CHAPTER IV

PHOTOCHEMISTRY OF
EPIMERIC 2-ACETYL-3,3-DIMETHYLNORBORNANES:
PRELIMINARY RESULTS.
INTRODUCTION

In the last few years, we have been investigating the photochemistry of vinyl halides with a view to understand the basic primary photoprocesses involved in this class of organic chromophoric groups. In this context, particularly the vinyl halides $1-5$ derived from camphene (Chart 4.01) were chosen and were extensively studied under a variety of conditions. This led to the following important findings:

1. Vinyl halides lacking substituents on the carbon bearing halogen ($R=H$) displayed extensively radical photo-behaviour giving the reduction products.

2. Competing ionic and radical behaviour implicating vinyl cationic and vinyl radical intermediates respectively was observed when a methyl substituent is introduced ($3, 4$).

3. In the presence of a phenyl substituent ($5$) a remarkable shift in the photobehaviour in favour of the ionic pathway occurred.

4. The polarity of the medium acted as a controlling factor in the photobehaviour. The above mentioned radical v/s ionic behaviour was observed only in polar medium such as methanol, while exclusive radical pathway leading to reduction products was observed in non-polar medium in spite of the presence of methyl and phenyl substituents.
5. Sensitization and quenching experiments indicated the involvement of the singlet excited state in the formation of ionic products while triplet state seemed to be responsible for the radical products. Based on these observations, a plausible mechanism involving electron transfer in the initially formed radical pair was suggested in order to account for the vinyl cation derived products. The dissociation of radical pair into vinyl radicals were assumed as intermediates in the formation of reduction products.

In probing further into these mechanistic aspects, the photochemistry of these vinyl halides was also explored in methanol containing oxygen. This study surprisingly led to a highly unexpected phenomenon. Under these conditions, halides 1 - 4 afforded essentially a single ketonic product viz. camphenilone, 6 (Scheme 4.01). Among the various pathways considered for the formation of camphenilone, the one of the possibilities is shown in scheme 4.02. The vinyl radical intermediate, 6A on combination with oxygen followed by hydrogen abstraction leads to the hydroperoxide, 6B. This on 0-0 homolysis and combination with hydrogen can give the tautomeric form of the ketone 8. The further steps in the formation of the observed camphenilone involves the α-cleavage of the ketone 8 resulting in the radical 6C followed by combination with oxygen as shown in above scheme.

In the light of the above considerations, it was
CHART 4.01

1. \( X = Br, R = H \)
2. \( X = I, R = H \)
3. \( X = Br, R = CH_3 \)
4. \( X = I, R = CH_3 \)
5. \( X = Br, R = Ph \)

SCHEME 4.01

\[ 1 \rightarrow 4 \stackrel{h\nu, MeOH}{\longrightarrow} \mathcal{O}_2 \rightarrow 6 \]

SCHEME 4.02

\[ \text{i) } O-O\text{-cleavage} \text{ ii) } H^+ \]
\[ \text{i) } O_2 \text{ ii) } H^+ \]

\[ \text{i) } O-O\text{-bond cleavage} \text{ ii) } H^+ \]

\[ \text{h\nu} \]

\[ \text{\alpha-cleavage} \]

8

9

10

11

12
thought worthwhile, initially, to study the photochemistry of the epimeric ketones 7 and 8 in an inert atmosphere to check the possibility of the occurrence of \( \alpha \)-cleavage (Norrish type-I cleavage) to generate the proposed radical intermediate (Scheme 4.02). Another important reason for the selection of these substrates was that the epimeric ketones, in general, are known to display differences in their photobehaviour. For example, we observed an altogether different type of photochemistry from the epimeric \( \alpha \)- and \( \beta \)-methoxy-4-caranones.

RESULTS

Preparations of 7 and 8

These ketones were prepared following a method developed in our laboratory (Scheme 4.03). The method consisted of the hydroboration/oxidation of (E)-\( \omega \)-methylcamphene which furnished essentially the endo-alcohol, 10. Chromic acid oxidation of 10 afforded the required 7 in good yield. The exo-isomer, 8 could be prepared by the base catalyzed equilibration of 7.

