow \begin{array}{c}
\text{Ph} \\
\text{H}
\end{array} + \begin{array}{c}
\text{ZnI}_2 \\
\text{Zn/ Cu (excess)} \ \\
\text{Ether}
\end{array}
\]

\[
\begin{array}{c}
\text{Ph} \\
\text{H}
\end{array} + \begin{array}{c}
\text{CH}_2\text{I}_2 \\
\text{H}
\end{array} \xrightarrow{\text{Zn/ Cu (excess) \ Ether}} \begin{array}{c}
\text{Ph} \\
\text{H}
\end{array} + \begin{array}{c}
\text{COPh}
\end{array}
\]

\[
\begin{array}{c}
\text{ICH}_2\text{ZnI}
\end{array}
\]

\[
\begin{array}{c}
\text{O}
\end{array} + \begin{array}{c}
\text{O}
\end{array}
\]
\( \alpha \)-Haloanions have been employed in many cases for the cyclopropanation of activated olefins, where the anion is resonance stabilized. For example, treatment of phenacylchloride with sodium hydride in the presence of methylvinylketone produced the corresponding cyclopropane (8) in 60 percent yield\(^{32}\).

\[
\text{PhCOCH}_2\text{Cl} + \begin{array}{c}
\text{NaH} \\
\text{PhH, HMPA}
\end{array} \rightarrow \begin{array}{c}
\text{COCH}_3 \\
\text{PhCO}
\end{array}
\]

Under the influence of a strong base the condensation of \( \alpha \)-halogeno esters with \( \alpha, \beta \)-unsaturated esters or nitriles yielded cyclopropanes and this is another method for the synthesis of cyclopropanes \(^{33,34}\).
Dehydrohalogenation of γ-chloropropyl sulphones or ketones was also used for the preparation of cyclopropanes. γ-Chloroketones\textsuperscript{35,36} or sulphones\textsuperscript{37} on treatment with a base such as sodium hydroxide, sodamide or potassium-t-butoxide undergo cyclization to give cyclopropanes (10,11).

\[
\text{Cl} \quad \overset{\text{O}}{\text{C\,\,\,Cl}} \quad \overset{\text{OH}}{\longrightarrow} \quad \overset{\text{OH}}{\text{C}} \quad \overset{\text{O}}{\text{C}}
\]

R\text{SO}_2\overset{\text{Cl}}{\text{C\,\,\,C}} \quad \overset{\text{KO} (\text{CH}_3)_3}{\longrightarrow} \quad \overset{\text{R\text{SO}_2}}{\text{C\,\,\,C}}

Eisch and Galle\textsuperscript{38} obtained some cyclopropyl sulphones (12) through the addition of organometallics to sulphonyl substituted allyl bromides.

\[
\text{R}\text{SO}_2 \quad \overset{\text{H}}{\text{H}} \quad + \quad \text{RMgX} \quad \longrightarrow \quad \begin{bmatrix}
\text{R} \\
\text{PhSO}_2-\text{CH-CH-CH}_2 \\
\text{MgX} \\
\text{Br}
\end{bmatrix} \quad \downarrow
\]

\[
\begin{array}{c}
\text{RSO}_2 \\
\text{H} \\
\text{R}
\end{array}
\]

R=CH\text{CH}=CH\text{CH}_2; \text{C}_6\text{H}_5; \text{CH}_2\text{C}_6\text{H}_5
The general synthetic utility of ylides in organic synthesis captured the imagination of organic chemists with the introduction of Wittig olefin synthesis. Considering the documentation of proton abstraction from carbon-bearing sulphur both in sulphides and sulphonium salts attention was directed towards utilization of these anions in synthesis.

Sulphur ylides, formally zwitterions in which a carbon ion achieves stabilization by interaction with an adjacent sulphonium centre, have been known for over forty years since the report of Ingold and Jessop on the isolation of dimethylsulphonium fluorenylide. A base catalysed ring closure of dimethyl-(o-aceto-p-tolyl) sulphonium methyl sulphonate necessitates invoking the first addition of a sulphur ylide to a carbonyl group. This class of intermediates found its practical application in organic synthesis by the excellent work of the groups of Corey and Franzen.
A few reports were found in the literature about the formation of cyclopropyl ketones by the reaction of phosphonium ylides with α,β-unsaturated ketones. For example, triphenylphosphonium methyldide reacts with mesitylstyrylketone resulting in the formation of cyclopropyl ketone (13).\(^{46}\)

![Chemical structure of reaction](attachment:image1)

Among all the synthetic routes available for the preparation of cyclopropanes the reaction of sulphur ylides with activated double bonds is more general, versatile and synthetically attractive. A wide variety of Michael acceptors have been explored with sulphur ylides. Excellent yields of cyclopropanes have been achieved with α,β-unsaturated ketones\(^{44,47-51}\), nitriles\(^{51}\), isonitriles\(^{52}\), sulphones\(^{53,54}\), sulphonamides\(^{55}\) and nitro compounds\(^{56}\) by using oxosulphonium methyldide.

One of the first examples of cyclopropanation involved the addition of dimethyloxosulphonium methyldide with chalcone to produce trans-1-benzoyl-2-phenylcyclopropane\(^{44}\).

![Chemical structure of reaction](attachment:image2)
Electron deficient double bonds promote the cyclopropanation reaction, because the electron withdrawing substituents on the olefin, not only activate the double bond but also stabilize the intermediate betaine. The presence of such intermediates is indicated by their facile collapse to cyclopropanes and supported by the stereochemistry of the product.

\[
\text{S}^+ - \text{C}^- \quad + \quad \text{E} \quad \rightarrow \quad \text{S}^+ \quad \text{C}^- \\
\]

\( \text{X} = \text{O} \) or electron pair

The reaction of dimethylsulphonium phenacylide with arylidenemalono-nitrile produces the corresponding cyclopropane, presumably via the intermediate (14)\textsuperscript{57}. This intermediate can be synthesised by the addition of a malononitrile anion to the vinylsulphonylum salt (15) followed by a proton shift. In both instances, the same cyclopropane was obtained in excellent yields.

\[
\text{PhCO}^- \quad \text{CHS(CH}_3)_2^- \quad + \quad \text{ArCH} = \text{C(CN)}_2^- \\
\]

14

\[
\text{CH(CN)}_2^- \quad + \quad \text{Ar} \quad \text{S(CH}_3)_2^- \quad \quad 15
\]
Bis-Michael systems were reported to undergo mono- or bis-cyclopropanation\textsuperscript{58,59} depending on the ratio of the ylide to the substrate.

In polyunsaturated compounds the site of the attack by sulphur ylides is specific. For example, dimethyloxosulphonium methyldide reacts with carvone to give 16, while the Simmon-Smith's procedure leads to a mixture of two possible isomers\textsuperscript{44}.

Caplin, Ollis and Sutherland\textsuperscript{61} described an unusual addition of a methylene group across the double bond. The methylene was supplied by dimethyloxosulphonium methyldide, but the stability of the product varies with the substituents on the chromone, and it was possible to isolate in a pure state only the tricyclic product (18) derived from 7-methoxychromone (17).
An outstanding example of the chemospecificity of the oxosulphonium ylides is the reaction with cephalosporin (19) derivatives without affecting the sensitive β-lactum.

An interesting application of cyclic sulphur ylides is the synthesis of spin systems - a reaction termed spiroannealation. The easy thermal rearrangement of some of the spiro products expands the usefulness of the process to the synthesis of gem-alkylated cyclopropanes.

The reactions of stabilized ylides with active olefins deserve special mention. The stabilized sulphonium ylides generally undergo cyclopropanation only. The success of this reaction contrasted to the failure to form epoxides even with saturated ketones suggests that the addition of stabilized ylides to
an enone requires the additional delocalization of charge over the conjugated system in the transition state for the reaction to occur. Ylides stabilized by only one group (ketone, ester, sulphone or cyano) normally cyclopropanate typical Michael acceptors. On the other hand, ylides stabilized by two such functions such as dimethylsulphonium dibenzoyl methyldide\textsuperscript{64} failed to react with even the relatively reactive Michael system, chalcone.

The reaction of dimethyl sulphonium phenacylide with trans-benzalacetone produces cis and trans-1,2-dibenzoyl-3-phenylcyclopropanes in which the cis-isomer predominates\textsuperscript{65}.

\[
\begin{align*}
\text{Ph} & = \text{Me} \\
\text{Ph} + \text{PhCOCHS(CH}_3)_2 \quad \xrightarrow{\text{PhH} \ 15 \ h} & \quad \text{Ph} \quad \text{Ph} \\
\end{align*}
\]

Reaction of tropone with the dimethylsulphonium phenacylides generated cyclopropanes involving attack only at the $\alpha,\beta$-double bond\textsuperscript{66}. The cyclopropanated dienone does condense further, but the reaction proceeds at the $\gamma,\delta$-position.
A number of cyclopropane derivatives\textsuperscript{67,68} have been synthesised successfully by the reaction of stabilised sulphonium ylides with activated olefins.

The same methodology was extended for the synthesis of cyclopropyl sulphones and cyclopropylketosulphones. $\alpha',\beta'$-Unsaturated sulphones gave cyclopropanes with dimethylsulphonium methylide and dimethyloxosulphonium methylide in contrast to the $\alpha',\beta'$-unsaturated carbonyl compounds which form epoxides and cyclopropanes respectively\textsuperscript{54}.

Naidu and Reddy\textsuperscript{69} utilized the same procedure to obtain a series of arylcyclopropylsulphones from dimethylsulphonium methylide and $\alpha',\beta'$-unsaturated sulphones. Naidu and Meera Rani\textsuperscript{70} reported stereospecific synthesis of
some 2-(arylcyclopropyl)styryl sulphones by the reaction of trimethylsulphonium iodide (1 mol) with bis(styryl)sulphones. Two moles of trimethylsulphonium iodide gave bis-2(arylcyclopropyl)sulphones.

Naidu and Nirmala\textsuperscript{71} synthesised trisubstituted cyclopropylketosulphones in a similar way using trimethyloxo sulphonium iodide.

Phase-transfer catalysis (ptc) has added another dimension to the applications of sulphur ylides in cyclopropanation reactions. The major advantage of the phase-transfer method lies in its simplicity and efficiency. The formation of cyclopropyl ketones by the reaction of dimethyl-
sulphoxonium methyldie with $\alpha$, $\beta$-unsaturated ketones under phase-transfer conditions was first demonstrated in 1973 by Merz and Markl.\textsuperscript{72}

\[ \text{ArCO} + (\text{CH}_3)_3\text{SOI} \rightarrow \text{ArCO} \]

Naidu and Sarada\textsuperscript{73} reported a series of bis(arylcyclopropyl)ketones from dibenzalacetones and dimethylphenacylsulphonium bromides using phase-transfer method.

\[ \text{O=C} \]

\[ + \]

\[ \text{CH}_2\text{Cl}_2, \text{BTEAC} \]

\[ \text{50\% aq. NaOH} \]

\[ 2\text{Ar'}\text{COCH}_2\text{S(CH}_3\text{)}_2\text{Br} \]

Recently Naidu and Reddy\textsuperscript{74} synthesised cyclopropylketosulphones by treating the bis(phenylsulphonyl)ethylene directly with dimethylsulphonium-phenacylides.
Similarly Naidu and Uma\textsuperscript{75} reported cyclopropylsulphones by simple addition of dimethylsulphonium phenacylides to unsaturated ketosulphones.

Cyclopropane, the first member of the alicyclic carbon compounds, differs largely in its chemical reactivity from the other members of the series as it resembles olefinic double bonded compounds. For example, cyclopropanes react with hydrogen, halogens and hydrogen halides to give the corresponding open chain compounds. This similarity has been attributed to the great amount of strain in the ring with three carbons. The facile cleavage of cyclopropanes has been utilized in synthetic intermediates. For example cyclopropane can be used to introduce n-propyl group on aromatic rings.

\[
\text{Cyclopropane} + \text{AlCl}_3 \rightarrow \text{CH}_2-\text{CH}_2-\text{CH}_3
\]
Carbon chain extension\textsuperscript{76,77} was possible by reductive cleavage of cyclopropanes.

\[
R^1 = R^2 = H, \text{ or } 3,4-(\text{OMe})_2
\]

Trost et al.\textsuperscript{78} exploited the exceptional reactivity of functionalized cyclopropanes like 1,1-bis(benzenesulphonyl)cyclopropane and it was proved to be a valuable synthon for propylene 1,3 dipole.
The characterisation of cyclopropanes by infrared bands in the regions 3100-2900 and 1100-800 cm\(^{-1}\) has been extensively documented\(^{30,79,80}\). The cyclopropanemethylene group gives rise to two high frequency bands (\(\geq CH_2\) symmetric = 3020 cm\(^{-1}\), \(\geq CH_2\) asymmetric = 3085 cm\(^{-1}\)) which can be used to distinguish from the other CH\(_2\) bands of alkane\(^{73}\). The substituents on the cyclopropane ring cause shifts in the position of bands. For example dicyclopentymethane shows bands at 3080 and 3020 cm\(^{-1}\), whereas dicyclopentylketone shows bands at 3110 and 3035 cm\(^{-1}\)\(^{72}\). A number of monosubstituted cyclopropanes showed one band at 3030-2995 cm\(^{-1}\) and another at 3039-3077\(^{30,81,82}\).

