Photochemical Transformations of α-Phellandrene

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U.v. irradiation of an ethereal solution of α-phellandrene (*p*-mentha-1,5-diene) (I) results in ring opening to give a mixture of geometrical isomers of 3,7-dimethylocta-1,3,5-triene (II) which, upon continued irradiation, forms at least six monomeric photoproducts. The major product (*ca.* 50%) is shown to be *exo*-6-isopropyl-2-methyl-bicyclo[3.1.0]hex-2-ene (XVa) on the basis of physical measurement and chemical degradation, and the second most important product (*ca.* 10%) is the *endo*-epimer (XVb). The configuration at C-6 in these products was determined by a stereospecific synthesis of dimethyl *t*-3-methylcyclopropane-*r*-1,*c*-2-dicarboxylate, (XIXa) which was identical with a degradation product of the main photoisomer (XVa), which is therefore the *exo*-6-isopropyl compound.

In 1960 Havinga and his co-workers[1] reported that irradiation of ethereal solutions of α-phellandrene (I) with u.v. light results in the formation of a mixture of the four possible geometrical isomers of the triene (II); these have since been isolated.[2] We have further irradiated the triene mixture, and found that, after initially increasing in intensity five-fold as described, the u.v. absorption of the solution at 265 nm eventually disappeared. Neither of the possible[3] 1,2,4-trienes was formed in appreciable yield, but a complex mixture of photoproducts resulted. The two principal photoisomers, produced in 50 and 10% yields, are described here.[4,5]

The major product, $C_{10}H_{16}$, gives n.m.r. signals indicative of the −CH=C(Me)− group, while its mass spectrum shows a parent ion peak at m/e 136. Dehydrogenation gave *m*- and *p*-cymene, and oxidative degradation led to isopropylsuccinic acid, so that by analogy with the photoisomerization of 1,5-hexadiene to bicyclo[2.1.1]hexane,[6] the structure (III) was first assigned to this compound.[4] Since there were no examples of bicyclo[2.1.1]hexene formation at the time of this work,[7] the product was re-examined.[5] Hydroboration and oxidation[8] gave a ketone (60%) with an i.r. maximum at 5·74 μm, indicative of a cyclopentanone rather than the bicyclo[2.1.1]hexanone[9] structure for the olefin (III). The ketone gave a crystalline benzylidene derivative establishing the presence of an α-methylene group, so that we can write the partial formula (IV) for the original hydrocarbon.

Since the photoproduct does not show the n.m.r. doublet generally associated with the presence of an isopropyl group, structures lacking this feature were considered. Thus the triene (II) might, by a plausible photochemical 1,3-hydrogen shift,[10] yield ocimene (V). This might (*cf.* ref. 11) yield the cyclobutanes (VI) (α-pinene) and (VII), or (VIII), which could arise as
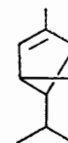
indicated in formula (IX). Direct comparison showed that the photoproduct is not α-pinene (VI), and the syntheses described below eliminated (VII) and (VIII).
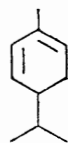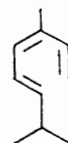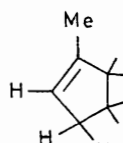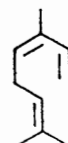

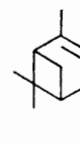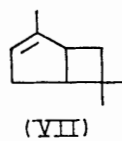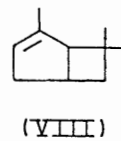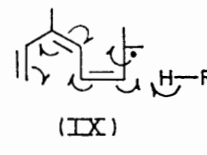The synthesis of (VII) was achieved by two routes. The first (Scheme 1), which also involved a synthesis of (VIII), was based on analogy with the photochemical addition[12] of isobutylene to 2-cyclohexenone at −80°. In the present work the photocondensation had to be

[1] R. J. de Kock, N. G. Minnaard, and E. Havinga, *Rev. Trav. chim.*, 1960, **79**, 922.

[2] J. E. Baldwin and S. M. Krueger, *J. Amer. Chem. Soc.*, 1969, **91**, 6444.

[3] K. J. Crowley, *Proc. Chem. Soc.*, 1964, 17.

[4] K. J. Crowley, *J. Amer. Chem. Soc.*, 1964, **86**, 5692 provides a preliminary account of some of these results; for a further report see ref. 5.

[5] J. Meinwald, A. Eckell, and K. L. Erickson, *J. Amer. Chem. Soc.*, 1965, **87**, 3532.

[6] R. Srinivasan, *J. Phys. Chem.*, 1963, **67**, 1367.

[7] For a review of bicyclo[2.1.1]hexane chemistry see J. Meinwald and Y. C. Meinwald, ' Recent Progress in Alicyclic Chemistry,' Vol. I, eds. H. Hart and G. Karabatsos, Academic Press, New York, 1966.

