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TERPENOIDS—XXXVII

STRUCTURE OF α-ELEMENE

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Abstract—On the basis of degradative and NMR studies, structure I is assigned to the hydrocarbon α-elemene, the principal component obtained during acetic acid-perchloric acid dehydration of elemol (II).

THE crystalline monocyclic alcohol, elemol(II) occurs in several natural products.[1] Acid catalysed dehydration of elemol has been studied by Ruzicka *et al.*[2] and Šorm *et al.*,[3] but no definite conclusion was drawn regarding the structure of products formed.

Treatment of elemol with acetic acid in presence of perchloric acid at room temperature gives a good yield of a product which essentially consists of hydrocarbons, as well as small quantities of acetoxy compounds. Chromatography of the hydrocarbon fraction on alumina yields a pure sesquiterpene hydrocarbon (60% of the hydrocarbon mixture) having molecular formula, $C_{15}H_{24}$. The purified sample shows a single intense absorption at 250 mμ (ε, 17,780) and on quantitative hydrogenation affords a hexahydroderivative, $C_{15}H_{30}$, which from its physical constants and the IR spectrum, was found to be identical with elemane[3] (III). The hydrocarbon, therefore, has an elemane skeleton with three double bonds. Only three hydrocarbons, β-elemene[4,5] (IV), α-elemene[3,5] (g) and δ-elemene[6] (VI) possessing the elemane framework are reported in the literature. The product is not identical with β- or δ-elemene, as it does not show IR absorption around 890 cm^{-1} $\left(\begin{smallmatrix}\diagdown\\ \diagup\end{smallmatrix}C{=}CH_2 \text{ grouping}\right)$.

Since Šorm *et al.* obtained α-elemene by dehydration of elemol with formic acid,[3] it was considered that the hydrocarbon obtained by a similar procedure might be identical with the α-elemene of the above authors.

This view was supported by the UV absorption data given for α-elemene (λ_{max} 252 mμ, ε 4169)[5] As a comparison of the ε values suggested that the α-elemene reported may be a mixture of several products, α-elemene was prepared by the formic acid procedure and the products chromatographed into several components. One of these (the major bulk) showed comparable UV absorption (λ_{max} 250 mμ, ε 15,140) and was identical with our hydrocarbon with the IR spectra superimposable.

* Contribution No. 517: National Chemical Laboratory, Poona-8, India.

[1] Clover, *Philipine J. Sci.* **2**, 41, ref. in Ber. Schimmel Co., II, 21 (1907); K. Kafuku, T. Ikeda and Y. Fujita, *J. Chem. Soc., Japan* **53**, 636 (1932).

[2] L. Ruzicka and M. Pfeiffer, *Helv. Chim. Acta* **9**, 841 (1926).

[3] F. Sorm, M. Holub, V. Sykora, J. Mieziva, M. Streibl, J. Pliva, B. Schneider and V. Herout, *Coll. Czech. Chem. Comm.* **18**, 512 (1953).

[4] V. Herout, O. Motl and F. Šorm, *Coll. Czech. Chem. Comm.* **19**, 990 (1954).

[5] V. Sykora, V. Herout and F. Šorm, *Coll. Czech. Chem. Comm.* **21**, 267 (1956).

[6] J. Gough, V. Powell and M. D. Sutherland, *Tetrahedron Letters* No. **21**, 763 (1961).

On the basis of IR and UV data the tentative structure (V)[7] suggested for α-elemene is untenable, as according to Woodward's rule[8] such a conjugated diene should show UV absorption at 237 ± 5 mμ.

The IR spectrum (Fig. 1) of pure α-elemene shows bands at 1818, 1634, 1002, 912, (—CH=CH$_2$), 1604 (conjugated C=C), 877 (CR$_1$R$_2$=CR$_3$R$_4$) and 809 cm^{-1} (—CH=CR$_1$R$_2$). The UV spectrum (λ_{max} 250 mμ, log ε 4·25) is very similar to that of neo-abietic acid (VII),[9] and different from abietic acid (VIII) or maalidiene (IX) which exhibit triple absorption[10] in the UV region. Only two structures (I & II) are therefore possible for α-elemene.