In the region 1100-800 cm\(^{-1}\), the cyclopropanes show two bands, one at 1026 cm\(^{-1}\) and another at 866 cm\(^{-1}\) (being deformation mode of the ring and CH deformation modes). In the spectra of a number of hydrocarbons with cyclopropane ring, the band at 866 cm\(^{-1}\) could not be identified\(^{83}\), however bands at 1020-1000 cm\(^{-1}\) were observed.

The band at 1020 cm\(^{-1}\) was considered to be characteristic of cyclopropane ring by several workers\(^{80,83-85}\). It was also suggested that one should use CH\(_2\) stretching frequency data (3100-3070 and 3030-2995 cm\(^{-1}\)) in addition to this 1020 cm\(^{-1}\) band correlation for the identification of cyclopropane. Washburn and Mahoney\(^{86}\) suggested that cyclopropane ring could be more definitely identified in the near infrared region by means of the first overtone (\(\geq 6098\) cm\(^{-1}\)) and combination band at \(\geq 4444\) cm\(^{-1}\).

Carbonyl group shows a characteristic strong band between 1800-1650 cm\(^{-1}\). Carbonyl group in conjugation with double bonds shifts to lower
frequencies\textsuperscript{87}. Similar such shifts were observed when cyclopropane ring is adjacent to carbonyl group\textsuperscript{88-90}. For example, acetone and alkyl cyclopropyl ketone\textsuperscript{87} show bands at 1720 cm\textsuperscript{-1} and 1704-1686 cm\textsuperscript{-1} respectively. Similarly bands for acetophenone were observed at 1695 cm\textsuperscript{-1} and for aryl cyclopropylketone\textsuperscript{91} at 1675 cm\textsuperscript{-1}.

A good number of proton magnetic resonance spectra of cyclopropane derivatives have been recorded. Hydrogens on the cyclopropane ring resonate in the region 0-2 ppm and cyclopropane itself exhibited signal at 0.22 ppm\textsuperscript{92}. Chemical shift data is useful in arriving at the orientation of substituents on cyclopropane\textsuperscript{93-97}.

However, coupling constant values are more useful. The geminal coupling constants in the range of -3.1 to -9.1 Hz were recorded for a number of substituted cyclopropanes\textsuperscript{84,90,96-101}. These values are in agreement with sp\textsuperscript{2} like hybridisation in three membered rings\textsuperscript{102}. Vicinal coupling constants for large number of substituted cyclopropanes including fused rings were recorded as \( J_{\text{cis}} = 7.0-12.6 \text{ Hz} \) and \( J_{\text{trans}} = 4.0-9.6 \text{ Hz} \)\textsuperscript{90,96,100}. The spread of \(^1\text{H} \) NMR signals of trisubstituted cyclopropanes which corresponds to either ABX or AMX patterns, permits the analysis of chemical shifts as well as coupling constants.

\(^{13}\text{C} \) NMR spectral data is also available for cyclopropanes, though not to the same extent of \(^1\text{H} \) NMR data. Cyclopropyl carbons resonated at upfield compared to the other allcyclic compounds. Burke and Lauterbur\textsuperscript{103} measured the \(^{13}\text{C} \) shifts for the cycloalkanes starting from cyclopropane to cycloheptadecane and compared these data for some linear alkanes. This
revealed the high field resonance position of cyclopropane relative to all the higher homologues. In cyclopropane both $^1\text{H}$ and $^{13}\text{C}$ nuclei resonate at relatively high fields.

A comparative study of the $^{13}\text{C}$-NMR spectra of stereoisomeric compounds helps to overcome the complications arising due to stereochemistry of di or trisubstituted cyclopropanes$^{104-106}$.

Large range of chemical shifts and the possibility of predicting the chemical shifts using the additive nature of substituents makes the $^{13}\text{C}$-NMR more useful than $^1\text{H}$-NMR for solving the stereochemical problems of cyclopropanes$^{107,108}$.

The potentiality of mass spectrometry is not exploited in the structural elucidation of cyclopropane derivatives. Very little information has been reported on the mass spectra of cyclopropane systems$^{109-112}$. A systematic study of the behaviour of these molecules under mass spectral conditions will not only throw light in understanding their molecular configurations and chemical bonding but also a valuable addition to the literature.

The fragmentation sequence of the substituted cyclopropanes results in the cleavage of the cyclopropyl ring invariably. The extent of ring cleavage in the transition state depends upon the stabilizing nature of the substituents. The structure of various disubstituted cyclopropanes were in fact determined by the use of mass spectral data$^{113-115}$. The mass spectral studies of cyclopropyl carbonyl compounds have been reported by Bravo and his co-
workers\textsuperscript{116}. The spectra showed molecular ions and in molecules where a benzoyl group is present, the signal at m/z 105 is the base peak. Other characteristic peaks include M\textsuperscript{+} - RCO and related fragments.

In spite of the various methods available for the preparation and study of cyclopropanes as reviewed in the earlier pages, only a few arylcyclopropyl sulphones have been reported in the literature. But there is no report on the preparation and structural studies of cyclopropyl sulphones with benzopyran moiety. It was therefore felt that the preparation of a number of (\textit{E})-7a-[2-(arylsulphonyl)ethenyl]-1a,7a-dihydro-1-arylbenzo[\textit{b}]cyclopropa-[\textit{e}]pyran-7(1\textit{H})-ones, would be quite interesting. Further a study of their infrared, nuclear magnetic resonance and mass spectra would be useful in establishing their stereochemical configurations. The following pages contain essentially a report of these studies.
CHAPTER II
EXPERIMENTAL

General Procedure for the preparation of phenacyl bromides The procedure followed was essentially that of Shevchuk and Dombrovskii\textsuperscript{117}. Bromine (0.1 mole) was added dropwise through a separatory funnel into a 500 ml round bottomed flask containing the appropriate acetophenone (0.1 mole) dissolved in ether (60 ml) and dioxan (30 ml). The contents of the flask were stirred by means of a magnetic stirrer. When the reaction was complete, the solution became colourless and stirring was discontinued. The reaction mixture was diluted with water and the aqueous layer was discarded. Evaporation of the ethereal layer afforded the appropriate phenacyl bromide and it was collected over a Büchner. The solid material was recrystallised from aqueous ethanol.

The phenacylbromides prepared are listed below:

\[ \text{R} \quad \ce{\text{O}} \quad \text{COCH}_2\text{Br} \]

<table>
<thead>
<tr>
<th>( R )</th>
<th>Yield (%)</th>
<th>m.p. ( (^\circ C) )</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>90</td>
<td>49.50 (50)</td>
<td>117</td>
</tr>
<tr>
<td>Cl</td>
<td>95</td>
<td>96.97 (96.5)</td>
<td>117</td>
</tr>
<tr>
<td>( \text{CH}_3 )</td>
<td>85</td>
<td>49.51 (51)</td>
<td>117</td>
</tr>
</tbody>
</table>
Preparation of dimethylphenacylsulphonium bromides The procedure adapted was same as that of Johnson and Amel. Dimethyl sulphide (15 ml) was added to the 50 ml flat bottomed flask containing the appropriate phenacyl bromide (0.05 mole) and stirred for a period of 2 h. The reaction mixture became a hard solid. After washing the product with dry ether it was recrystallised from a mixture of ethanol and ether.

The dimethylphenacylsulphonium bromides prepared are listed below:

\[
R \text{O} \text{COCH}_2\text{SMe}_2\text{Br}
\]

<table>
<thead>
<tr>
<th>R</th>
<th>Yield (%)</th>
<th>m.p (°C)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>85</td>
<td>140-41 (139-40)</td>
<td>118</td>
</tr>
<tr>
<td>Cl</td>
<td>90</td>
<td>128-29 (128-29)</td>
<td>119</td>
</tr>
<tr>
<td>CH₃</td>
<td>90</td>
<td>112-13 (112-13)</td>
<td>119</td>
</tr>
</tbody>
</table>

General procedure for the preparation of dimethylsulphonium phenacylides These stable ylides were prepared according to the procedure of Trost. Into a 250 ml three-necked flask containing a well stirred solution of sodium hydroxide (10 g in 125 ml of water), cooled to 5° under nitrogen atmosphere was added portion wise an appropriate dimethylphenacylsulphonium bromide (0.05 mole). Stirring was discontinued when all the solid material dissolved and the contents of the flask were extracted with chloroform in 10-15 ml quantities several times, until no more solid was left on evaporation of
chloroform extract. The combined chloroform extracts were dried over
anhydrous sodium sulphate. The solvent on evaporation gave a pale oily
product, which solidified in vacuo over phosphorous pentoxide. It was
recrystallised from a mixture of chloroform and carbon tetrachloride.

The dimethylsulphoniumphenacylides prepared are listed below:

\[
\text{R} \quad \text{○} \quad \text{COCHSMe}_2
\]

<table>
<thead>
<tr>
<th>R</th>
<th>Yield (%)</th>
<th>m.p (℃)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>78</td>
<td>76-77 (78-79)</td>
<td>65</td>
</tr>
<tr>
<td>Cl</td>
<td>70</td>
<td>105-107 (106-107)</td>
<td>R5S</td>
</tr>
<tr>
<td>CH₃</td>
<td>80</td>
<td>93-94</td>
<td>119</td>
</tr>
</tbody>
</table>

General procedure for the preparation of (E)-7a-[[2-(arylsulphonyl)ethenyl]-
1a,7a-dihydro-1-arylbenzo[b]cyclopropa[e]pyran-7(1H)-ones (II 1-39)
(E)-3-[[2-(arylsulphonyl)ethenyl]-4H-1-benzopyran-4-one (0.001 mole) and
dimethyl sulphonium phenacylide (0.001 mole) were dissolved in 10-15 ml of
chloroform and refluxed on a water bath. The course of the reaction was
monitored by thin layer chromatography. The period of reaction varied from
15-90 minutes. The reaction mixture was allowed to stand for 2-3 h. The
compound crystallised out, was collected over a Büchner. Recrystallisation
of the product twice from a mixture of chloroform and light petroleum (3:1)
afforded an analytical sample.
(E)-7a-[2-(Phenylsulphonyl)ethenyl]-1a,7a-dihydro-1-benzoylbenzo[b]cyclopenta[e]pyran-7(1H)-one (II-1) Cyclopropanation was effected by refluxing a mixture of 0.312 g (0.001 mole) of (E)-3-[2-(phenylsulphonyl)ethenyl]-4H-1-benzopyran-4-one and 0.18 g (0.001 mole) of dimethylsulphonium phenacylide in 10 ml of chloroform for 30 minutes on a water bath. On working up, as described in the general procedure, the product isolated was collected over a Buchner. Recrystallisation of the solid material, twice from light petroleum ether and chloroform mixture (1:3) yielded (0.3 g, 63%) colourless crystals, m.p. 168-70°.

Anal. Calcd. for C_{25}H_{18}O_5S: C 69.76; H 4.18.
Found: C 69.5; H 4.20.

IR (KBr): 3040, 1670, 1650 (C=O), 1600 (C=C), 1310 (SO$_2$ asym), 1145 (SO$_2$ sym), 1040 (ring deform), 980 (S CH out-of-plane) and 860 cm$^{-1}$.

$^1$HNMR (CDCl$_3$): $\delta$ 3.63 (1H, d, H-1), 5.15 (1H, d, H-1a; $^3$J$_{H-1, H-1a}$ = 4.5 Hz), 6.70-7.76[16H, m, ArH (14) + vinyl H (2)].

M.S. m/z (% relative intensity): 430 (6.3), 310 (16.7), 289 (50), 263 (2.6), 261 (12.5), 246 (6.3), 205 (2.1), 184 (2.1), 171 (10.4), 158 (2.1), 143 (2.1), 141 (18.8), 121 (64.6), 120 (4.2), 118 (2.1), 115 (18.8), 105 (100), 92 (8.4), 89 (4.2) and 77 (41.6).

(E)-7a-[2-([(4-Bromophenyl)sulphonyl])ethenyl]-1a,7a-dihydro-1-benzoylbenzo[b]cyclopenta[e]pyran-7(1H)-one (II-2) (E)-3-[2-([(4-Bromophenyl)sulphonyl] ethenyl]-4H-1-benzopyran-4-one (0.391 g, 0.001 mole) was added to a solution of dimethylsulphonium phenacylide (0.18 g, 0.001 mole) in chloroform (15 ml) and refluxed for 60 minutes on a water bath. On working up the reaction
mixture as described in the general procedure the product obtained was collected at the pump. Recrystallisation of the compound from a mixture of chloroform and light petroleum (3:1), afforded 0.45 g (79%) of pure II-2 as colourless crystals, m.p. 180-82°.

Anal. Calcd. for $C_{25}H_{17}O_5SBr$: C 58.93; H 3.33. Found: C 58.50; H 3.40.

IR (KBr): 3050, 1665 (C=O), 1600 (C=C), 1320 (SO_2 asym), 1150 (SO_2 sym), 1060 (ring deform), 975 (δ CH out-of-plane) and 860 cm\(^{-1}\).