Photolysis of endo-2-acetyl-3,3-dimethylnorbornane, 7

Irradiation of 7 in methanol using lamp A afforded a reaction product (10 hr) comprising five components of RT's 1.25 (7%), 2.94 (4%), 3.80 (49%), 4.84 (22%) and 5.54 (18%). The component of RT 2.94 was recognised as unreacted 7 by its
GLC behaviour. Preparative GLC of the product after removing the low boiler (RT 1.25) by fractional distillation, furnished the major component (RT 3.80) in pure form, however, the other components could not be obtained pure.

Characterization of the component of RT 3.80: The elemental analysis and the observed molecular ion at m/e 166 in its mass spectrum suggested that the product is isomeric with the starting ketone. However, the IR spectrum indicated the presence of an olefinic and a tertiary hydroxyl functions. The presence of these functionalities was further corroborated by its PMR spectrum (Fig.4.01).

In view of the formation of unsaturated tertiary alcohol from the saturated ketone \( \text{7} \), a variety of likely photochemical pathways were considered. An examination of the structural features of the ketone, \( \text{7} \), reveals that a Norrish type-II elimination should expeditiously occur because of stereoelectronic factors leading to an intermediate \( \text{13} \).

At this point it is interesting to note that one of the photoproducts \( ^* \) (RT 3.41) observed in the initial stages of photolysis (2 hr) readily diminished (GLC) with concomitant increase in the major product, during the course of the reaction. This observation prompted us to suspect that probably the ketone \( \text{13} \) could have been the likely intermediate responsible for the observed product (RT 3.80), as a result of N-II cyclization. This secondary photoprocess can lead

\*The PMR spectrum of the crude material obtained from one of the early aliquotes showed the presence of vinylic protons (5.66 s) and an additional methyl ketone signal (2.00) suggesting the likely presence of an intermediate ketone such as \( \text{13} \).
to a pair of tertiary alcohols 11 and 12 as shown in Scheme 4.04. A detailed examination of the PMR spectrum showed that the compound, on hand, could be represented by 11, the distinction between the two structures could be made by the observed three singlets for three methyl groups while the structure 12 possesses only two methyl groups.

The separation of the components of RT 4.84 and 5.54, and characterization are in progress.

In order to check the intermediacy of the ketone 13 in the formation of the spiro alcohol, 11, its synthesis was considered necessary. The method outlined in Scheme 4.05 involves a copper-catalysed 1,4-addition of the cyclopentyl-grignard 14 to mesityl oxide. As the saturated analogue of the bromide, 14A, could be conveniently prepared, its grignard reaction with mesityl oxide was initially attempted. However, this resulted in a complex mixture of products and therefore could not be used as a preparative method.

Another sequential approach of some merit has also been depicted in Scheme 4.05. Reformtsky reaction of 15 with cyclopentenone 16 followed by dehydration was anticipated to furnish the product with a cyclopentadienyl moiety, 16A. Since, acidic reagents are to be involved in some of the further steps, a likely but undesirable participation of cyclopentadienyl system becomes apparent. Besides this,
the required selective hydrogenation of one of the double bonds in 16A would also constitute a difficult step. From these considerations, it was decided to synthesize the saturated analogue of the ketone 13. The method employed in its synthesis has been outlined in Scheme 4.06.

The olefinic ester 17 could be conveniently prepared by the method suggested above for 16A. Catalytic hydrogenation, hydrolysis of the ester followed by the reaction with thionyl chloride afforded the acyl halide 20. The latter acid chloride was converted to its diazo derivative 21 by treatment with diazomethane and its photolysis in the presence of methanol furnished the homologated ester 22. Alkaline hydrolysis of 23 afforded the corresponding acid 24 which was transformed into the required ketone 26 (PMR: Fig.4.02) by the reaction of diazoketone 25 with HI as shown in the scheme.