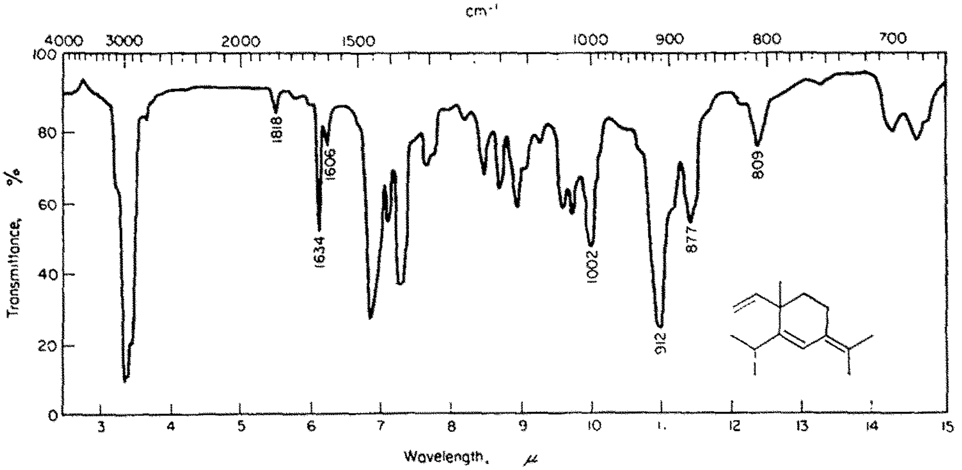

FIG. 1. Infrared spectrum of α-elemene (liquid film)

To eliminate the possibility of structure V the NMR spectrum was examined. This shows 4 olefinic protons out of 24·35 protons present in the molecule which is consistent with structures I and X, and not with V, which should show 6 olefinic protons. It is possible to account for all the peaks in the NMR spectrum on the basis of the structures I and X, NMR data and assignments are shown in Fig. 2.

In conformity with these structures α-elemene on ozonization gives formaldehyde and acetone as volatile components.

To decide between the structures (I and X) two sets of reactions were considered. The first route involved preparation of the tetrahydro derivative followed by ozonization to give ketones XI or XII, both of which are reported in literature.[11,12] Hydrogenation of α-elemene in ethyl acetate in presence of palladium on charcoal gives tetrahydro-α-elemene. The IR spectrum of tetrahydro-α-elemene shows the absence of vinyl group, but exhibits bands at 1640 and 888 cm^{-1}, suggesting isomerization of the isopropylidene group to the isopropenyl form. Ozonization of such a product (XIII or

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[7] J. Pliva, M. Horak, V. Herout and F. Šorm, *The Terpenes, Coll. of Spectra and Physical Constants* **1**, S23 (1960).

[8] R. B. Woodward, *J. Amer. Chem. Soc.* **63**, 1123 (1941).

[9] G. C. Harris and T. F. Sanderson, *J. Amer. Chem. Soc.* **70**, 339 (1948)

[10] G. Buchi, M. S. Wittenau and D. M. White, *J. Amer. Chem. Soc.* **81**, 1968 (1959) and references cited therein.

[11] V. Sykora, V. Herout and F. Šorm, *Coll. Czech. Chem. Comm.* **19**, 566 (1954).

[12] V. Sykora, V. Herout and F. Šorm, *Coll. Czech. Chem. Comm.* **20**, 220 (1955).