(E)-7a-[2-[(4-Chlorophenyl)sulphonyl]ethenyl]-1a,7a-dihydro-1-benzoylbenzo[b]cyclopropa[e]pyran-7(1H)-one(II-3) A mixture of 0.347 g (0.001 mole) of (E)-3-[2-[(4-chlorophenyl)sulphonyl]ethenyl]-4H-1-benzopyran-4-one and 0.18 g (0.001 mole) of dimethylsulphonium phenacyclide in 15 ml of chloroform were refluxed on a water bath for 60 minutes. The product was isolated as per the general procedure described and on recrystallisation of the material twice from a mixture of light petroleum and chloroform (1:3) afforded 0.3 g (57%) of pure compound II-3 as colourless crystals, m.p. 178-79°.

Anal. Calcd. for $C_{25}H_{17}O_5SCl$: C 64.59; H 3.66. Found: C 64.60; H 3.70.

IR (KBr): 3060, 1650 (C=O), 1610 (C=C), 1310 (SO_2 asym), 1140 (SO_2 sym), 1070 (ring deform), 980 (δ CH out-of-plane) and 860 cm\(^{-1}\).

$^1$H NMR (CDCl_3): δ 3.64 (1H, d, H-1), 5.18 (1H, d, H-1a; $^3$J_H-1, H-1a = 4.5 Hz), 6.71-7.76 [(15H, m, ArH (13) + vinyl H (2)].
(E)-7a-[2-[(4-Phenylsulphonyl)]ethenyl]-1a,7a-dihydro-5-bromo-1-benzo[\text{b}](E)cyclopropa[e]pyran-7(1H)-one (II-4) To a solution of 0.391 g (0.001 mole) of (E)-3-[2-(phenylsulphonyl)ethenyl]-6-bromo-4H-1-benzopyran-4-one in 15 ml chloroform was added 0.18 g (0.001 mole) of dimethylsulphonium phenacylide and refluxed for 30 minutes on a water bath. On working up the reaction mixture, as described in the general procedure, the product obtained was collected over a Buchner. The material was recrystallised from a mixture of chloroform and light petroleum to give 0.45 g (79%) of an analytical sample of II-4 as yellow crystals, melting at 182-83°.

Anal. Calcd. for C_{25}H_{17}O_{5}SBr: C 58.93; H 3.33.
Found: C 58.8; H 3.30.

IR (KBr): 3040, 1670, 1655 (C=O), 1600 (C=C), 1300 (SO_2 asym), 1140 (SO_2 sym), 1060 (ring deform), 980 (\text{CH out-of-plane}) and 870 cm\(^{-1}\).

\(^1\text{H} NMR (\text{CDCl}_3): \delta 3.53 (1H, d, J-H-1), 5.10 (1H, d, H-la; 3J_{H-1, H-la} = 4.5 Hz), 6.30-7.65 [15H, m, ArH (13) + vinyl H (2)].

(E)-7a-[2-[(4-Bromophenyl)sulphonyl]ethenyl]-1a,7a-dihydro-5-bromo-1-benzo[\text{b}](E)cyclopropa[e]pyran-7(1H)-one (II-5) Cyclopropanation was accomplished by refluxing a mixture containing 0.47 g (0.001 mole) of (E)-3-[2-[(4-bromophenyl)sulphonyl]ethenyl]-6-bromo-4H-1-benzopyran-4-one and 0.18 g (0.001 mole) of dimethylsulphonium phenacylide in 10 ml of chloroform for a period of 60 minutes. On working up the reaction mixture as per the general procedure, the compound obtained was recrystallised twice from a mixture of chloroform and light petroleum to afford 0.52 g (80%) of II-5 as yellow needle shaped crystals, melting at 198-99°.
Anal. Calcd. for C$_{25}$H$_{16}$O$_5$SBr$_2$: C 51.02; H 2.72.

Found: C 51.0; H 2.9.

IR (KBr): 3060, 1650 (C=O), 1600 (C=C), 1310 (SO$_2$ asym), 1140 (SO$_2$ sym), 1070 (ring deform), 980 (S-CH out-of-plane) and 860 cm$^{-1}$.

($E$)-7a-[2-[4-Chlorophenyl)sulphonyl]ethenyl]-1a,7a-dihydro-5-bromo-1-benzoylbenzo[b]cyclopropa[e]pyran-7(1H)-one (II-6) A mixture containing 0.426 g (0.001 mole) of ($E$)-3-[2-[(4-chlorophenyl)sulphonyl]ethenyl]-6-bromo-4H-1-benzopyran-4-one, and 0.18 g (0.001 mole) of dimethylsulphonium phenacylide in 10 ml of chloroform was refluxed for 30 minutes on a water bath. The product formed was collected over a Büchner. Recrystallisation of the above material from a mixture of solvents (chloroform, light petroleum 3:1) afforded 0.48 g (79%) of pure II-6 as light yellow crystals, m.p. 176-77$^0$.

Anal. Calcd. for C$_{25}$H$_{16}$O$_5$SBrCl: C 55.19; H 2.94.

Found: C 55.0; H 3.0.

IR (KBr): 3040, 1670, 1650 (C=O), 1600 (C=C), 1310 (SO$_2$ asym), 1150 (SO$_2$ sym), 1060 (ring deform), 990 (S-CH out-of-plane) and 870 cm$^{-1}$.

($E$)-7a-[2-[(Phenylsulphonyl)ethenyl]-1a,7a-dihydro-5-chloro-1-benzoylbenzo[b]cyclopropa[e]pyran-7(1H)-one (II-7) A solution of ($E$)-3-[2-(phenylsulphonyl)ethenyl]-6-chloro-4H-1-benzopyran-4-one (0.347 g, 0.001 mole) and dimethylsulphonium phenacylide (0.18 g, 0.001 mole) in chloroform (10 ml) was refluxed on a water bath for 15 minutes. The reaction mixture was
allowed to stand for 2 h at room temperature and the product crystallised
was collected over a Buchner. It was recrystallised from a mixture of
chloroform and l-lith petroleum to give 0.38 g (72%) of II-7 as light yellow
crystals melting at 187-88°.

Anal. Calcd. for C_{25}H_{17}O_{5}SCl: C 64.58; H 3.65.
Found: C 64.5; H 3.7.

IR (KBr): 3040, 1650 (C=O), 1600 (C=C), 1310 (SO_{2} asym), 1140 (SO_{2}
sym), 1060 (ring deform), 980 (S CH out-of-plane) and 870 cm^{-1}.

(E)-7a-[2-[(4-Bromophenyl)sulphonyl]ethenyl]-1a,7a-dihydro-5-chloro-1-
benzoylbenzo[b]cyclopropa[e]pyran-7(1H)-one (II-8) Cyclopronation was
effected by refluxing a solution containing 0.426 g (0.001 mole) of (E)-3-[2-
[(4-bromophenyl)sulphonyl]ethenyl]-6-chloro-4H-1-benzopyran-4-one and 0.18 g
(0.001 mole) of dimethylsulphonium phenacylilide in 15 ml of chloroform, on a
water bath, for a period of 30 minutes. On working up the reaction mixture
as described in the general procedure, the product separated was collected
over a Buchner and was recrystallised twice from a mixture of chloroform
and light petroleum to yield 0.46 g (76%) of II-8 as yellow crystals, m.p.
192-93°.

Anal. Calcd. for C_{25}H_{16}O_{5}BrCl: C 55.19; H 2.94.
Found: C 55.1; H 3.0.

IR (KBr): 3040, 1650 (C=O), 1600- (C=C), 1320 (SO_{2} asym), 1140 (SO_{2}
sym), 1060 (ring deform), 975 (S CH out-of-plane) and 870 cm^{-1}. 
(E)-7a-[2-[(4-Chlorophenyl)sulphonyl]ethenyl]-1a,7a-dihydro-5-chloro-1-benzo[b]cyclopropa[e]pyran-7(1H)-one (II-9) Dimethylsulphonium-phenacylide (0.18 g, 0.001 mole) was added to a solution of (E)-3-[2-[(4-chlorophenyl)sulphonyl]ethenyl]-6-chloro-4H-1-benzopyran-4-one (0.381 g, 0.001 mole) in chloroform (10 ml) and refluxed on a water bath for 30 minutes. The reaction mixture was worked up as per the general procedure and the product was collected at the pump. Recrystallisation of the solid material from chloroform and light petroleum mixture (3:1) afforded 0.35 g (62%) of II-9 as colourless crystals melting at 200-201°.


Found: C 60.0; H 3.1.

IR (KBr): 3060, 1650 (C=O), 1600 (C=C), 1310 (SO₂ asym), 1140 (SO₂ sym), 1060 (ring deform), 980 (CH out-of-plane) and 870 cm⁻¹.

(E)-7a-[2-(Phenylsulphonyl)ethenyl]-1a,7a-dihydro-5-methyl-1-benzo[b]cyclopropa[e]pyran-7(1H)-one (II-10) To a solution of 0.326 g (0.001 mole) of (E)-3-[2-(phenylsulphonyl)ethenyl]-6-methyl-1-benzopyran-4-one in 10 ml of chloroform, 0.18 g (0.001 mole) of dimethylsulphonium phenacylide was added and refluxed on a water bath for 60 minutes. The product was worked up as described in the general procedure and the compound was collected over a Buchner. Recrystallisation of the compound from a mixture of chloroform and light petroleum (3:1) gave 0.35 g (70%) of pure II-10 as colourless crystals melting at 186-187°.
Anal. Calcd. for $\text{C}_{26}\text{H}_{20}\text{O}_{5}\text{S}$: C 70.27; H 4.5.

Found: C 70.6; H 4.6.

IR (KBr): 3040, 1650 (C=O), 1610 (C=C), 1310 (SO$_2$ asym), 1145 (SO$_2$ sym), 1080 (ring deform), 980 ($\delta$ CH out-of-plane) and 865 cm$^{-1}$.

$^1$H NMR (CDCl$_3$): $\delta$ 2.3 (3H, s, CH$_3$), 3.63 (1H, d, H-1), 5.15 (1H, d, H-1a; $^3$$J_{H-1,H-1a}$ = 4.5 Hz), 6.63-7.56 [15H, m, ArH (13) + vinyl H (2)].

(E)-7a-[2-[(4-Bromophenyl)sulphonyl]ethenyl]-1a,7a-dihydro-5-methyl-1-benzoylbenzo[b]cyclopropa[e]pyran-7(1H)-one (II-11) A mixture of 0.405 g (0.001 mole) of (E)-3-[2-[(4-bromophenyl)sulphonyl]ethenyl]-6-methyl-4H-1-benzopyran-4-one and 0.18 g (0.001 mole) of dimethylsulphonium phenacylide in 15 ml of chloroform was refluxed on a water bath for 60 minutes. The product formed was collected over a Büchner after the completion of the reaction. Recrystallisation of the filtered material from a mixture of chloroform and light petroleum (3:1) gave an analytical sample (0.52 g, 89%) as colourless crystals, m.p. 179-80$^\circ$.

Anal. Calcd. for $\text{C}_{26}\text{H}_{19}\text{O}_{5}\text{SBr}$: C 59.65; H 3.63

Found: C 60.0; H 3.6.

IR (KBr): 3080, 1670, 1655 (C=O), 1610 (C=C), 1305 (SO$_2$ asym), 1140 (SO$_2$ sym), 1080 (ring deform), 990 ($\delta$ CH out-of-plane) and 870 cm$^{-1}$.

$^1$H NMR (CDCl$_3$): $\delta$ 2.27 (3H, s, CH$_3$), 3.60 (1H, d, H-1), 5.12 (1H, d, H-1a; $^3$$J_{H-1,H-1a}$ = 4.51 Hz), 6.60-7.50 [14H, m, ArH (12) + vinyl H (2)].
(E)-7a- [2-[(4-Chlorophenyl)sulphonyl]ethenyl]-1a,7a-dihydro-5-methyl-1-benzoylbenzo[b]cyclopropa[e]pyran-7(1H)-one (II-12) To a solution containing 0.361 g (0.001 mole) of (E)-3-[2-[(4-chlorophenyl)sulphonyl] ethenyl]-6-methyl-4H-1-benzopyran-4-one in 15 ml of chloroform, 0.18 g (0.001 mole) of dimethylsulphonium phenacylide was added and refluxed on a water bath for 60 minutes. The reaction mixture on working up as per the general procedure, gave a crystalline product which was collected over a Büchner. Recrystallisation of the product from a mixture of chloroform and light petroleum (3:1) gave 0.4 g (74%) of II-12 as colourless crystals, melting at 216-180°.

Anal. Calcd. for C26H19O5SCl: C 65.2; H 3.97.
Found: C 65.4; H 3.8.

IR (KBr): 3060, 1650 (C=O), 1610 (C=C), 1310 (SO2 asym), 1150 (SO2 sym), 1060 (ring deform), 980 (\(\delta\) CH out-of-plane) and 870 cm\(^{-1}\).

(E)-7a- [2-(Phenylsulphonyl)ethenyl]-1a,7a-dihydro-5-methoxy-1-benzoylbenzo[b]cyclopropa[e]pyran-7(1H)-one (II-13) Cyclopropanation was achieved by refluxing a solution of 0.342 g (0.001 mole) of (E)-3-[2-(phenylsulphonyl)-ethenyl]-6-methoxy-4H-1-benzopyran-4-one and 0.18 g (0.001 mole) of dimethylsulphonium phenacylide in 10 ml of chloroform on a water bath for 60 minutes. On working up the reaction mixture as per the general procedure, a colourless crystalline product was obtained. Recrystallisation of the product from a mixture of chloroform light petroleum (3:1), afforded 0.42 g (81%) of II-13 as colourless crystals, melting at 205-206°.
Anal. Calcd. for C_{26}H_{20}O_{6}S: C 67.82; H 4.34.