The observed spiro alcohol 11 in the photolysis of 7 has been proposed to arise from a secondary photoprocess of the intermediate ketone 13. As it was not possible to prepare this ketone in order to establish its intermediacy and its saturated analogue 26 could be synthesized, it was decided to photolyze the latter ketone under the conditions employed for 7. This photolysis was expected to furnish a spiro alcohol which would be identical with the hydrogenated spiro alcohol 11 obtained from 7.
Scheme 4.03

1. \( \text{B}_2\text{H}_6 \)
2. \( \text{H}_2\text{O}_2 - \text{NaOH} \)

Scheme 4.04

1. \( \text{h}_\omega \)
2. \( \text{CH}_3\text{OH} \)

Scheme 4.05

1. \( \text{MgBr} \)
2. \( \text{Complex mixture} \)
3. \( \text{i) Reformatsky} \)
4. \( \text{ii) POC}_3 \)
To our great surprise, photolysis of 26 under the conditions employed for 7, afforded a complex mixture of products. Nevertheless, one of the products was accentuated in GLC when mixed with the hydrogenated product of 11. The unexpected complexity observed in the photolysis of 26 may be due to the absence of double bond in the cyclopentane ring. Establishing the intermediacy of the proposed ketone 13 in the formation of spiro alcohol 11 needs further work to be done.

Photoirradiation of exo-2-acetyl-3,3-dimethylnorbornane, 8:
The photolysis of 8 in methanol was carried out by employing lamp A and the product obtained therefrom, was found to comprise four components with RT's 2.74 (5%), 3.14 (6%), 3.96 (26%) and 4.38 (63%). Preparative GLC of the total product enabled us to obtain the major component (RT 4.38) in pure form and the third component as a 3:2 mixture with the last component. The first component was recognised as the unreacted starting ketone, 8, from its GLC behaviour.

Component of RT 4.38: The IR spectrum of this component indicated it to be a tertiary alcohol. From its elemental analysis and the observed molecular ion peak at m/e 166, the molecular formula of this component could be computed as C_{11}H_{18}O isomeric with the starting ketone, 8.

The PMR spectrum (Fig.4.03) of the component displayed two 3H singlets at 1.10 and 1.30 indicating the
presence of two quaternary methyls. The downfield signal at 1.30 is suggestive of a methyl function on a carbon carrying a hydroxyl group. Besides this the spectrum was conspicuous by the absence of -COCH₃ absorption (present in the starting 8), clearly indicating the occurrence of NII cyclization resulting in a cyclobutanol. Therefore, the product, on hand, could be represented by either of the structures 27 and 28, differing in stereochemistry (Scheme 4.07).

Component of RT 3.96: Although this component could not be obtained pure, its isolation as a mixture with the last component and spectral data of the mixture were sufficient enough for its characterization. The IR and the PMR data indicated this component also to have arisen from a N II cyclization. The PMR spectrum contained all the signals of the major component (RT 4.38) and in addition it displayed two 3H singlets of greater intensity at 1.13 and 1.30. Thus, this data clearly indicated that this component and the one previously described, are stereoisomers and also could be represented by either of the structures 27 and 28.

There have been some attempts reported in the literature for distinguishing such stereoisomers on the basis of their PMR spectral data. The methyl groups of these isomers in hindered positions are known to resonate in considerably more downfield region compared to those of the corresponding
unhindered alcohols. Based on such a consideration, the component corresponding to RT 4.38 can be assigned the structure 27 and the other component of RT 3.96, 28. However, as such a difference in present case is very small, the structural assignments become tentative.

DISCUSSION

It may be recalled that the study of the photochemistry of these ketones was undertaken to check the occurrence of \( \alpha \)-cleavage, leading to a pathway for the formation of camphe-nilone in the photolysis of 1 - 5. It, therefore, becomes apparent from the observed results that \( \alpha \)-cleavage is not a favoured process \(^*\) in both the ketones, 7 and 8 indicating that the pathways suggested in Scheme 4.01 are not operating.