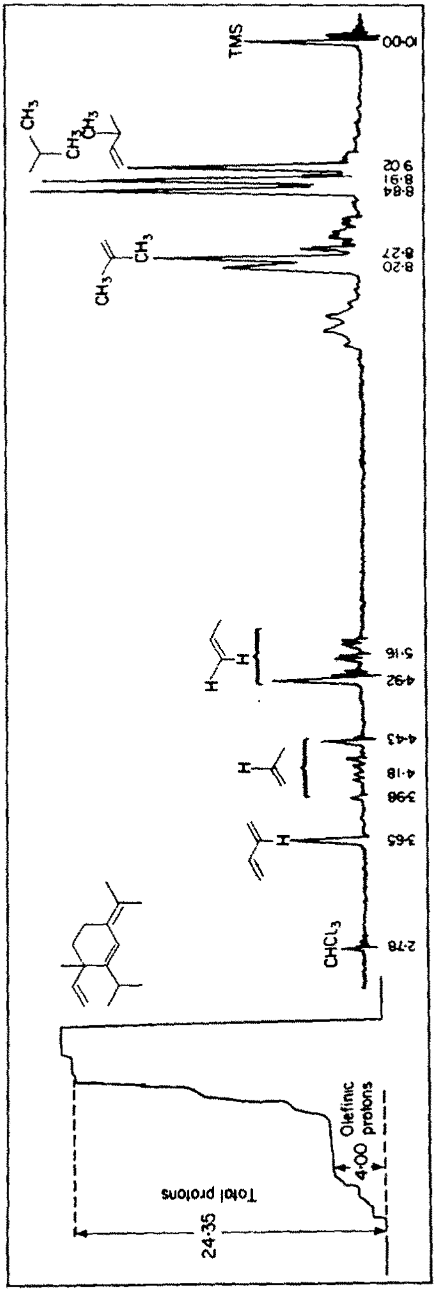

FIG. 2. NMR spectrum of α-elemene

XIV) would give two more ketones (XV and XVI) in addition to the ketones (XI and XII) mentioned above.

Ketone (XV) not reported, was synthesized. Tetrahydroelemol benzoate (XVII), prepared by hydrogenation of elemol benzoate[5] was pyrolysed to the hydrocarbon (XVIII). This has IR absorption bands at 3080, 1775, 1639 and 888 cm^{-1} (Fig. 3) indicating the presence of terminal methylene group. Presence of $\rangle C{=}CH_2$ group was further confirmed by ozonolysis, which furnishes formaldehyde and the norketone (XV), characterized as its semicarbazone, m.p. 159°. The IR spectrum of this ketone shows an intense band at 1710 cm^{-1} for a carbonyl function in the side chain and 1354 cm^{-1} due to methyl keto grouping. Methyl keto function in XV was further confirmed by reconvertion to tetrahydroelemol[13] on reaction with methyl magnesium iodide.

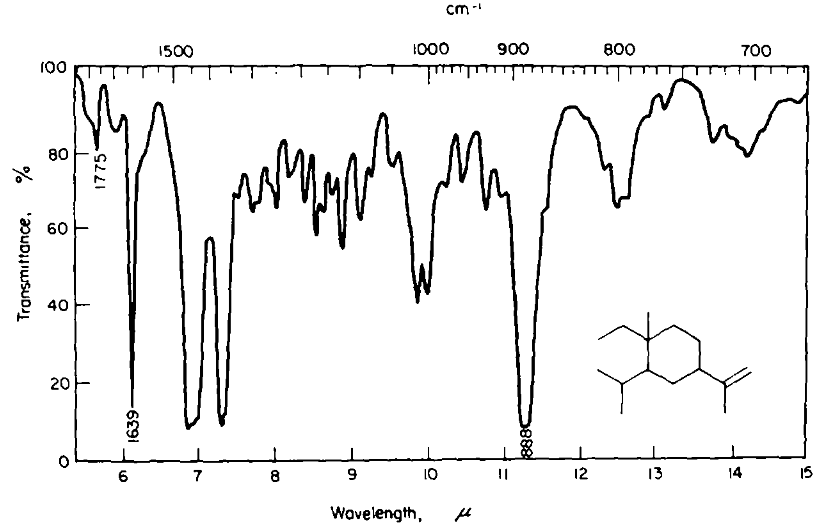

FIG. 3. Infrared spectrum of tetrahydroelemene (liquid cell 0.025 mm)

A small quantity of ketone (XII) was also obtained with a semicarbazone, m.p. 169–170° (lit.[12,14] 169–172°, 169°). The IR spectrum of this C_{12}-ketone is completely identical with the ketone, $C_{12}H_{22}O$, obtained by chromic acid oxidation of tetrahydroelemol.