Found: C 67.9; H 4.5.

IR (KBr): 3040, 1670, 1650 (C=O), 1610 (C=C), 1320 (SO_{2} asym), 1140 (SO_{2} sym), 1080 (ring deform), 980 (\delta \text{CH out-of-plane}) and 870 cm^{-1}.

{^1H} NMR (CDCl_{3}): 8 3.66 (1H, d, H-1), 3.73 (3H, s, CH_{3}O), 5.13 (1H, d, H-1a; J_{H-1,H-1a} = 4.5 \text{ Hz}), 6.63-7.56 [15H, m, ArH (13H) + vinyl H (2)].

(\varepsilon)-7a-[2-[(4-Bromophenyl)sulphonyl]ethenyl]-1a,7a-dihydro-5-methoxy-1-benzo[b]cyclopropa[e]pyran-7(1H)-one (II-14) A solution containing 0.342 g (0.001 mole) of (\varepsilon)-3-[2-[(4-bromophenyl)sulphonyl]ethenyl]-6-methoxy-4H-1-benzopyran-4-one and 0.18 g (0.001 mole) of dimethylsulphonyl phenacylde in 15 ml of chloroform was refluxed on a water bath for 60 minutes. On working up the reaction mixture, the solid material obtained was collected over a Büchner. This product on recrystallisation from a solvent mixture (chloroform and light petroleum, 3:1) afforded 0.42 g (81%) of an analytically pure sample II-14 as colourless crystals, m.p. 198-99\(^{0}\).

Anal. Calcd. for C_{26}H_{19}O_{6}SBr: C 57.8; H 3.52.

Found: C 57.9; H 3.6.

IR (KBr): 3060, 1660, 1645 (C=O), 1600 (C=C), 1300 (SO_{2} asym), 1140 (SO_{2} sym), 1060 (ring deform), 990 (\delta \text{CH out-of-plane}) and 860 cm^{-1}.

{^1H} NMR (CDCl_{3}): 8 3.56 (1H, d, H-1), 3.73 (3H, s, CH_{3}O), 5.16 (1H, d, H-1a; J_{H-1,H-1a} = 4.5 \text{ Hz}), 6.36-7.56 [14H, m, ArH (12) + vinyl H (2)].
(E)-7a-[2-[(4-Chlorophenyl)sulphonyl]ethenyl]-1a,7a-dihydro-5-methoxy-1-
benzoylbenzo[b]cyclopropa[e]pyran-7(1H)-one (II-15) A mixture of 0.422 g
(0.001 mole) of (E)-3-[2-[(4-chlorophenyl)sulphonyl]ethenyl]-6-methoxy-4H-1-
benzopyran-4-one and 0.18 g (0.001 mole) of dimethylsulphonium phenacylide
in 10 ml of chloroform was refluxed on a water bath for 60 minutes. The
product obtained on working up the reaction mixture as per the general
procedure, was collected over a Büchner by filtration. The filtered material
on recrystallisation from a mixture of chloroform and light petroleum (3:1)
gave 0.52 g (86%) of II-15 as colourless crystals, m.p. 186-87⁰.

Anal. Calcd. for C_{26}H_{19}O_6SCl: C 63.09; H 3.84.
Found: C 63.20; H 3.90.

IR (KBr): 3040, 1660, 1645 (C=O), 1600 (C=C), 1320 (SO₂ asym), 1140
(SO₂ sym), 1060 (ring deform), 980 (δCH out-of-plane) and 870 cm⁻¹.

(E)-7a-[2-(Phenylsulphonyl)ethenyl]-1a,7a-dihydro-1-(4-chlorobenzoyl)benzo[b]-
cyclopropa[e]pyran-7(1H)-one (II-16) Cyclopropanation was accomplished by
refluxing a mixture of 0.312 g (0.001 mole) of (E)-3-[2-(phenylsulphonyl)-
ethenyl]-4H-1-benzopyran-4-one and 0.215 g (0.001 mole) of dimethyl-
sulphonium 4-chlorophenacylide in 15 ml of chloroform, on a water bath for
a period of 60 minutes. On working up the reaction mixture as described in
the general procedure, the solid material obtained was collected over a
Büchner by filtration. Recrystallisation of the product from a mixture of
chloroform and light petroleum afforded 0.32 g (51%) of II-16 as colourless
crystalline solid melting at 184-85⁰.
Anal. Calcd. for C_{25}H_{17}O_5Cl: C 64.59; H 3.66.

Found: C 64.40; H 3.80.

IR (KBr): 3080, 1675 (C=O), 1600 (C=C), 1310 (SO_2 asym), 1150 (SO_2 sym), 1010 (ring deform), 980 (C-H out-of-plane) and 855 cm^{-1}.

^1H NMR (CDCl_3): \( \delta \) 3.58 (1H, d, H-1), 5.15 (1H, d, H-1a; \( J_{H-1,H-1a} = 4.5 \) Hz), 6.71-7.76 [15H, m, ArH (13) + vinyl (2)].

M.S. m/z (% relative intensity): 466 (1.3), 464 (3.8), 346 (3.8), 344 (7.7), 325 (6.4), 323 (15.4), 282 (1.3), 280^+(5.1), 205 (1.3), 184 (2.6), 179 (1.3), 177 (1.3), 171 (10.3), 151 (2.6), 149 (5.1), 141 (42.2), 139 (100), 121 (28.2), 120 (5.1), 118 (1.3), 113 (15.4), 111 (38.4), 104 (3.8) 92 (10.1) and 77 (28.2).

(E)-7a-[2-[(4-Bromophenyl)sulphonyl]ethenyl]-1a,7a-dihydro-1-(4-chlorobenzo[b]cyclopropa[e]pyran-7(1H)-one (II-17) To a solution of 0.391 g (0.001 mole) of (E)-3-[2-[(4-bromophenyl)sulphonyl]ethenyl]-4H-1-benzopyran-4-one in 15 ml of chloroform, 0.215 g (0.001 mole) of dimethylsulphonium 4-chlorophenacylide was added and refluxed on a water bath for 60 minutes. The reaction mixture on working up as per the general procedure, gave a solid which was collected over a Büchner. This product on recrystallisation from chloroform and light petroleum (3:1) afforded 0.4 g (66%) of II-17 as colourless crystalline solid, melting at 190-92^0.

Anal. Calcd. for C_{25}H_{16}O_5SBrCl: C 55.19; H 2.94.

Found: C 55.30; H 2.90.

IR (KBr): 3080, 1670 (C=O), 1610 (C=C), 1310 (SO_2 asym), 1150 (SO_2 sym), 1040 (ring deform), 980 (C-H out-of-plane) and 860 cm^{-1}.

^1H NMR (CDCl_3): \( \delta \) 3.5 (1H, d, H-1), 5.15 (1H, d, H-1a; \( J_{H-1,H-1a} = 4.5 \) Hz), 6.69-7.76 [14H, m, ArH (12) + vinyl H (2)].
(E)-7a-[2-[(4-Chlorophenyl)sulphonyl]ethenyl]-1a,7a-dihydro-1-(4-chlorobenzoyl)-benzo[b]cyclopropa[e]pyran-7(1H)-one (II-18) A mixture of 0.347 g (0.001 mole) of (E)-3-[2-[(4-chlorophenyl)sulphonyl]ethenyl]-4H-1-benzopyran-4-one and 0.215 g (0.001 mole) of dimethylsulphonium 4-chlorophenacylide were dissolved in 10 ml of chloroform and refluxed on a water bath for 60 minutes. On working up the reaction mixture as described in the general procedure, a solid material obtained was recrystallised from a mixture of chloroform and light petroleum (3:1), yielding 0.35 g (62%) of II-18 as colourless crystals melting at 203-204°.

Anal. Calcd. for C_{25}H_{16}O_{5}SCl_{2}: C 60.2; H 3.2. Found: C 60.70; H 3.1.

IR (KBr): 3080, 1670 (C=O), 1600 (C=C), 1310 (SO_2 asym), 1150 (SO_2 sym), 1040 (ring deform), 970 (SCH out-of-plane) and 860 cm⁻¹.

(E)-7a-[2-(Phenylsulphonyl)ethenyl]-1a,7a-dihydro-5-bromo-1-(4-chlorobenzoyl)benzo[b]cyclopropa[e]pyran-7(1H)-one (II-19) To a solution of 0.391 g (0.001 mole) of (E)-3-[2-(phenylsulphonyl)ethenyl]-6-bromo-4H-1-benzopyran-4-one in 15 ml of chloroform, 0.215 g (0.001 mole) of dimethylsulphonium-4-chlorophenacylide was added and refluxed on a water bath for 30 minutes. The product from the reaction mixture was worked up as per the general procedure and the compound was collected using a Buchner. The material on recrystallisation from a mixture of chloroform and light petroleum (3:1), gave 0.38 g (63%) of pure II-19 as colourless crystals melting at 196-97°.
Anal. Calcd. for $C_{25}H_{16}O_5SBrCl$: C 55.19; H 2.94.

Found: C 55.10; H 3.0.

IR (KBr): 3080, 1670 (C=O), 1600 (C=C), 1310 (SO$_2$ asym), 1150 (SO$_2$ sym), 1040 (ring deform), 990 ($\delta$ CH out-of-plane) and 860 cm$^{-1}$.

$^1$H NMR (CDCl$_3$): $\delta$ 3.53 (1H, d, H-1), 5.12 (1H, d, H-1a; $^3$J$_{H-1,H-1a}$ = 4.5 Hz), 6.56-7.78 [14H, m, ArH (12) + vinyl H (2)].

$^{(E)}$-7a-[(2-[(4-Bromophenyl)sulphonyl]ethenyl]-1a,7a-dihydro-5-bromo-1-(4-chlorobenzoyl)benzo[b]cyclopropa[e]pyran-7(1H)-one (II-20) Cyclopropanation was effected by refluxing a solution containing a mixture of 0.47 g (0.001 mole) of $^{(E)}$-3-[2-[(4-bromophenyl)sulphonyl]ethenyl]-6-bromo-4H-1-benzopyran-4-one and 0.215 g (0.001 mole) of dimethylsulphonium 4-chlorophenacyclide in 15 ml of chloroform on a water bath for 60 minutes. The product obtained from the reaction mixture was collected on a Buchner and recrystallised using chloroform and light petroleum (3:1) mixture, to get 0.58 g (85%) of II-20 as colourless crystals melting at 178-79$^0$.

Anal. Calcd. for $C_{25}H_{15}O_5SBr_2Cl$: C 48.19; H 2.41.

Found: C 48.0; H 2.50.

IR (KBr): 3080, 1670 (C=O), 1610 (C=C), 1310 (SO$_2$ asym), 1150 (SO$_2$ sym), 1040 (ring deform), 980 ($\delta$ CH out-of-plane) and 860 cm$^{-1}$.

$^{(E)}$-7a-[2-[(4-Chlorophenyl)sulphonyl]ethenyl]-1a,7a-dihydro-5-bromo-1-(4-chlorobenzoyl)benzo[b]cyclopropa[e]pyran-7(1H)-one (II-21) Addition of 0.215 g (0.001 mole) of dimethylsulphonium 4-chlorophenacyclide to a solution containing 0.426 g (0.001 mole) of $^{(E)}$-3-[2-[(4-chlorophenyl)sulphonyl]-
ethenyl]-6-bromo-4H-1-benzopyran-4-one in 15 ml of chloroform and refluxing on a waterbath for a period of 60 minutes gave a solid material on working out the reaction mixture as per the general procedure. The product was collected at the pump and recrystallised from a solvent mixture (chloroform, light petroleum, 3:1) to get 0.54 g (84%) of pure II-21 as colourless crystals melting at 201-202°.

Anal. Calcd. for C_{25}H_{15}O_5SBrCl_2: C 51.90; H 2.59.

Found: C 52.1; H 3.0.

IR (KBr): 3080, 1670 (C=O), 1600 (C=C), 1310 (SO_2 asym), 1150 (SO_2 sym), 1020 (ring deform), 980 (S CH out-of-plane) and 855 cm\(^{-1}\).

(E)-7a-[(2-(Phenylsulphonyl)ethenyl]-1a,7a-dihydro-5-chloro-1-(4-chlorobenzoyl)-benzo[b]cyclopropa[e]pyran-7(1H)-one (II-22) A mixture of 0.347 g (0.001 mole) of (E)-3-[(2-(phenylsulphonyl)ethenyl]-6-chloro-4H-1-benzopyran-4-one and 0.215 g (0.001 mole) of dimethylsulphonium 4-chlorophenacylide was dissolved in 15 ml of chloroform and refluxed on a water bath for 60 minutes. On working up of the reaction mixture as described in the general procedure, the product obtained was collected at the pump. Recrystallisation of the solid material from chloroform-light petroleum mixture (3:1) gave 0.32 g (57%) of pure II-22 as pale yellow crystals melting at 189-90°.

Anal. Calcd. for C_{25}H_{16}O_5SCl_2: C 60.12; H 3.20.

Found: C 60.0; H 3.4.