The absence of \( \alpha \)-cleavage in 8 is somewhat surprising when compared to the reported photobehaviour of the analogous methyl ketones, 29 and 30, in norbornyl series (Scheme 4.08). The ketone 29 has been reported to give exclusively products 31 and 32 arising from \( \alpha \)-cleavage. Many interesting findings emerge out when a comparison is made between the photobehaviour of the present substrates and the corresponding nor-ketones 29 and 30. The observed N II cyclization in 8 could be understood

\(^*\) \( \alpha \)-Cleavage in these ketones may not be completely ruled out as some minor products were not characterized; however, this cleavage as a major process has not occurred.
in terms of the available \( \gamma \)-hydrogens from the gem-dimethyl groups. This may be a special situation in the exo-configuration wherein \( \gamma \)-hydrogens are sufficiently close in space to the carbonyl function for a facile hydrogen abstraction, making it a more competitive pathway than \( \alpha \)-cleavage.

The endo-ketone 7 has furnished products arising essentially from N II elimination followed by secondary photoprocess of the intermediate ketone 13; besides this, the products from N II cyclization similar to those of 8, were conspicuously absent. It is interesting to note that the 1,4-biradicals supposed to be involved in a N II process have preferred to undergo an elimination rather than cyclization. This difference in the photobehaviour could be ascribed to the presence of favourable orbital overlap leading to elimination. It may be observed that the corresponding endo-norketone 30 afforded products originating from both N II elimination and cyclization (Scheme 4.08); at the same time, this ketone did not also afford any product arising from \( \alpha \)-cleavage. A few more examples of different photobehaviour of exo- and endo- epimeric ketones are also known.

It may be pointed out that in the photochemistry of acyclic ketones, a wide range of N II cyclization: N II elimination ratios have been reported. In this context, the
Scheme 4.06

Raney Ni
\[
\begin{align*}
\text{i)} & \quad \text{Raney Ni} \\
\text{ii)} & \quad \text{OH} \\
\text{iii)} & \quad \text{SOCl}_2 \\
\text{iv)} & \quad \text{CH}_2\text{N}_2 \\
\end{align*}
\]

17

18: \( R = \text{CO}_2\text{Me} \)
19: \( R = \text{CO}_2\text{H} \)
20: \( R = \text{COCl} \)
21: \( R = \text{COCH}_2\text{N}_2 \)

\[
\begin{align*}
\text{i)} & \quad \text{h}_2\text{O}/\text{MeOH} \\
\text{ii)} & \quad \text{OH} \\
\text{iii)} & \quad \text{SOCl}_2 \\
\text{iv)} & \quad \text{CH}_2\text{N}_2 \\
\end{align*}
\]

21

22: \( R = \text{CO}_2\text{Me} \)
23: \( R = \text{CO}_2\text{H} \)
24: \( R = \text{COCl} \)
25: \( R = \text{COCH}_2\text{N}_2 \)

26

Scheme 4.07

8

\[
\begin{align*}
\text{h}_2\text{O} & \quad \text{CH}_3\text{OH} \\
\end{align*}
\]

27

28

Scheme 4.08

\[
\begin{align*}
\text{h}_2\text{O} & \quad \text{CH}_3\text{CN} \\
\end{align*}
\]

29

31

32

\[
\begin{align*}
\text{h}_2\text{O} & \quad \text{CH}_3\text{CN} \\
\end{align*}
\]

30

\[
\begin{align*}
\text{h}_2\text{O} & \quad \text{CH}_3\text{CN} \\
\end{align*}
\]
present epimeric ketones 7 and 8 show a remarkable reaction selectivity in their photolysis. The exo-ketone 8 afforded products entirely originating from N II cyclization while the endo-isomer 7 furnished product of N II elimination.

Although the present study is preliminary in nature, some characteristic features of the photochemistry of these two ketones have emerged as follows:

1. The epimeric ketones 7 and 8 have displayed an altogether different type of photobehaviour showing reaction selectivity.

2. The photochemistry of these ketones appears to have been directed by the presence of methyl groups in comparison with the corresponding norketones.