Tetrahydro-α-elemene on ozonization furnishes only a small quantity of monoketonic fraction, which after extensive chromatography could be resolved into two fractions: (i) IR bands at 1712 cm^{-1} for a carbonyl function on a six-membered ring and 1412 cm^{-1} for —CO—CH$_2$- grouping, and (ii) IR bands at 1709 cm^{-1} due to keto group in side chain and 1358 cm^{-1} for the methyl keto function. However, no crystalline semicarbazone could be obtained from these ketones. The main ozonization product appears to be a keto-aldehyde which can be explained by assuming the presence of XIX in tetrahydro-α-elemene, probably formed by 1,4- addition to the conjugated system. Acetone and formaldehyde were detected as volatile components of ozonolysis. Thus these experiments do not lead to any definite conclusion.

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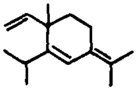
[13] V. Sykora, V. Herout, J. Pliva and F. Šorm, *Coll. Czech. Chem. Comm.* **19**, 124 (1954).

[14] L. Ruzicka and A. G. van Veen, *Liebigs Ann.* **476**, 70 (1929).

α-Elemene was selectively ozonized according to the procedure[9] employed for neo-abietic acid. The neutral portion of ozonolysis on chromatography over alumina yields a ketone, $C_{12}H_{18}O$ with IR bands at 1675 and 1610 cm^{-1} due to α-β unsaturated cyclohexenone, 1820, 1002 and 912 cm^{-1}, characteristic of vinyl group. This proves that only the isopropylidene double bond has been cleaved during ozonization. The volatile fragment of ozonization was identified as acetone. The ketone shows UV absorption at λ_{max} 239 mμ (log ε 3·9).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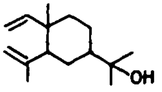

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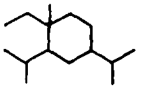
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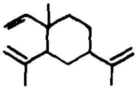
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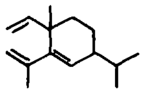
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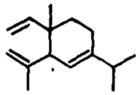
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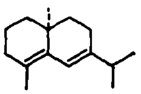
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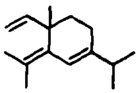
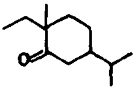
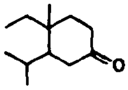

X



XI



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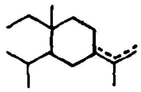
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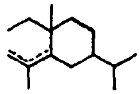
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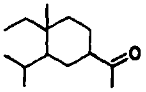

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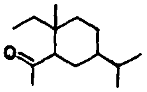
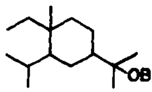
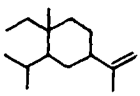


XVI



XVII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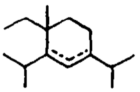
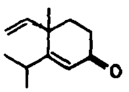
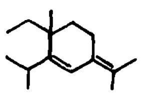
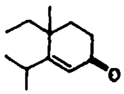

XIX



XX


XXI



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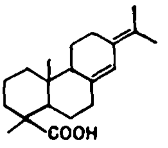
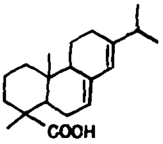


VII



VIII

On hydrogenation in methanol solution in presence of palladium charcoal, a tetrahydro product, $C_{12}H_{22}O$ (IR bands at 1706 and 1408 cm^{-1}) is formed which has a semicarbazone, m.p. 169° which shows no depression in melting point on admixture with the semicarbazone of XII. This establishes the structure XX for the unsaturated ketone and hence the structure I for α-elemene.

In a subsequent experiment, α-elemene was selectively hydrogenated to dihydro-α-elemene (XXI), which shows a single intense absorption at 248 mμ (log ε 4·1) indicating that the conjugated diene system remains unaffected during hydrogenation, further confirmed by IR bands at 1623 and 1606 cm^{-1} due to a conjugated diene system.