IR (KBr): 3080, 1670 (C=O), 1600 (C=C), 1300 (SO_2 asym), 1150 (SO_2 sym), 1010 (ring deform), 970 (S CH out-of-plane) and 845 cm\(^{-1}\).
(E)-7a-[2-[(4-Bromophenyl)sulphonyl]ethenyl]-1a,7a-dihydro-5-chloro-1-(4-chlorobenzoyl)-benzo[b]cyclopropa[e]pyran-7(1H)-one (II-23) A solution containing a mixture of 0.426 g (0.001 mole) of (E)-3-[2-[(4-bromophenyl)sulphonyl]ethenyl]-6-chloro-4H-1-benzopyran-4-one and 0.215 g (0.001 mole) of dimethylsulphonium 4-chlorophenacylide in 10 ml of chloroform was refluxed on a waterbath for 60 minutes. By adapting the general procedure described earlier, the reaction mixture was worked up to yield a solid material. Recrystallisation of the product from a mixture of chloroform and light petroleum (3:1) afforded 0.52 g (81%) of II-23 as colourless crystals melting at 172-73°.

Anal. Calcd. for C_{25}H_{15}O_{5}SBrCl_{2}: C 51.9; H 2.59.

Found: C 51.8; H 2.6.

IR (KBr): 3080, 1670 (C=O), 1610 (C=C), 1310 (SO_{2} asym), 1150 (SO_{2} sym), 1010 (ring deform), 970 (S CH out-of-plane) and 860 cm^{-1}.

(E)-7a-[2-[(4-Chlorophenyl)sulphonyl]ethenyl]-1a,7a-dihydro-5-chloro-1-(4-chlorobenzoyl)benzo[b]cyclopropa[e]pyran-7(1H)-one (II-24) A mixture of 0.381 g (0.001 mole) of (E)-3-[2-[(4-chlorophenyl)sulphonyl]ethenyl]-6-chloro-4H-1-benzopyran-4-one and 0.215 g (0.001 mole) of dimethylsulphonium 4-chlorophenacylide was dissolved in 15 ml of chloroform and refluxed on a waterbath for a period of 30 minutes. The reaction mixture was worked up as per the general procedure to yield a solid product. The product was recrystallised from chloroform - light petroleum (3:1) mixture to afford 0.50 g (94%) of II-24 as pure colourless crystals melting at 189-90°.
Anal. Calcd. for C_{25}H_{15}O_5Cl_3: C 56.23; H 2.81.
Found: C 56.5; H 2.90.

IR (KBr): 3080, 1670 (C=O), 1610 (C=C), 1310 (SO_2 asym), 1150 (SO_2 sym), 1010 (ring deform), 970 (δ CH out-of-plane) and 860 cm\(^{-1}\).

\(^1\)H NMR (CDCl_3): δ 3.53 (1H, d, H-1), 5.10 (1H, d, H-1a; J_{H-1,H-1a} = 4.5 Hz), 6.68-7.63 [13H, m, ArH (11) + vinyl H (2)].

\((E)-7a-[2-(Phenylsulphonyl)ethenyl]-1a,7a-dihydro-5-methyl-1-(4-chlorobenzoyl)-benzo[b]cyclopropa[e]pyran-7(1H)-one (II-25)\) Cyclopropanation was effected by refluxing a solution containing 0.326 g (0.001 mole) of \((E)-3-[2-(phenylsulphonyl)ethenyl]-6-methyl-4H-1-benzopyran-4-one and 0.215 g (0.001 mole) of dimethylsulphonium 4-chlorophenacylide in 15 ml of chloroform, on a waterbath for a period of 45 minutes. On working up the reaction mixture as described in the general procedure, a solid material was isolated. Recrystallisation of the product from chloroform and light petroleum mixture (3:1) gave 0.45 g (94%) of II-25 as yellow crystals, m.p. 169-70°.

Anal. Calcd. for C_{26}H_{19}O_5SCl: C 65.20; H 3.97.
Found: C 65.7; H 4.0.

IR (KBr): 3080, 1670 (C=O), 1610 (C=C), 1310 (SO_2 asym), 1150 (SO_2 sym), 1010 (ring deform), 980 (δ CH out-of-plane) and 860 cm\(^{-1}\).

\(^1\)H NMR (CDCl_3): δ 2.30 (3H, s, CH_3), 3.53 (1H, d, H-1), 5.10 (1H, d, H-1a; J_{H-1,H-1a} = 4.5 Hz), 6.68-7.56 [14H, m, ArH (12) + vinyl H (2)].
(E)-7a-[2-[(4-Bromophenyl)sulphonyl]ethenyl]-1a,7a-dihydro-5-methyl-1-(4-chlorobenzoyl)-benzo[b]cyclopropa[e]pyran-7(1H)-one (II-26) To a solution containing 0.326 g (0.001 mole) of (E)-3-[2-[(4-bromophenyl)sulphonyl]ethenyl]-6-methyl-4H-1-benzopyran-4-one in 15 ml of chloroform was added to 0.215 g (0.001 mole) of dimethylsulphonium 4-chlorophenacylide and refluxed on a waterbath for a period of 60 minutes. The reaction mixture was worked up as per the general procedure to get the product. Recrystallisation of this material from chloroform - light petroleum mixture (3:1) afforded 0.51 g (91%) of II-26 as colourless crystals melting at 192-93°.

Anal. Calcd. for C_{26}H_{18}O_{5}SBrCl: C 55.96; H 3.23.
Found: C 55.5; H 3.20.

IR (KBr): 3080, 1670 (C=O), 1610 (C=C), 1310 (SO\textsubscript{2} asym), 1150 (SO\textsubscript{2} sym), 1040 (ring deform), 970 (S CH out-of-plane) and 850 cm\textsuperscript{-1}.

\(^1\)H NMR (CDCl\textsubscript{3}): \(\delta\) 2.28 (3H, s, CH\textsubscript{3}), 3.53 (1H, d, H-1), 5.10 (1H, d, H-1a; \(^3\)J\textsubscript{H-1,H-1a} = 4.5 Hz), 6.50-7.56 [13H, m, ArH (11) + vinyl H (2)].

(E)-7a-[2-[(4-Chlorophenyl)sulphonyl]ethenyl]-1a,7a-dihydro-5-methyl-1-(4-chlorobenzoyl)-benzo[b]cyclopropa[e]pyran-7(1H)-one (II-27) (E)-3-[2-[(4-Chlorophenyl)sulphonyl]ethenyl]-6-methyl-4H-1-benzopyran-4-one (0.361 g; 0.001 mole) and dimethylsulphonium 4-chlorophenacylide (0.215 g, 0.001 mole) were dissolved in 15 ml of chloroform and refluxed on a waterbath for a period of 60 minutes. The reaction mixture on working up as in the earlier methods, afforded a solid product. On recrystallisation of the solid product from a mixture of chloroform and light petroleum (3:1), 0.4 g (78%) of II-27 as light yellow crystals melting at 218-26°, was obtained.
Anal. Calcd. for $C_{26}H_{18}O_5SCL_2$: C 60.8; H 3.50.

Found: C 61.0; H 3.60.

IR (KBr): 3080, 1670 (C=O), 1600 (C=C), 1310 (SO$_2$ asym), 1150 (SO$_2$ sym), 1010 (ring deform), 980 (≠ CH out-of-plane) and 860 cm$^{-1}$.

$^1$H NMR (CDCl$_3$): 2.27 (3H, s, CH$_3$), 3.53 (1H, d, H-1), 5.10 (1H, d, H-1a; $^3$J$_{H-1,H-1a}$ = 4.51 Hz), 6.60-7.43 [13H, m, ArH (11) + vinyl H (2)].

(E)-7a-[2-(Phenylsulphonyl)ethenyl]-1a,7a-dihydro-5-methoxy-1-(4-chlorobenzoyl)benzo[b]cycloprop[a]pyran-7(1H)-one (II-28) To a solution of 0.342 g (0.001 mole) of (E)-3-[2-(phenylsulphonyl)ethenyl]-6-methoxy-4H-1-benzopyran-4-one in 15 ml of chloroform, 0.215 g (0.001 mole) of dimethylsulphonium 4-chlorophenacylide was added and refluxed on a water bath for 45 minutes. On working up of the reaction mixture, a solid product was isolated. Recrystallisation of this solid material from chloroform - light petroleum mixture (3:1) afforded 0.38 g (77%) of II-28 as colourless crystals melting at 196-97$^0$.

Anal. Calcd. for $C_{26}H_{19}O_5SCL$: C 63.09; H 3.84.

Found: C 63.0; H 3.9.

IR (KBr): 3080, 1670 (C=O), 1610 (C=C), 1310 (SO$_2$ asym), 1150 (SO$_2$ sym), 1010 (ring deform), 980 (≠ CH out-of-plane) and 860 cm$^{-1}$.

$^1$H NMR (CDCl$_3$): 3.53 (1H, d, H-1), 3.73 (3H, s, CH$_3$O), 5.10 (1H, d, H-1a; $^3$J$_{H-1,H-1a}$ = 4.5 Hz), 6.63-7.50 [14H, m, ArH (12) + vinyl H (2)].
(E)-7a-[2-[(4-Bromophenyl)sulphonyl]ethenyl]-1a,7a-dihydro-5-methoxy-1-(4-chlorobenzoyl)benzo[b]cyclopropa[e]pyran-7(1H)-one (II-29) A mixture containing 0.342 g (0.001 mole) of (E)-3-[2-[(4-bromophenyl)sulphonyl]-ethenyl]-6-methoxy-4H-1-benzopyran-4-one and 0.215 g (0.001 mole) of dimethylsulphonium 4-chlorophenacylde in 10 ml of chloroform was refluxed on a water bath for 45 minutes. The product was worked up from the reaction mixture as per the general procedure. Recrystallisation of the product from a mixture of chloroform and light petroleum (3:1) afforded 0.4 g (70%) of pure II-29 as pale yellow crystals melting at 194-95°.

Anal. Calcd. for C26H18O6SBrCl: C 54.4; H 3.13.

Found: C 54.5; H 3.10.

IR (KBr): 3080, 1675 (C=O), 1600 (C=C), 1310 (SO2 asym), 1150 (SO2 sym), 1040 (ring deform), 970 (C CH out-of-plane) and 860 cm⁻¹.

1H NMR (CDCl3): S 3.56 (1H, d, H-1), 3.73 (3H, s, CH3O), 5.10 (1H, d, H-1a; 3JH-1, H-1a = 4.5 Hz), 6.50-7.43 [13H, m, ArH (11) + vinyl H (2)].

(E)-7a-[2-[(4-Chlorophenyl)sulphonyl]ethenyl]-1a,7a-dihydro-5-methoxy-1-(4-chlorobenzoyl)benzo[b]cyclopropa[e]pyran-7(1H)-one (II-30) Cyclopropanation was accomplished by refluxing 0.422 g (0.001 mole) of (E)-3-[2-[(4-chlorophenyl)sulphonyl]-ethenyl]-6-methoxy-4H-1-benzopyran-4-one and 0.215 g (0.001 mole) of dimethylsulphonium 4-chlorophenacylde in 15 ml of chloroform on a water bath for 30 minutes. The reaction mixture was worked out as described in the general procedure, to isolate the product. The solid product was recrystallised from chloroform - light petroleum mixture (3:1) to give 0.42 g (79%) of II-30 as colourless crystals melting at 16-87°.
Anal. Calcd. for $\text{C}_{26}\text{H}_{18}\text{O}_6\text{SCl}_2$: C 58.97; H 3.40.
Found: C 58.50; H 3.50.

IR (KBr): 3060, 1670 (C=O), 1600 (C=C), 1310 (SO$_2$ asym), 1150 (SO$_2$ sym), 1010 (ring deform), 970 (S CH out-of-plane) and 860 cm$^{-1}$.

$^1$H NMR (CDCl$_3$): $\delta$ 3.51 (1H, d, H-1), 3.68 (3H, s, CH$_3$O), 5.10 (1H, d, H-1a; $^3$J$_{H-1,H-1a}$ = 4.5 Hz), 6.71-7.45 [13H, m, ArH (11) + vinyl H (2)].

(E)-7a-[2-(Phenylsulphonyl)ethenyl]-1a,7a-dihydro-1-(4-methylbenzoyl)-benzo[b]cyclopropa[e]pyran-7(1H)-one (II-31) To a solution of 0.312 g (0.001 mole) of (E)-3-[2-(phenylsulphonyl)ethenyl]-4H-1-benzopyran-4-one in 15 ml of chloroform 0.213 g (0.001 mole) of dimethylsulphonium 4-methylphenacylde was added and refluxed on a waterbath for 30 minutes. The product from the reaction mixture was isolated on working up as per the general procedure. Recrystallisation of this product from a mixture of chloroform and light petroleum mixture (3:1) gave 0.4 g (90%) of II-31 as pale yellow crystals melting at 192-94$^\circ$.

Anal. Calcd. for $\text{C}_{26}\text{H}_{20}\text{O}_5\text{S}$: C 70.27; H 4.50.
Found: C 70.0; H 4.70.

IR (KBr): 3050, 1670 (C=O), 1600 (C=C), 1315 (SO$_2$ asym), 1140 (SO$_2$ sym), 1040 (ring deform), 990 (S CH out-of-plane) and 860 cm$^{-1}$.