3. The 1,4-biradical derived from \( \rightdownarrow \)-hydrogen abstraction in the endo-ketone 7 have preferred to eliminate rather than cyclize. This observation has already been rationalized in terms of orbital disposition in the respective 1,4-biradical intermediates involved. Further, the ketone 7 has shown regioselectivity in hydrogen abstraction which could be attributed to the available conformational and stereoelectronic requirements in it.

The study of the nature of the excited states responsible for the primary photoprocess, solvent effect on product distribution and isolation/characterization of the minor products are in progress.
EXPERIMENTAL

General remarks remain the same as described in experimental section of Chapter II.

Preparation of norbornyl ketones 7 and 8: (Scheme 4.03).

**Hydroboration of (E)-α-methylcamphene:** To a stirred solution of 9 (30.06 g, 0.20M) in dry THF (100 ml) was added 1M solution of diborane in THF (∼ 70 ml) in a dropwise manner, at 0°, maintaining an atmosphere of N₂. After stirring the reaction mixture for 21 hr at room temperature, it was again cooled to 0° and 3N aqueous sodium hydroxide (30 ml) was cautiously added followed by 30% hydrogen peroxide (30 ml). The reaction mixture was further stirred for 2 hr and worked up in a standard manner (experimental, Chapter III) to afford 10, b.p. 125-130°/15 mm (27.0 g, 80%).

**IR:** 3600 cm⁻¹.

**PMR:** (60 MHz) 1.01 (s, 6H, 2 t-CH₃s), 1.13 (d, 6 Hz, 3H, -C(OH)-CH₃) and 3.70 (m, 1H, -CH-OH).

**MS:** m/e 168 (M⁺)

**Oxidation of the alcohol 10:** Chromic acid solution (∼ 60 ml) was slowly added to a stirred solution of 10 (20.2 g, 0.12M) in ether (150 ml) at 15° (40 min.). The reaction mixture was further stirred for about an hour and worked up in the usual manner to get the required ketone, endo-2-acetyl-3,3-dimethyl-norbornane, 7, b.p. 100-105°/15 mm, 17.00 g, 85%.

**UV:** λmax (MeOH) 290 nm (ε 25)
IR: 1709 cm$^{-1}$.

PMR: (90 MHz) 1.02 and 1.20 (2s, 3H each, t-CH$_3$s), 2.09 (s, 3H, -CO-CH$_3$), 2.38 (bs, 2H methines at C$_1$ and C$_2$).

MS: m/e 166 (M$^+$)

exo-2-Acetyl-3,3-dimethylnorbornane, 8: The ketone 7 (8.30 g, 0.05M) was introduced in one portion into sodium methoxide (prepared from 0.88 g of Na) in absolute methanol (50 ml), maintaining the temperature around 15°. The reaction mixture was then refluxed for 10 hr and was subjected to a standard work up to obtain the ketone, 8, b.p. 90-94°/12 mm (7.40 g, 88%).

UV: $\lambda_{\text{max}}$ (MeOH) 285 nm ($\varepsilon$ 20).

IR: 1709 cm$^{-1}$.

PMR: (90 MHz) 0.91 and 1.23 (2s, 3H each, t-CH$_3$s), 2.07 (s, 3H, -CO-CH$_3$) and 2.31 (m, 2H, methines at C$_1$ and C$_2$).

MS: m/e 166 (M$^+$).

Photolysis of 7: A solution of 7 (1.16 g, 7.0 mmol) in methanol (220 ml) was irradiated with lamp A almost till the disappearance of the starting material (10 hr). The product obtained after the removal of solvent was found to comprise five components (GLC: Column A, 110°, 30 ml/min) with RT's 1.25 (7%), 2.94 (4%), 3.80 (49%), 4.84 (22%) and 5.54 (18%).