Dihydro-α-elemene (XXI) on selective ozonization gives the unsaturated ketone (XXII), λ_{max} 239 mμ, log ε 3·86. The IR spectrum exhibits strong bands at 1672 and 1608 cm^{-1} due to α-β unsaturated cyclohexenone. Hydrogenation affords dihydro product, $C_{12}H_{22}O$, which gives a semicarbazone, m.p. 170°, identical in all respects with that of the ketone XII. This gives additional support for structure I but it is possible that α-elemene may contain a small proportion of the isomer X.

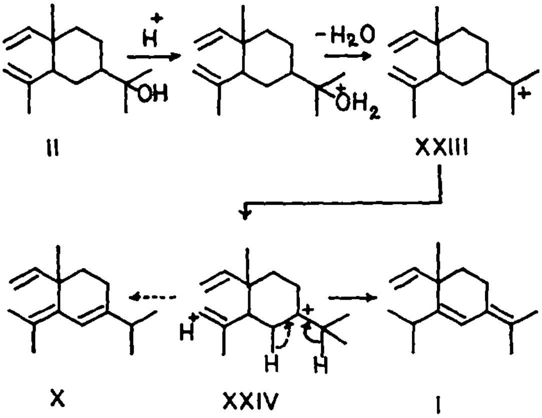
Recently, Leeuwen and Huisman[15] have reported the acid-catalysed dehydration of tertiary alcohols, and the results support the view that α-elemene may contain small amount of the isomer X.

The fractions eluted before α-elemene on the alumina column and which show much lower UV absorption (λ_{max} 250 mμ, log ε 2·8 to 3·6) might contain the optically active δ-elemene (VI), which may be responsible for the terminal methylenic absorption (890 cm^{-1}) observed by Sorm *et al.* for their α-elemene.

Mechanism for the formation of α-elemene from elemol

The sequence of the reactions shown in Scheme I, appears to account satisfactorily for the formation of α-elemene and accompanying products. Elemol (II) through protonation, forms the carbonium ion intermediate (XXIII), which can rearrange itself to a new ion (XXIV). Elimination of a proton together with simultaneous migration of the isopropenyl double bond would give rise to I or X. In view of the great tendency of the carbonium ion intermediate (XXIII or XXIV) to lose a proton, the reaction of this intermediate with the CH_3COO^- ion may give rise to acetoxy compounds, small amounts of which are actually formed during the formation of α-elemene.

Scheme I



EXPERIMENTAL

M.p. are uncorrected. Specific rotations were determined in chloroform solution. Light petroleum refers to fraction b.p. 60–80°. UV absorption spectra were measured in ethanol with a Beckman Model DK-2 Spectrophotometer. IR spectra were measured with a Perkin-Elmer (Model 137b) Infracord Spectrophotometer.

Isolation of elemol (II). Higher boiling fractions of Java citronella oil were used for the isolation of elemol, m.p. 52–53°, $[\alpha]_D$ −5·82° (*c*, 3·4) (Found: C, 81·4; H, 12·04. $C_{15}H_{26}O$ requires: C, 81·02;

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[15] P. H. Van Leeuwen and H. O. Huisman, *Rec. Trav. Chim.* **80**, 1115 (1961).

H, 11.79%). The IR spectrum showed complete identity with the spectrum of elemol available in literature.

Reaction of elemol with acetic acid-perchloric acid. To a solution of elemol (61 g) in glacial acetic acid (600 ml), perchloric acid (15 ml 60%) was added. The reaction mixture was allowed to stand at room temp (25–27°) for 72 hr with continuous stirring, then diluted with a large excess water and extracted with ether. The extract was washed with aqueous sodium hydrogen carbonate, then with water, dried (Na_2SO_4) and evaporated leaving crude α-elemene (52 g).