M.S. m/z (% relative intensity): 444 (6.4), 325 (2.6), 324 (11.5), 323 (1.3), 303 (56.3), 277 (1.3), 275 (10.3), 260 (6.4), 205 (1.3), 184 (2.6), 171 (20.5), 158 (9.0), 157 (1.3), 141 (7.7), 129 (5.1), 121 (7.18), 119 (100), 104 (1.3), 92 (3.8), 91 (19.2), 89 (2.6), 77 (9.0).
(E)-7a-[2-[(4-Bromophenyl)sulphonyl]ethenyl]-1a,7a-dihydro-1-(4-methylbenzoyl)benzo[b]cyclopropa[e]pyran-7(1H)-one (II-32) A mixture of 0.391 g (0.001 mole) of (E)-3-[2-[(4-bromophenyl)sulphonyl]ethenyl]-4H-1-benzopyran-4-one and 0.215 g (0.001 mole) of dimethylsulphonium 4-methylphenacylide in 15 ml of chloroform was refluxed on a waterbath for 60 minutes. On working up the reaction mixture as described in the general procedure, the product separated was collected as a crystalline solid, on a Buchner. Recrystallisation of the product from a mixture of chloroform and light petroleum (3:1) gave 0.45 g (86%) of II-32 as colourless crystals, m.p. 170-72°.

Anal. Calcd. for C_{26}H_{19}O_{5}SBr: C 59.65; H 3.63.

Found: C 60.0; H 3.70.

IR (KBr): 3080, 1680, 1660 (C=O), 1600 (C=C), 1320 (SO₂ asym), 1140 (SO₂ sym), 1045 (ring deform), 980 (δ CH out-of-plane) and 860 cm⁻¹.

M.S. m/z (% relative intensity): 524 (2.1), 522 (2.1), 405 (2.1), 404 (4.2), 403 (2.1), 402 (4.2), 340 (2.1), 338 (2.1), 303 (14.6), 275 (2.1), 220 (2.1), 218 (2.1), 205 (2.1), 184 (2.1), 171 (18.8), 158 (2.1), 157 (4.2), 156 (2.1), 154 (6.3), 129 (6.3), 121 (18.8), 120 (10.4), 119 (100), 104 (2.1), 92 (6.1), 91 (37.5), 89 (2.1), 77 (4.2).

(E)-7a-[2-[(4-Chlorophenyl)sulphonyl]ethenyl]-1a,7a-dihydro-1-(4-methylbenzoyl)benzo[b]cyclopropa[e]pyran-7(1H)-one (II-33) Cyclopropanation was effected by refluxing a solution containing 0.337 g (0.001 mole) (E)-3-[2-[(4-chlorophenyl)sulphonyl]ethenyl]-4H-1-benzopyran-4-one and 0.215 g (0.001 mole) of dimethylsulphonium 4-methylphenacylide in 15 ml of chloroform on a
waterbath for a period of 30 minutes. The reaction mixture was worked out as per the general procedure to get the product as a crystalline solid. The product on recrystallisation from a mixture of chloroform and light petroleum (3:1) afforded 0.390 g (81%) of II-33 as light yellow crystals melting at 164-65°.

Anal. Calcd. for C_{26}H_{19}O_{5}SCl: C 65.20; H 3.97.

Found: C 65.10; H 3.90.

IR (KBr): 3080, 1680, 1660 (C=O), 1605 (C=C), 1330 (SO₂ asym), 1150 (SO₂ sym), 1040 (ring deform), 970 (CH out-of-plane) and 860 cm⁻¹.

(E)-7a-[2-(Phenylsulphonyl)ethenyl]-1a,7a-dihydro-5-methyl-1-(4-methylbenzoyl)benzo[b]cyclopropa[e]pyran-7(1H)-one (II-34) To a solution of 0.326 g (0.001 mole) of (E)-3-[2-(phenylsulphonyl)ethenyl]-6-methyl-4H-1-benzopyran-4-one in 15 ml of chloroform was added 0.215 g (0.001 mole) of dimethylsulphonium 4-methylphenacylide and was refluxed on a waterbath for 45 minutes. The reaction mixture when worked out as per the general procedure gave a crystalline solid. The product on recrystallisation from chloroform - light petroleum mixture (3:1) gave 0.32 g (70%) of II-34 as colourless crystals, m.p. 202-203°.

Anal. Calcd. for C_{27}H_{22}O_{5}S: C 70.74; H 4.80.

Found: C 70.80; H 4.90.

IR (KBr): 3060, 1665 (C=O), 1600 (C=C), 1305 (SO₂ asym), 1140 (SO₂ sym), 1040 (ring deform), 970 (CH out-of-plane) and 870 cm⁻¹.
^1H NMR (CDCl₃): δ 2.10 (3H, s, CH₃), 2.30 (3H, s, CH₃), 3.40 (1H, d, H-1a, 5.0 (1H, d, H-1a; 3J_H-1,H-1a = 4.5 Hz), 6.35-7.30 [14H, m, ArH (12) + vinyl H (2)].

(E)-7a-[2-[(4-Bromophenyl)sulphonyl]ethenyl]-1a,7a-dihydro-5-methyl-1-(4-methylbenzoyl)benzo[b]cyclopropa[e]pyran-7(1H)-one (II-35) To a mixture of 0.405 g (0.001 mole) of (E)-3-[2-[(4-bromophenyl)sulphonyl]ethenyl]-6-methyl-4H-1-benzopyran-4-one and 0.215 g (0.001 mole) of dimethylsulphonium 4-methylphenaclylde, 15 ml of chloroform was added and refluxed on a water bath for 60 minutes. The reaction mixture on working up as described in the general procedure, gave a crystalline solid. Recrystallisation of this product from chloroform - light petroleum mixture (3:1) afforded 0.410 g (76%) of II-35 as colourless crystals melting at 208-210°C.

Anal. Calcd. for C₂₇H₂₁O₅SBr: C 60.34; H 3.91.
Found: C 60.10; H 4.0.

IR (KBr): 3060, 1680, 1670 (C=O), 1610 (C=C), 1310 (SO₂ asym), 1150 (SO₂ sym), 1035 (ring deform), 980 (6 CH out-of-plane) and 870 cm⁻¹.

(E)-7a-[2-[(4-Chlorophenyl)sulphonyl]ethenyl]-1a,7a-dihydro-5-methyl-1-(4-methylbenzoyl)benzo[b]cyclopropa[e]pyran-7(1H)-one (II-36) Cyclopropanation was achieved by refluxing a solution containing 0.361 g (0.001 mole) of (E)-3-[2-[(4-chlorophenyl)sulphonyl]ethenyl]-6-methyl-4H-1-benzopyran-4-one and 0.215 g (0.001 mole) of dimethylsulphonium 4-methylphenaclylde, in 15 ml of chloroform, on a waterbath for a period of 90 minutes. On working up the
reaction mixture as per the general procedure, a solid material was isolated. The solid product on recrystallisation from chloroform - light petroleum mixture (3:1) yielded 0.380 g (77%) of II-36 as colourless crystals, m.p. 193-95°.

Anal. Calcd. for C\textsubscript{27}H\textsubscript{21}O\textsubscript{5}S\textsubscript{5}Cl: C 65.78; H 4.26.
Found: C 65.20; H 4.4.

IR (KBr): 3060, 1680, 1670 (C=O), 1610 (C=C), 1310 (SO\textsubscript{2} asym), 1150 (SO\textsubscript{2} sym), 1040 (ring deform), 980 (S CH out-of-plane) and 870 cm\textsuperscript{-1}.

\(^1\text{H} NMR (CDCl\textsubscript{3}): S 2.30 (3H, s, CH\textsubscript{3}), 2.40 (3H, s, CH\textsubscript{3}), 3.70 (1H, d, H-1), 5.30 (1H, d, H-1a; \(^3\)J\textsubscript{H-1,H-1a} = 4.5 Hz), 6.80-7.80 [13H, m, ArH (11) + vinyl H (2)].

(E)-7a-[2-(Phenylsulphonyl)ethenyl]-1a,7a-dihydro-5-methoxy-1-(4-methylbenzoyl)benzo[b]cyclopropa[e]pyran-7(1H)-one (II-37) To a mixture of 0.312 g (0.001 mole) of (E)-3-[2-(phenylsulphonyl)ethenyl]-6-methoxy-4H-1-benzopyran-4-one and 0.215 g (0.001 mole) of dimethylsulphonium 4-methylphenacylide, 15 ml of chloroform was added and refluxed on a waterbath for 30 minutes. The reaction mixture was worked up as described in the general procedure and the product separated as a crystalline solid was collected at the pump. On recrystallisation of the product from a mixture of chloroform - light petroleum (3:1), 0.35 g (73%) of II-37 was obtained as colourless crystals melting at 205-206°.

Anal. Calcd. for C\textsubscript{27}H\textsubscript{22}O\textsubscript{6}S: C 68.35; H 4.64.
Found: C 68.5; H 4.8.
IR (KBr): 3060, 1680, 1660 (C=O), 1610 (C=C), 1310 (SO₂ asym), 1150 (SO₂ sym), 1030 (ring deform), 975 (S CH out-of-plane) and 875 cm⁻¹.

¹H NMR (CDCl₃): δ 2.40 (3H, s, CH₃), 3.71 (1H, d, H-1), 3.83 (3H, s, CH₃O), 5.32 (1H, d, H-1a; 3J_H-1,H-1a = 4.4 Hz), 6.99-7.81 [14H, m, ArH (12) + vinyl H (2)].

(E)-7a-[2-[(4-Bromophenyl)sulphonyl]ethenyl]-1a,7a-dihydro-5-methoxy-1-(4-methylbenzoyl)benzo[b]cyclopropa[e]pyran-7(1H)-one (II-38) A mixture of 0.342 g (0.001 mole) of (E)-3-[2-[(4-bromophenyl)sulphonyl]ethenyl]-6-methoxy-4H-1-benzopyran-4-one and 0.215 g (0.001 mole) of dimethyl-sulphonium 4-methylphenacylidie was dissolved in 10 ml of chloroform and refluxed on a waterbath for 90 minutes. On working up as per the general procedure, the reaction mixture yielded a crystalline solid. Recrystallisation of the solid product from chloroform - light petroleum mixture (3:1) gave 0.42 g (76%) of II-38 as colourless crystals, m.p. 176-78⁰.

Anal. Calcd. for C₂₇H₂₁O₆SBr: C 58.58; H 3.79.
Found: C 58.3; H 3.80.

IR (KBr): 3080, 1680, 1660 (C=O), 1610 (C=C), 1320 (SO₂ asym), 1140 (SO₂ sym), 1020 (ring deform), 990 (S CH out-of-plane) and 875 cm⁻¹.

M.S. m/z (% relative intensity): 554 (1.3), 552 (1.3), 404 (1.3), 402 (1.3), 340 (2.6), 333 (38.5), 305 (6.4), 303 (3.8), 220 (1.3), 218 (2.6), 214 (2.6), 205 (3.8), 201 (14.1), 157 (9.0), 156 (9.0), 154 (15.4), 151 (34.6), 150 (100), 148 (1.3), 134 (7.7), 129 (5.1), 122 (3.9), 119 (96.2), 107 (5.1), 91 (5.1).
(E)-7a-[2-[(4-Chlorophenyl)sulphonyl]ethenyl]-1a,7a-dihydro-5-methoxy-1-(4-methylbenzoyl)benzo[b]cyclopropa[e]pyran-7(1H)-one (II-39) Cyclopropanation was achieved by refluxing a solution containing 0.422 g (0.001 mole) of (E)-3-[2-[(4-chlorophenyl)sulphonyl]ethenyl]-6-methoxy-4H-1-benzopyran-4-one and 0.215 g (0.001 mole) of dimethylsulphonium 4-methylphenacylde in 15 ml of chloroform on a waterbath for a period of 60 minutes. The reaction mixture was worked up as per the general procedure, to get the product as crystalline solid. It was recrystallised from a mixture of chloroform and light petroleum (3:1) to afford 0.400 g (79%) of II-39 as colourless crystals melting at 171-72°C.

Anal. Calcd. for C_{27}H_{21}O_{6}SCl: C 63.72; H 4.13.

Found: C 63.4; H 4.20.

IR (KBr): 3080, 1680, 1665 (C=O), 1610 (C=C), 1320 (SO_2 asym), 1150 (SO_2 sym), 1035 (ring deform), 960 (≤ CH out-of-plane) and 850 cm\(^{-1}\).
CHAPTER III
DISCUSSION

In recent times the use of sulphur ylides as synthetic intermediates has become very important. Among these ylides, dimethylsulphonium methylide (1) and dimethylsulphoxonium methylide (2) have been quite extensively studied for their reactions with aldehydes\textsuperscript{120-123}, ketones\textsuperscript{44,120}, $\alpha,\beta$-unsaturated ketones\textsuperscript{34,48,124}, nitriles\textsuperscript{125,126}, isonitriles\textsuperscript{52}, sulphones\textsuperscript{54,55,127,128}, sulphonamides\textsuperscript{55} and nitro\textsuperscript{56} compounds. Both ylides are nucleophiles and effective in transferring methylene group to certain electrophilic unsaturated linkages.