Fractional distillation of the total material afforded two cuts: fraction 1 b.p. 90-100° (bath)/30 mm (60 mg) fraction 2, b.p. 105-110°C (bath)/7 mm (698 mg). The GLC of the fraction
1 indicated to be a mixture possessing the component of RT 1.25 as a major constituent and therefore was not analysed. Preparative GLC of fraction 2 (Column C, 170°, 50 ml/min.) yielded the component of RT 2.94 and 3.80 pure, and the other two components of RT 4.84 and 5.54 as a mixture. The GLC and the PMR data of the component 2.94 showed it to be the unreacted unreacted._

Spiro (3.4)2,2,4-trimethyl-oct-6-ene-4-ol, 11 (RT 3.80).

IR: 3695, 3130, 1650, 1365, 1360 and 1150 cm⁻¹.

PMR: (90 MHz, Fig.4.01) 1.04, 1.07 (2s, 3H each, t-CH₃'s), 1.35 (s, 3H, -C(OH)CH₂) and 5.77 (m, 2H, -CH=CH).

MS: m/e 166 (M⁺, 50%), 151(49%), 148(48%), 134(58%), 108(94%), 99(91%), 93 (base peak) and 85 (62%).

Analysis: Found: C, 79.55; H, 10.90. C₁₁H₁₈O requires:
C, 79.46; H, 10.92%.

The isolation and characterization of the components of RT's 4.84 and 5.54 are in progress.

Preparation of the intermediate ketone, 26

Methyl 2-bromo-2-methylpropenoate:

To isobutyric acid (70.40g, 0.80M) was added thionyl chloride (112.0 g, 0.95M, freshly distilled) with stirring at room temperature (75 min.). The mixture was heated at 80° for 30 minutes and the excess thionyl chloride was distilled off. Bromine (135.0 g) was introduced into the reaction pot at 80-90° with stirring (30 min.). The temperature
was raised to 100°C and the stirring was continued (5 hr).
The reaction mixture was cooled and absolute methanol (46 ml)
added, and the resulting solution was refluxed (2 hr). Cooled
reaction mixture was poured into ice-cold water and extracted
with ether (150 ml x 3). The organic extract was washed
successively with water, sodium hydrogen sulfite, sodium
carbonate, water, brine and dried. Evaporation of the solvent
furnished the product, **16**, b.p. 90-95°/100 mm (74.0 lg, 51%).

IR: 1735 cm⁻¹

PMR: (80 MHz) 1.91 (s, 6H, Br-C(CH₃)₂) and 3.78 (s, 3H, -OCH₃).

*Reformatsky reaction of cyclopentanone with the above bromide, 16*
(Scheme 4.05). A mixture of cyclopentanone (16.80 g, 0.20 M),
activated zinc dust (19.60 g, 0.30 M) and sodium dry benzene
(100 ml) was stirred and heated to reflux maintaining anhydrous
conditions. Freshly distilled **16** (27.10 g in 20 ml benzene)
was slowly introduced (3 hr) and the stirring was continued
(5 hr).

The cooled reaction mixture was decanted and washed
with 10% hydrochloric acid (50 ml) followed by water (200 ml).
The benzene extract was azeotropically distilled using a
Dean-Stark apparatus till no more water separated (1 hr).
Phosphorous oxychloride (freshly distilled, 2 ml) was intro-
duced and the distillation was continued as long as there was
collection of water (1 hr). The cooled benzene solution was
successively washed with water, 10% aqueous sodium carbonate,
water, brine and was dried. Removal of benzene afforded the product 17, b.p. 88-90°/10 mm (10.40 g, 41%).

IR: 1740 and 1640 cm⁻¹.

PMR: (80 MHz) 1.30 (s, 6H, -C(CH₂)₂), 3.60 (s, 3H, -OCH₃) and 5.42 (m, 1H, -C=CH).

Hydrogenation of 17 (Scheme 4.06): A mixture of 17 (8.40 g, 0.05 M), Raney Ni (freshly prepared, ~9 g) and ethanol (50 ml) was stirred (6 hr) in Parr hydrogenation apparatus under 3 atm. pressure (H₂). The catalyst was filtered off and the solvent distilled out to get the required product, 18, b.p. 90-95°/10 mm (7.57 g, 90%).

IR: 2941, 2857, 1730, 1470, 1430, 1390, 1365, 1260, 1190 and 1145 cm⁻¹.