Isolation of α-elemene (I). The crude product was successively filtered through grade III (1 kg) and grade II (1 kg) alumina. The product eluted with light petroleum consisted mainly of hydrocarbons (40 g) which were subjected to careful chromatography on alumina (grade I, 3·3 kg).

In all 16 × 50 ml fractions with light petroleum were collected. Considering the physical constants of the chromatographic subfractions and their IR and UV spectra, fractions (2 to 14) were essentially pure samples of α-elemene. Fraction 8, after distillation showed maximum UV absorption, λ_{max} 250 mμ (log ε 4·25). The physical data relating to pure α-elemene are given below. The constants are determined on fraction 8, b.p. 120–130° (bath)/7 mm n_D^{26} 1·5130; $[\alpha]_D$ +116° (*c*, 14·85), d_4^{30} 0·8782. (Found: C, 88·3; H, 12·0. $C_{15}H_{24}$ requires: C, 88·16; H, 11·84%).

IR bands at: 1818, 1634, 1606, 1002, 912, 877, and 809 cm^{-1}.

Hydrogenation of α-elemene to hexahydro-α-elemene (III). A solution of α-elemene (0.546 g) in acetic acid (20 ml) was hydrogenated over Adams catalyst (20 mg), until the equivalent of 3·1 moles of hydrogen had been absorbed. After removal of catalyst, the filtrate afforded 0·5 g of the saturated hydrocarbon (elemane) which was purified by chromatography on alumina (grade I, 25 g), followed by distillation over sodium. It had the following properties, b.p. 130–132° (bath)/8 mm, n_D^{30} 1·4620 d_4^{30} 0·8387, M_R 68·85. $C_{15}H_{30}\sqrt{\overset{=}{\text{nil}}}$ requires 69·27; $[\alpha]_D$ ±0 (*c*, 15·6). (Found: C, 85·8; H, 14·4. $C_{15}H_{30}$ requires: C, 85·63; H, 14·37%).

IR spectrum was found to be identical with that of elemane described in literature.[3]

Dehydration of elemol with formic acid. A solution of elemol (8 g) in formic acid (98%, 36 ml) was maintained at 80–90° for 1 hr. The product was chromatographed on alumina (grade I, 300 g) and eluted with light petroleum. The third fraction (2·1 g) showed a high refractive index, n_D^{27} 1·5130 and was filtered again through alumina (grade I, 160 g) and distilled, b.p. 135–145° (bath)/8 mm, n_D^{27} 1·5126, $[\alpha]_D$ +98° (*c*, 5·2). (Found: C, 88·1; H, 11·15. $C_{15}H_{24}$ requires: C, 88·16; H, 11·84%). UV spectrum λ_{max} 250 mμ (log ε 4·18). The IR spectrum showed very good agreement with that of α-elemene obtained by the acetic acid-perchloric acid method. Slightly low values for specific rotation and UV absorption indicate the presence of trace impurities.

Tetrahydroelemol benzoate (XVII). Elemol benzoate was prepared[5] and a solution containing elemol benzoate (19·33 g) in acetic acid (150 ml) in presence of 0·4 g of Adams catalyst, absorbed 3200 ml hydrogen corresponding to 2·04 moles hydrogen in about 3 hr. The hydrogenated product was purified by distillation in vacuum to yield 18 g pure tetrahydro-elemol benzoate (XVII), b.p. 175–180° (bath)/1 mm, n_D^{25} 1·5010. (Found: C, 79·68; H, 10·96. $C_{22}H_{34}O_2$ requires: C, 79·95; H, 10·37%). IR bands at: 1710, 1280 and 712 cm^{-1}.

Tetrahydro elemene (XVIII). Tetrahydroelemol benzoate (17·5 g) was heated in a distillation flask at 210–230° (bath temp) *in vacuo* (100 mm). The distillate was taken up in ether and freed from benzoic acid by washing with small portions of sodium-bicarbonate solution. The ethereal extract containing the neutral portion, was washed with water, dried and solvent evaporated. The hydrocarbon (12·02 g) was further purified by chromatography over alumina (grade I, 0.7 kg) and then distilled *in vacuo* over sodium (8·64 g), b.p. 128–129°/9 mm, $[\alpha]_D$ 7·59° (clean), n_D^{26} 1·4748, d_4^{30} 0·8537, M_R 68·37. $C_{15}H_{28}\sqrt{\overset{=}{1}}$ requires 68·8 (Found: C, 86·8; H, 13·5. $C_{15}H_{28}$ requires: C, 86·46; H, 13·54%). IR bands at: 3077, 1775, 1639, and 888 cm^{-1}.