The ylide (1) reacts with a wide variety of aldehydes and ketones by overall methylene transfer to form an oxirane. Truce et al.\textsuperscript{54,55,127}, reacted dimethylsulphonium methylide (1) with $\alpha,\beta$-unsaturated sulphones and reported the formation of cyclopropyl sulphones (3). From our laboratories,

\[
\text{C}_6\text{H}_5\text{SO}_2\text{CH=CH-C}_6\text{H}_5 + (\text{CH}_3)_2\overset{+}{\overset{-}{\overset{\text{S}}{\text{CH}_2}}} \text{DMSO KO-t-Bu} \to \text{C}_6\text{H}_5\text{SO}_2\text{CH-CH-C}_6\text{H}_5
\]

(3)
a number of cyclopropyl sulphones\textsuperscript{129,130}, ketones\textsuperscript{73}, ketosulphones\textsuperscript{71,75}, bis(arylsulphonyl)ethylenes\textsuperscript{74} were reported by using dimethylsulphonium methyldie, dimethylsulphoxonium methyldie and dimethylsulphonium phenacylde.

With an aim to cyclopropanate the side chain ethylenic bond of [(arylsulphonyl)ethenyl]benzopyranones (I a–o) under phase transfer catalysis some of the compounds were treated with dimethylphenacylsulphonium bromide in the presence of BTEAC as catalyst, dichloromethane and 50 per cent sodium hydroxide as solvents. On working up the reaction mixture, the dichloromethane layer did not yield any product. The compounds obtained on acidification of sodium hydroxide layer proved to be the starting materials.
themselves. This was confirmed by TLC, melting point and mixed melting point with an authentic sample. Hence no cyclopropanation of the compound had taken place. It appears from literature survey that the pyran ring is sensitive to alkalies\textsuperscript{131-133}, which may be hindering the cyclopropanation of the side chain ethylenic bond.

In another attempt to cyclopropanate the ethylenic bond of the side chain of \[((arylsulphonyl)ethenyl]benzopyranone, the stable ylide dimethylsulphonium phenacyl]ide in refluxing chloroform has been used in refluxing to avoid the alkaline medium in the reaction. In this reaction the product obtained on chemical analysis showed the cyclopropanation of the \[((arylsulphonyl)ethenyl]benzopyranones occurring. But surprisingly the \textsuperscript{1}H NMR spectral data indicated the cyclopropanation to occur at the C-2 double bond of the pyrone instead at the side chain ethylenic bond of the molecule.
By using this procedure a series of (E)-7α-[2(aryl)sulphonyl)ethenyl]-1α,7a-dihydro-1-aryl-benzo[b]cyclopropa[e]pyran-7(1H)-ones (II 1-39) have been prepared.

where

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The yields and melting points of all the (E)-7a-[2(arylsulphonyl)ethenyl] 1a,7a-dihydro-1-arylsulphonato[b]cyclopropa[e]pyran-1(7H)-ones (II 1-39) prepared under the present investigation are presented in Table II-1.

**Table II-1**

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INFRARED ABSORPTION SPECTRA

The infrared absorption spectral study of \((\text{E})-7a-[2-(arylsulphonyl)-ethenyl]~1a,7a\text{-dihydro-1-aryloylbenzo}[\text{b}]\text{cyclopropa}[\text{e}]\text{pyran-1(7H)-ones (II 1-39)}\) have been undertaken with a view to confirm the configuration assigned to them on the basis of their method of preparation. The important bands of all these compounds are presented in Table II-2 and the spectra of two of these compounds are reproduced in figures 7 and 8. The spectral features of these cyclopropylsulphones can best be discussed by considering the frequencies associated with the following type of vibrations.

**Cyclopropane ring deformation mode**

The deformation mode\(^{80,83-85}\) of the cyclopropane ring was found to display normally an intense and some times weak band\(^{134}\) at 1026 cm\(^{-1}\) region. This band was considered to be the most characteristic of the cyclopropane ring. The compounds synthesised in the present investigation (see Table II-2) have exhibited bands in the region 1080-1010 cm\(^{-1}\). This data may be considered as the positive evidence for the presence of cyclopropane ring in all these compounds.

**C-H Deformation vibration mode**

A band at 866 cm\(^{-1}\) has been observed for many cyclopropanes\(^{87,135}\) along with 1026 cm\(^{-1}\) band\(^{83}\). All the compounds under present investigation exhibited medium to weak bands in the region 875-845 cm\(^{-1}\).
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</tr>
<tr>
<td>35</td>
<td>Cl</td>
<td>Cl</td>
<td>1635 A</td>
<td>1670</td>
<td>990</td>
<td>1010</td>
<td>860</td>
<td>1310</td>
<td>1150</td>
<td></td>
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<tr>
<td>36</td>
<td>Cl</td>
<td>Cl</td>
<td>1635 A</td>
<td>1670</td>
<td>990</td>
<td>1010</td>
<td>860</td>
<td>1310</td>
<td>1150</td>
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<td></td>
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<td>37</td>
<td>Cl</td>
<td>Cl</td>
<td>1635 A</td>
<td>1670</td>
<td>990</td>
<td>1010</td>
<td>860</td>
<td>1310</td>
<td>1150</td>
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<td></td>
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<tr>
<td>38</td>
<td>Cl</td>
<td>Cl</td>
<td>1635 A</td>
<td>1670</td>
<td>990</td>
<td>1010</td>
<td>860</td>
<td>1310</td>
<td>1150</td>
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<td></td>
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<tr>
<td>39</td>
<td>Cl</td>
<td>Cl</td>
<td>1635 A</td>
<td>1670</td>
<td>990</td>
<td>1010</td>
<td>860</td>
<td>1310</td>
<td>1150</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>
C=C Stretching frequency

The C=C stretching frequencies of all the new cyclopropyl compounds are presented in Table II-2. The C=C stretching frequency bands for an enormous variety of substituted ethylenes\(^{136-147}\) appear between 1680-1620 cm\(^{-1}\). The intensity of \(\nu\) C=C band is generally weak and decreases as the symmetry in the molecule increases. But in the case of all these compounds a very strong band in the region 1610-1600 cm\(^{-1}\) is observed. This band may be due to the ethylenic bond present in the side chain of the molecule. This spectral data also indicates that the ethylenic bond in the side chain is not cyclopropanated.

\[\text{C-H Out-of-plane deformation}\]

All the cyclopropyl compounds synthesised in the present investigation exhibited a strong band in the region 990-960 cm\(^{-1}\). All the [(arylsulphonyl)-ethenyl]benzopyranones before cyclopropanation also showed a strong band in the region 975-960 cm\(^{-1}\) (see Table I-7 p.\textbf{44}). Very characteristic absorption due to the C-H out-of-plane deformation in disubstituted ethylenic compounds has been observed near 990-960 cm\(^{-1}\) and this band\(^{129,142,148-154}\) has been used to confirm the trans nature of the ethylenic bond. The presence of this characteristic band in both the sets of compounds indicate the presence of ethylenic bond as well as its trans configuration. The presence of ethylenic bond in cyclopropyl compounds indicates that the ethylenic bond present in the side chain of original benzopyran has not been cyclopropanated.
Sulphonyl group frequency

It has been extensively documented$^{144,155,156}$ about the SO$_2$ group absorptions in the regions 1340-1290 and 1165-1120 cm$^{-1}$. These bands were assigned to asymmetric and symmetric stretchings respectively. All compounds under the present investigation (II 1-39) exhibited strong bands in the region 1330-1300 cm$^{-1}$ (asymmetric stretchings) and 1150-1140 cm$^{-1}$ (symmetric stretchings) (see Table II-2 and also fig. 7 and 8).

NUCLEAR MAGNETIC RESONANCE SPECTRA

$^1$H-NMR spectra

It has been observed that protons attached to the cyclopropane ring resonate in the region $S$ 0-2 ppm$^{92}$. The upfield chemical shifts of cyclopropanes have diagnostic importance. For a number of cyclopropanes, the configurations of substituents have been established from chemical shifts$^{93-97}$ as well as coupling constants$^{157}$ of cyclopropane ring protons. Vicinal coupling constants$^{90,96-100}$ of cyclopropanes are in the range of $J_{\text{trans}} = 4.0$ to 9.6 Hz and $J_{\text{cis}} = 7.0$ to 12.6 Hz; $J_{\text{trans}} < J_{\text{cis}}$.

The $^1$H NMR spectra of (E)-3-[(2-(phenylsulphonyl)ethenyl]4H-1-benzopyran-4-one (I a) and its corresponding cyclopronated compound (II-1) are reproduced in fig. 9 and 10 and the $^1$H NMR spectral characteristics of these two compounds are presented in Table II-3.
Table II-3

$^1$H NMR data of (E)-3-[2-(phenylsulphonyl)ethenyl]-4H-1-benzopyran-4-one (I a)

<table>
<thead>
<tr>
<th>R</th>
<th>R'</th>
<th>values in ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>2H</td>
<td>Ar H and vinyl H</td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>H</td>
<td>8.60 (1H,s)</td>
</tr>
<tr>
<td>H</td>
<td>H</td>
<td>7.20-7.81 (11H, m)</td>
</tr>
</tbody>
</table>

$^1$H NMR data of (E)-7a-[2-(phenylsulphonyl)ethenyl]-1a,7a-dihydro-1-benzoyl-benzo[b]cyclopropa[e]pyran-7(1H)-one (II-1).

<table>
<thead>
<tr>
<th>R</th>
<th>R'</th>
<th>R''</th>
<th>values in ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>hydrogen proton</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>J$_{HA,HB}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Ar H and vinyl H</td>
</tr>
<tr>
<td>H</td>
<td>H</td>
<td>H</td>
<td>5.15 (1H,d)</td>
</tr>
<tr>
<td>H</td>
<td>H</td>
<td>H</td>
<td>3.63 (1H,d)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>4.50 (Hz)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>6.70-7.76 (16H, m)</td>
</tr>
</tbody>
</table>
A careful comparison of the spectral data indicate that the proton at C-2 of I a shows a resonance signal at δ 8.2 ppm and the signals due to vinylic protons of the side chain δ 6.2-7.5 ppm merged with the complex multiplets of aromatic protons (δ 7.20-7.81 ppm). The cyclopropanated product II-1 shows two new resonance signals at δ 5.15 ppm and δ 3.63 ppm with the absence of the signal at δ 8.6 ppm (C-2 proton) which was present in the original product. A complex multiplet appeared for II-1 also in the region δ 6.7-7.76 ppm which may constitute for aromatic protons as well as for the free ethylenic protons of the side chain.

The appearance of two new proton signals at δ 5.15 ppm and δ 3.63 ppm the absence of signal at δ 8.6 ppm and the normal presence of complex multiplets in the region δ 6.70-7.76 ppm without much change, represent the ethylenic as well as aromatic protons. This also clearly indicates that the cyclopropanation of the molecule occurred across the C₂-C₃ double bond of the benzopyran ring rather than at the ethylenic bond of the side chain.

Caplin et al. for a cyclopropanated product of benzo-4-pyrone (4), reported ¹H NMR signals for Hₓ and Hₐ or B around δ 4.8 ppm and δ 1.8 ppm respectively. The spectrum has been analysed as an ABX spectrum and the coupling constant JₓBₓ = 4.5 cps was reported by them and the same J value was obtained for the compound (II-1) under present study. The protons Hᵧ and Hₐ are absent in the compound II-1 under present investigation.
The $^1$H NMR spectral data of the nineteen new cyclopropanated products (II 5, 4, 10, 11, 13, 14, 16, 17, 19, 24-30, 34, 36 and 37) are presented in Table II-4. The spectra of two of the compounds (II 10 and 14) are reproduced in figures 11 and 12.