PMR: (80 MHz) 1.13 (s, 6H, -C(CH₃)₂), 1.31-2.33 (m, 9H, 4x -CH₂ and one methine proton) and 3.65 (s, 3H, -OCH₃).

MS: m/e 111 (M⁺ - 59, 8%), 109(10%), 102(47%), 95(17%), 87(18%), 83(23%), 79(35%), 69(61%), 67(90%) and 59 (base peak).

Analysis: Found: C, 70.71; H, 10.67. C₁₀H₁₈O₂ requires: C, 70.59; H, 10.59%.

Alkaline hydrolysis of 18: To a stirred solution of 10% aq. NaOH (20 ml) and 95% ethanol (40 ml) was added 18 (6.81 g, 40.0 mmol) in one portion and the reaction mixture was refluxed for 2 hr. The required acid was obtained by the treatment of the cooled
residue with 10% hydrochloric acid. Isolation and purification was effected by a standard procedure to get pure acid, 19 b.p. 85-87°/3 mm (5.69 g, 91%).

PMR: (90 MHz) 1.16 (s, 6H, -CO-CH3), 1.33-2.31 (m, 9H, 4-CH2 and the methine proton) and 6.38 (bs, 1H, -COOH).

Homologation of the Acid, 19: Treatment of the above acid, 19 (3.59 g, 23.0 mmol) with thionyl chloride (8.21 g, 69.0 mmol) as described previously afforded the acid chloride, 20, b.p. 80-90°(bath)/10 mm (3.52 g, 88%).

IR: 1800 cm⁻¹.

PMR: (80 MHz) 1.23 (s, 6H, -CO-CH3) and 1.39 - 2.32 (m, 9H, 4-CH2 and the methine proton).

A solution of 20 (3.48 g, 20.0 mmol) in ether (15 ml) was added dropwise to an ethereal solution of diazomethane (250 ml, prepared from 10 g of nitrosomethylurea) at 0-5°. After the addition, the solution was kept at room temperature (2 hr) and the excess of diazomethane and ether were removed at 35°C on a water bath to get an yellow oil, 21.

IR: 1620 and 2150 cm⁻¹.

A solution of the above oil, 21 in absolute methanol (200 ml) was irradiated with lamp A employing a corex filter. The reaction was monitored by evolution of nitrogen and was stopped when the evolution ceased (1.5 hr). Removal of the solvent afforded the product, 22, b.p. 90-95°(bath)/6 mm (2.98 g, 81%).
IR: 1735 cm\(^{-1}\).

PMR: (90 MHz) 0.96 (s, 6H, -C(CH\(_3\))\(_2\)), 1.04 - 1.91 (m, 9H, 4\(\times\) CH\(_2\) and the methine proton) and 2.22 (s, 2H, -CH\(_2\)-COOCH\(_3\)) and 3.64 (s, 3H, -OCH\(_3\)).

MS: m/e 169 (M\(^+\) - 15, 6%), 153 (28%), 137(7%), 115(51%), 111(89%), 110(base peak),101(76%), 95(75%), 73(84%) and 69(83%).

Analysis: Found: C, 71.82; H, 10.76. C\(_{11}\)H\(_{20}\)O\(_2\) requires: C, 71.74; H, 10.87%.

4-Cyclopentyl-4-methyl 2-pentanone, 26: The following sequence of reactions was employed in preparing the ketone, 26. The ester 22 was converted to the corresponding acid chloride. Treatment of the latter with diazomethane furnished the diazoketone which on reaction with hydroiodic acid afforded the required ketone.

The ester obtained from the above photolysis, 22 (2.94 g, 16.0 mmol) was hydrolyzed with 10% NaOH to get the acid 23, b.p. 110-120\(^\circ\)(bath)/3 mm (2.58 g, 95%).

PMR: (80 MHz) 1.00 (s, 6H, -C(CH\(_3\))\(_2\)), 1.12 - 1.96 (m, 9H, 4\(\times\) CH\(_2\) and the methine proton) and 2.21 (s, 2H, -CH\(_2\)COOH).