Ozonization of tetrahydroelemene (XVIII). (from pyrolysis of tetrahydro elemol benzoate). Tetrahydroelemene (7·9 g) was ozonized in chloroform solution (in 3 batches) at −28°. The combined ozonide after removal of solvent *in vacuo*, was decomposed with water and extracted with ether. The organic material was then separated into neutral (7·7 g) and acidic material (0·190 g). Presence of formaldehyde in the volatile fraction was confirmed by its dimedone derivative, m.p. 189°, a mixed m.p. with an authentic sample was undepressed. The neutral portion was separated by chromatography over alumina grade III, 240 g). In all 28 × 40 ml fractions with light petroleum were collected and IR spectra of the fractions taken. Fractions 7–28 (22 × 40 ml) eluted (2·5 g) of the ketone (XV), b.p. 160–164° (bath)/4·5 mm, n_D^{26} 1·4710 (Found: C, 80·6; H, 12·3. $C_{14}H_{26}O$ requires: C, 79·93; H, 12·46%). IR bands at: 1710 and 1354 cm^{-1}.

Semicarbazone was crystallized from aqueous ethanol, m.p. 159° (Found: N, 15·8. $C_{15}H_{29}ON_3$ requires: N, 15·72%).

Subsequent petroleum ether fractions (20 × 40 ml) gave only traces of carbonyl compound.

Elution of the chromatographic column with light petroleum–benzene (1:1, 10 × 40 ml) gave (0·3 g) ketone (XII), b.p. 150–155° (bath)/11 mm, $n_D^{26.5}$ 1·4740, $[\alpha]_D$ +5·024 (*c*, 5·97). (Found: C, 79·1; H, 12·1. $C_{12}H_{22}O$ requires: C, 79·06; H, 12·16%). IR bands at: 1714 and 1418 cm^{-1}.

This ketone gave a semicarbazone, which was crystallized from aqueous methanol, m.p. 169–170° (lit. m.p. 169–172° and 169°)[12,14] (Found: N, 16·95. $C_{13}H_{25}ON_3$ requires: N, 17·56%).

Tetrahydroelemol from ketone (XV). The methyl ketone (400 mg) was stirred and refluxed for 6 hr with Grignard reagent prepared from magnesium (0·7 g) and methyl iodide (3·5 g) in dry ether (50 ml). After decomposition with ice and dil sulphuric acid, the reaction product yielded 0·34 g tetrahydroelemol, purified by sublimation *in vacuo*, m.p. 55°. (Found: C, 78·93; H, 13·08. $C_{15}H_{30}O$ requires: C, 79·57; H, 13·36%).

Partial hydrogenation of α-elemene. α-Elemene (17·83 g) was hydrogenated in ethyl acetate (150 ml) in presence of 5% palladium charcoal catalyst (3 g). Hydrogenation ceased after 4560 ml (1·98 moles) hydrogen had been absorbed in about 2·5 hr yielding 17·33 g tetrahydroelemene which was purified by vacuum distillation, b.p. 140–145° (bath)/9 mm, n_D^{27} 1·4716, d_4^{30} 0·8529, M_R 68·25. $C_{15}H_{28}\sqrt{1}$ requires 68·8, $[\alpha]_D$ −12·4° (*c*, 1·3).

Since no definite conclusion could be drawn, details regarding ozonization of tetrahydro-α-elemene are not given.