Table II-4

$^1$H NMR spectral data$^{*}$ of (E)-7a-[2(arylsulphonyl)ethenyl]-1a,7a-dihydro-1-
arylcyclopenta[b]pyran-7-(1H)-ones

<table>
<thead>
<tr>
<th></th>
<th>H</th>
<th>Cyclopropanyl protons $^a$</th>
<th>Coupling constant $^b$</th>
<th>Ar H and vinyl H $^c$</th>
<th>Substituents $^d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>II 1</td>
<td>$^a$H</td>
<td>H</td>
<td>$^b$H</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$^a$H</td>
<td>$^a$H</td>
<td>$^a$H</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>5.15</td>
<td>3.63</td>
<td>4.50</td>
<td>6.70-7.76(16H)</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>5.18</td>
<td>3.64</td>
<td>4.50</td>
<td>6.71-7.76(15H)</td>
<td>-</td>
</tr>
<tr>
<td>10</td>
<td>5.10</td>
<td>3.53</td>
<td>4.50</td>
<td>6.30-7.65(15H)</td>
<td>-</td>
</tr>
<tr>
<td>11</td>
<td>5.15</td>
<td>3.63</td>
<td>4.50</td>
<td>6.63-7.56(16H)</td>
<td>2.30(3H)</td>
</tr>
<tr>
<td>18</td>
<td>5.12</td>
<td>3.60</td>
<td>4.50</td>
<td>6.60-7.50(14H)</td>
<td>2.27(3H)</td>
</tr>
<tr>
<td>13</td>
<td>5.13</td>
<td>3.66</td>
<td>4.50</td>
<td>6.63-7.56(15H)</td>
<td>3.73(3H)</td>
</tr>
<tr>
<td>14</td>
<td>5.16</td>
<td>3.56</td>
<td>4.50</td>
<td>6.36-7.56(14H)</td>
<td>3.73(3H)</td>
</tr>
<tr>
<td>16</td>
<td>5.15</td>
<td>3.58</td>
<td>4.50</td>
<td>6.71-7.76(15H)</td>
<td>-</td>
</tr>
<tr>
<td>17</td>
<td>5.15</td>
<td>3.58</td>
<td>4.50</td>
<td>6.69-7.76(14H)</td>
<td>-</td>
</tr>
<tr>
<td>19</td>
<td>5.12</td>
<td>3.53</td>
<td>4.50</td>
<td>6.56-7.78(14H)</td>
<td>-</td>
</tr>
<tr>
<td>24</td>
<td>5.10</td>
<td>3.53</td>
<td>4.50</td>
<td>6.68-7.63(13H)</td>
<td>-</td>
</tr>
<tr>
<td>25</td>
<td>5.10</td>
<td>3.53</td>
<td>4.50</td>
<td>6.68-7.56(14H)</td>
<td>2.30(3H)</td>
</tr>
<tr>
<td>26</td>
<td>5.10</td>
<td>3.53</td>
<td>4.50</td>
<td>6.50-7.56(13H)</td>
<td>2.28(3H)</td>
</tr>
<tr>
<td>27</td>
<td>5.10</td>
<td>3.53</td>
<td>4.51</td>
<td>6.60-7.43(13H)</td>
<td>2.27(3H)</td>
</tr>
<tr>
<td>28</td>
<td>5.10</td>
<td>3.53</td>
<td>4.50</td>
<td>6.63-7.50(14H)</td>
<td>3.73(3H)</td>
</tr>
<tr>
<td>29</td>
<td>5.10</td>
<td>3.56</td>
<td>4.50</td>
<td>6.50-7.43(13H)</td>
<td>3.73(3H)</td>
</tr>
<tr>
<td>30</td>
<td>5.10</td>
<td>3.51</td>
<td>4.50</td>
<td>6.71-7.45(13H)</td>
<td>3.68(3H)</td>
</tr>
<tr>
<td>31</td>
<td>5.00</td>
<td>3.40</td>
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<td>6.35-7.30(14H)</td>
<td>2.10(3H)</td>
</tr>
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<td>32</td>
<td>5.32</td>
<td>3.71</td>
<td>4.40</td>
<td>6.99-7.81(14H)</td>
<td>2.40(3H)</td>
</tr>
</tbody>
</table>

$^*$ Solvent CDCl$_3$ - 90 MHz spectra

$^**$Chemical shift (ppm)
The spectra of all these compounds showed the resonance signals of
cyclopropane protons in the regions 6 5.10-5.32 and 6 3.4-3.70 ppm corres-
ponding to H_A and H_B respectively. The appearance of resonance signal for
H_A at a much lower field (6 5.0-5.3 ppm) may be due to the deshielding
effect of oxygen atom attached to the cyclopropane carbon. The same may
be attributed to the appearance of resonance signal for H_B around 6 3.5-3.6
ppm due to the carboxyl group bonded to the cyclopropyl carbon. The
coupling constant value J_HA-HB = 4.5 cps., indicates that the protons in
cyclopropane ring are in trans position. The protons of substituents CH_3
and CH_2CH_2 showed signals as singlets in the 1H NMR spectra as
expected.

13C NMR spectra

13C NMR spectra of two cyclopropanated products (II 16 and 26) have
been recorded to confirm the position of cyclopropane ring in the molecule.
The spectra are reproduced in figures 13 and 14 and their important
chemical shifts are presented in Table II-5.

Table II-5

| Compound | R   | R'  | R''  | Chemical shifts of cyclo-
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th>propyl carbons 1a</th>
<th>1</th>
<th>7a</th>
</tr>
</thead>
<tbody>
<tr>
<td>II-16</td>
<td>H</td>
<td>H</td>
<td>Cl</td>
<td>66.2</td>
<td>40.6</td>
<td>32.1</td>
</tr>
<tr>
<td>II-26</td>
<td>CH_3</td>
<td>Br</td>
<td>Cl</td>
<td>66.3</td>
<td>40.7</td>
<td>32.3</td>
</tr>
</tbody>
</table>

* 22.64 MHz spectra, solvent CDCl_3, 6 values from TMS
**FIG. 13**

**1H NMR OF SAMPLE HM1/COCl3**

- **OP**: 22.2 ppm
- **BY**: 8.0 ppm
- **DI**: -128.8 ppm
- **TO**: 185.4 ppm
- **SV**: 5484.595 ppm

**HR/FT**: 671

- **AG**: 45.01 ppm
- **SR**: 0 ppm
- **TL**: 297 ppm

- **LV**: 3.5 ppm
- **CA**: 0 ppm
- **ED**: 15.7 ppm
- **DI**: 20.23 ppm
- **HM/CH**: 119.13 ppm

**PPM/CH**: 5.251

Chemical structure diagram with labeled peaks.
Cromble and his co-workers\textsuperscript{158} studied $^{13}$C NMR spectra of isoprenoids containing a cyclopropane ring (5). They have assigned $^{13}$C chemical shifts in the range of $\delta$ 31-35 ppm for the cyclopropane carbon attached to a vinylic side chain.

\[
\begin{array}{c}
R' \\
\Downarrow \\
\Downarrow \\
R'' \\
\end{array}
\]

In the present investigation $^{13}$C chemical shifts also appeared in the region $\delta$ 32.1-32.33 ppm for cyclopropane carbon (7a) attached to a vinylic side chain for the compounds II 16 and 26.

Weiner and Malivmovski\textsuperscript{159} made a comparative study of the $^{13}$C NMR shifts of methanes, benzenes, vinyl groups, methyl ketones and cyclopropanes. In cyclopropanes, they have assigned a $^{13}$C chemical shift value of $\delta$ 36.8 ppm for a carbon bearing a benzoyl group and a value of $\delta$ 41.2 ppm for the carbon bearing a carbonyl group. On the basis of the above information, for the compounds in the present study $^{13}$C chemical shift of C-I attached to the carbonyl group can be assigned to the value $\delta$ 40.6 and 40.7 ppm (see Table II-5). The chemical shifts of C-I a of the cyclopropane ring attached to the oxygen atom resonated at $\delta$ 66.2 and 66.3 ppm and this down field shift of the signals may be due to the deshielding effect of the oxygen attached to the cyclopropane ring.
A mass spectral study of (E)-7a[2-(arylsulphonyl)ethenyl]-1a,7a-dihydro-1-arylybenzo(b)cyclopropa(e)pyran-7(1H)ones has been undertaken with a view to confirm their structures. The mass spectra of II-1, 16, 31, 32 and 38 have been recorded and the data are presented in Table II-6 and two spectra are reproduced in Fig.15 and 16. The mass spectral fragmentation of (E)-7a[2(phenylsulphonyl)ethenyl]-1a,7a-dihydro-1-(4-methylbenzoyl)benzo(b)cyclopropa(e)pyran-7(1H)one (II-31) as a typical example of this series of compounds is presented in Scheme-2.

The mass spectrum of (E)-7a-[2-(phenylsulphonyl)ethenyl]-1a,7a-dihydro-1-(4-methylbenzoyl)benzo(b)cyclopropa(e)pyran-7(1H)one (II-31) showed the molecular ion M⁺, at m/z 444 with an intensity of 6.4 per cent. The decomposition of the molecular ion in one mode of fragmentation gave an ion at m/z 325 (2.6%) with the loss of C₈H₇O⁺. In another mode of decomposition the molecular ion on the loss of C₁₈H₁₃O₄S⁺ led to the formation of the ion at m/z 119 with an intensity of 100 per cent. This ion becomes the base peak in the spectrum. The molecular ion on the loss of C₁₄H₁₂O₃S gave the radical ion at m/z 184 (2.6%). This radical ion on successive losses of C₂H₂, C₃H and HCO⁻ fragments led to the formation of ions at m/z 158 (9%), m/z 121 (71.8%) and m/z 92 (3.8%) respectively. The molecular ion on the loss of C₈H₇O₂S might have led to the formation of the cation C₁₈H₁₃O₃⁺ at m/z 277 (1.3%). The loss of PhSO₂⁻ from the molecular ion might have led to the formation of the ion at m/z 303 (56.3%) which in turn led to the formation of the ion at m/z 275 (10.3%) with the loss of CO molecule. The molecular ion, on the loss of C₇H₄O₂ may lead
Table 11-6

Mass spectral data* of (E)-7a(2-arylsulphonyl)ethenyl-1a,7a-dihydro-1-arylbenzo(9)-cyclopropa(e)pyran-7(1H)-ones

![Chemical structure image]

<table>
<thead>
<tr>
<th>Compd.</th>
<th>R</th>
<th>R′</th>
<th>R''</th>
<th>m₁</th>
<th>m₂</th>
<th>m₃</th>
<th>m₄</th>
<th>m₅</th>
<th>m₆</th>
<th>m₇</th>
<th>m₈</th>
<th>m₉</th>
<th>m₁₀</th>
<th>m₁₁</th>
<th>m₁₂</th>
<th>m₁₃</th>
<th>m₁₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>II-1</td>
<td>H</td>
<td>H</td>
<td>H</td>
<td>430</td>
<td>-</td>
<td>310</td>
<td>289</td>
<td>263</td>
<td>261</td>
<td>246</td>
<td>205</td>
<td>184</td>
<td>158</td>
<td>121</td>
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<td>92</td>
<td>77</td>
</tr>
<tr>
<td>16</td>
<td>H</td>
<td>H</td>
<td>Cl</td>
<td>466</td>
<td>325</td>
<td>346</td>
<td>325</td>
<td>297</td>
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<td>205</td>
<td>184</td>
<td>-</td>
<td>121</td>
<td>141</td>
<td>92</td>
<td>113</td>
<td>115</td>
</tr>
<tr>
<td>31</td>
<td>H</td>
<td>H</td>
<td>CH₃</td>
<td>444</td>
<td>325</td>
<td>324</td>
<td>303</td>
<td>277</td>
<td>275</td>
<td>260</td>
<td>205</td>
<td>184</td>
<td>158</td>
<td>121</td>
<td>119</td>
<td>92</td>
<td>91</td>
</tr>
<tr>
<td>32</td>
<td>H</td>
<td>Br</td>
<td>CH₃</td>
<td>524</td>
<td>405</td>
<td>404</td>
<td>303</td>
<td>275</td>
<td>340</td>
<td>-</td>
<td>184</td>
<td>158</td>
<td>121</td>
<td>119</td>
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<td>CH₂O</td>
<td>Br</td>
<td>CH₃</td>
<td>554</td>
<td>404</td>
<td>333</td>
<td>305</td>
<td>-</td>
<td>214</td>
<td>-</td>
<td>-</td>
<td>151</td>
<td>119</td>
<td>122</td>
<td>91</td>
<td>91</td>
<td>91</td>
</tr>
</tbody>
</table>

* m/z intensities as percentage of base peak

\[
\begin{align*}
m_1 &= -R_1^+ \quad \text{mz} \quad R_1^+ \\
m_2 &= -R_2^+ \quad \text{mz} \quad R_2^+ \\
m_3 &= -R_3^+ \quad \text{mz} \quad R_3^+ \\
m_4 &= -R_4^+ \quad \text{mz} \quad R_4^+ \\
m_5 &= -R_5^+ \quad \text{mz} \quad R_5^+ \\
m_6 &= -R_6^+ \quad \text{mz} \quad R_6^+ \\
m_7 &= -R_7^+ \quad \text{mz} \quad R_7^+ \\
m_8 &= -R_8^+ \quad \text{mz} \quad R_8^+ \\
m_9 &= -R_9^+ \quad \text{mz} \quad R_9^+ \\
m_{10} &= -R_{10}^+ \quad \text{mz} \quad R_{10}^+ \\
m_{11} &= -R_{11}^+ \quad \text{mz} \quad R_{11}^+ \\
m_{12} &= -R_{12}^+ \quad \text{mz} \quad R_{12}^+ \\
m_{13} &= -R_{13}^+ \quad \text{mz} \quad R_{13}^+ \\
m_{14} &= -R_{14}^+ \quad \text{mz} \quad R_{14}^+ \\
\end{align*}
\]
to the formation of the radical ion at m/z 324 (11.5%). This radical ion with the loss of SO₂ and C₈H₇O may lead to the formation of the ions at m/z 260 (6.4%) and at m/z 205 (1.3%).

The mass spectra of the compounds II 1, 16, 32 and 38 showed similar patterns of fragmentation.

Cyclopropanation of carvone has been studied by Corey and Chaykovsky⁴⁴ and later by other workers⁶⁰,¹⁶⁰.

When cyclopropanation was attempted with dimethyloxosulphonium methylide, the double bond in the ring got cyclopropanated exclusively rather than the double bond present in the side chain of carvone.

\[
\text{R} + (\text{CH₃})₂\text{SOCH₂} → \text{R} - \text{SOCH₂}
\]

The cyclopropanation studies of (E)-3[2-(arylsulphonyl)ethenyl]-4H-1-benzopyran-4-ones (I a-o) with dimethylox sulphonium phenacylilide in the present investigation also led to the cyclopropanation of the double bond present in the benzopyran ring rather than the vinylic group present in the side chain.

The infrared, the nuclear magnetic resonance (¹H and ¹³C) and mass spectral studies confirm the structures of all the compounds investigated.
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