Treatment of the acid, 23 (2.55 g, 15.0 mmol) with thionyl chloride followed by a standard work up furnished the acid chloride, 24, b.p. 90-100\(^\circ\)(bath)/10 mm (2.54 g, 90%).

IR: 1800 cm\(^{-1}\).
Addition of a solution of the acid chloride (2.54 g, 13.5 mmol) in ether (15 ml) to excess of diazomethane and a standard work up as described previously afforded the required diazoketone, 25.

IR: 1625 and 2100 cm⁻¹.

To a stirred solution of diazoketone 25 in chloroform (35 ml) was slowly introduced 48% aqueous hydroiodic acid at room temperature, till the evolution of nitrogen ceased (HI required 4.5 ml). The reaction mixture was diluted with water (50 ml) and two layers were separated. The aqueous layer was repeatedly extracted with ether and the combined organic extract was successively washed with water, aqueous sodium thiosulfate, water, brine and dried. The removal of solvent furnished the required ketone, 26 as a colourless liquid, b.p. 120-125°(bath)/12 mm (1.59 g, 70%).

IR: 1710 cm⁻¹.

PMR: (90 MHz, Fig. 4.02) 0.94 (s, 6H, -CiCn^), 2.13 (s, 3H, -CO-CH^) and 2.33 (s, 2H, -CH2-CO).

MS: m/e 153 (M⁺ - 15, 8%), 139(4%), 128(10%), 111(53%), 110(base peak), 99(20%), 95(48%), 81(23%) and 69(72%).

Analysis: Found: C, 78.51; H, 11.82. C_{11}H_{20}O requires: C, 78.57; H, 11.91%.

Photolysis of exo-ketone, 8: Irradiation of a solution of 8 (831 mg, 5.0 mmol) in methanol (220 ml) with lamp A was carried out till 95% conversion of the starting ketone (10 hr)
The product obtained after the removal of solvent, b.p. 100-105°(bath)/7 mm (582 mg, 70%) comprised (GLC: Column A, 110°, 30 ml/min) four components of RT's 2.74(5%), 3.14(6%), 3.96(26%) and 4.38 (63%). Preparative GLC (Column C, 160°, 60 ml/min.) of the total product furnished the last component in a pure form and the third component as a 3:2 mixture with the last one. The first component was found by its GLC behaviour to be the unreacted 8.

Tricyclo[4.2.1.0^{2.5}]2,4-dimethylnonane-4-ol, 27 (RT 4.38).

IR: 3355, 1450, 1383, 1271, 1200 and 1120 cm^{-1}.

PMR: (60 MHz, Fig. 4.03), 1.10 (s, 3H, t-CH₃), 1.30 (s, 3H, -C(OH)-CH₃) and 2.05 (bs, 2H, bridgehead protons).

MS: m/e 166 (M^+, 49%), 146 (50%), 123 (base peak), 116(73%), 108(78%), 107(82%), 91 (66%) and 80(81%).

Analysis: Found: C, 79.54; H, 10.89; C_{11}H_{18}O requires: C, 79.46; H, 10.92%.

The mixture of 28 (RT 3.96) and 27 (RT 4.38):

IR: 3360, 1455, 1380, 1200 and 1130 cm^{-1}.

PMR: (60 MHz) 1.10 (s, 3H, t-CH₃, signal of low intensity), 1.13 (s, 3H, t-CH₃, signal of high intensity) and 1.30 (s, 6H, 2x t-CH₃ signal of high intensity).
FIG. 401. PMR SPECTRUM OF SPIRO (3,4) 2,2,4-TRIMETHYL-
OCT-6-ENE-4-OL, 11 (90 MHz)
FIG. 4.02. PMR SPECTRUM OF
4-CYCLOPENTYL-4-METHYL-2-PENTANONE, 26
(90 MHz)
FIG. 4-03. PMR SPECTRUM OF TRICYCLO (4,2,1,0²,⁵) 2α, 4β-DIMETHYLNONANE
4α-OL 27 (60 MHz)
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