Selective ozonization of α-elemene (I). α-Elemene (3·7 g) was ozonized in chloroform solution (40 ml) at −30°. The oxygen flow was adjusted to obtain about 0·2 g ozone per hr. The ozonization was stopped after exactly 1 hr and then decomposed and the neutral product taken up in ether and filtered through alumina (grade II, 100 g). Light petroleum eluted 2·6 g unchanged α-elemene. Elution with benzene and benzene–ether (1:1) yielded unsaturated ketone (0·8 g). This fraction was further chromatographed on alumina (grade II, 30 g). Light petroleum eluted a very small quantity of carbonyl containing fraction which was not further examined. Light petroleum–benzene (1:1, 5 × 10 ml) eluted 450 mg of pure α-β-unsaturated ketone, b.p. 148–155° (bath)/5 mm, n_D^{26} 1·4985. (Found: C, 81·1; H, 10·14. $C_{12}H_{18}O$ requires: C, 80·85; H, 10·18%). UV spectrum λ_{max} 239 mμ (log ε 3·9). IR bands at: 1820, 1678, 1634, 1610, 1002, 912 and 801 cm^{-1}.

Hydrogenation of α-β-unsaturated ketone (XX). The ketone (400 mg) in methanol (10 ml) was subjected to catalytic hydrogenation with palladium-charcoal catalyst (10%) until absorption corresponding to 2 moles hydrogen. The product (380 mg) was purified by distillation *in vacuo*, b.p. 140–150° (bath)/6 mm, n_D^{27} 1.4755 (Found: C, 79·77; H, 11·65. $C_{12}H_{22}O$ requires: C, 79·06; H, 12·16%). IR bands at: 1706 and 1408 cm^{-1}.

The semicarbazone prepared was crystallized from aqueous methanol, m.p. 169–170°, mixed m.p. with the authentic sample of semicarbazone from (XII) remained undepressed. (Found: N, 17·9; $C_{13}H_{25}ON_3$ requires: N, 17·56%). The IR spectra (in nujol) of the two specimens were identical.

Hydrogenation of α-elemene to dihydro-α-elemene (XXI). α-Elemene (2·36 g) in methanol (25 ml) was hydrogenated in presence of palladium-charcoal catalyst (0·25 g, 5%) until absorption of hydrogen corresponding to one double bond (339 ml, 1 mole). The catalyst was filtered and the filtrate after the removal of solvent distilled *in vacuo*, b.p. 125–135° (bath)/4 mm, $n_D^{23.5}$ 1·5000; $[\alpha]_D$ −8·84° (*c*, 7·8). (Found: C, 86·8; H, 12·7. $C_{15}H_{26}$ requires: 87·3; H, 12·7%). UV spectrum λ_{max} 248 mμ (log ε 4·1). IR bands at: 1623, 1606, 1464, 1379, 1299, 1176, 1145, 1111, 1037, 892, 878, 820 and 796 cm^{-1}.

Selective ozonization of dihydro-α-elemene (XXI). Ozonization of dihydro-α-elemene (2 g) was carried out as for selective ozonization of α-elemene. The ozonide was decomposed and the organic material extracted with ether. The product obtained was filtered through a short column of alumina. Light petroleum eluted unchanged dihydro-α-elemene (1 g). Benzene eluted the α-β-unsaturated ketone (0·9 g). The distilled product had the following properties, b.p. 152–158° (bath)/5 mm, n_D^{23} 1·4891. (Found: C, 79·0; H, 11·1. $C_{12}H_{20}O$ requires: C, 79·94; H, 11·18%). UV spectrum: λ_{max} 239 mm (log ε 3·86). IR bands at: 1672 and 1608 cm^{-1}.

Hydrogenation of α-β-unsaturated ketone (XXII). The ketone (481 mg) in methanol (10 ml) was hydrogenated in presence of palladium-charcoal catalyst (0·2 g, 5%) until hydrogen uptake had ceased (1 hr, 70 ml), the product was obtained in the usual way through chromatography and distillation. The semicarbazone was crystallized from aqueous ethanol, m.p. 170° (mixed m.p. with an authentic sample of the semicarbazone of XII remained undepressed).

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