[8] H. C. Brown and C. P. Garg, *J. Amer. Chem. Soc.*, 1961, **83**, 2951.

[9] J. Meinwald and P. G. Gassman, *J. Amer. Chem. Soc.*, 1963, **85**, 57; G. Büchi and I. M. Goldman, *ibid.*, 1957, **79**, 4741.

[10] R. B. Woodward and R. Hoffmann, ' The Conservation of Orbital Symmetry,' Academic Press, New York, 1970.

[11] K. J. Crowley, *Tetrahedron*, 1965, **21**, 1001; W. G. Dauben and R. L. Cargill, unpublished work cited in W. G. Dauben and W. T. Wipke, *Pure Appl. Chem.*, 1964, **9**, 539.

[12] E. J. Corey, J. D. Bass, R. Le Mahieu, and R. B. Mitra, *J. Amer. Chem. Soc.*, 1964, **86**, 5570.

effected at 0° owing to the lower solubility of cyclo-pentenone in ether. Polymer formation was thereby greatly enhanced, but the two expected products were obtained, together with small amounts of other isomers.

SCHEME 1
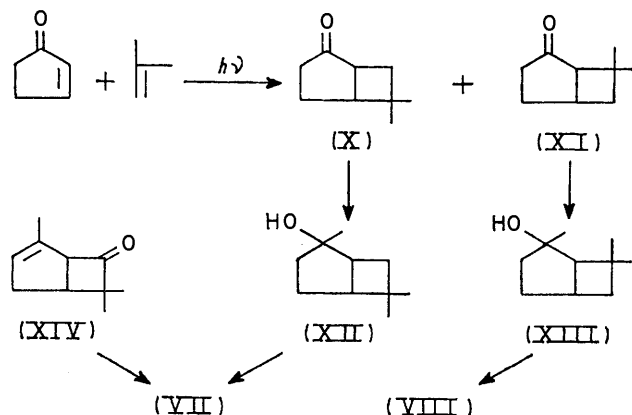
The major product was assigned structure (X) by analogy, and from examination of its i.r. and n.m.r. spectra; in particular the two methyl groups gave singlets at δ 1·03 and 1·20, while in the second product (XI), the corresponding three-proton singlets are at δ 0·84 and 1·20. The diamagnetic shift of the higher-field protons of (XI) can be ascribed to the shielding effect of the carbonyl group,[13] since one of the methyl groups of (XI) will lie almost directly above the trigonal atom.

With methyl-lithium both ketones gave the corresponding tertiary alcohols (XII) and (XIII), the i.r. and n.m.r. spectra of which are in accord with the assigned structures. These were dehydrated with phosphoryl chloride in pyridine, and both gave mixtures of two hydrocarbons, each in the ratio ca. 4 : 1. The major product (VII) from (XII) showed two singlet three-proton resonances (δ 0·94 and 1·08). The mixture from (XIII) could not be separated, but appeared from its n.m.r. spectrum to be mainly the expected product (VIII). The minor hydrocarbon from each dehydration was probably the corresponding exocyclic olefin.

A second synthesis of (VII) was achieved by reduction of the cyclobutanone (XIV).[14] Wolff–Kishner reduction at room temperature [15] was unsuccessful but the high-temperature Huang-Minlon modification [16] yielded the hydrocarbon (VII), which gave i.r. and n.m.r. spectra identical with those obtained earlier.

Having thus excluded (VII) and (VIII) for the major photoproduct, the isopropyl structure (XVa), which accords with the partial structure (IV), was subsequently established. This structure, which has analogous pre-cedents in the literature,[17] contains a vinylcyclopropane chromophore, in agreement with the u.v. maximum at

205·5 nm (ε 5200). Treatment with ozone and then with performic acid gave the crude keto-acid (XVIa). On oxidation with sodium hypobromite, this yielded the crystalline diacid (XVIIIa), the anhydride of which gives i.r. maxima at 5·54 and 5·68 μm, suggesting a glutaric anhydride. Its diester (XIXa), with refluxing 10% methanolic potassium hydroxide, yielded a mixture of acids, re-esterification of which gave the starting material (37%) and its acylic isomer (XXI) (56%). The same reaction was effected less cleanly by heating a 6% solution of (XIXa) in 2,2,4-trimethylpentane at 280° for 20 h. This ring-opening is analogous to that des-cribed [18] for homocaronic acid, and reverse Michael reactions are known to be brought about merely by heat.[19]

The ring-opened diacid (XX) shows $\lambda_{max.}$ 206 nm, suggestive of an αβ-unsaturated acid, either α or β sub-stituted,[20] while the n.m.r. spectrum of its methyl ester

shows an olefinic splitting pattern indicative of a 1,2-*trans*-disubstituted conjugated double bond. The syn-

[13] L. M. Jackman and S. Sternhell, ' Applications of NMR Spectroscopy in Organic Chemistry,' 2nd edn., Pergamon Press, London, 1969, pp. 88—92.
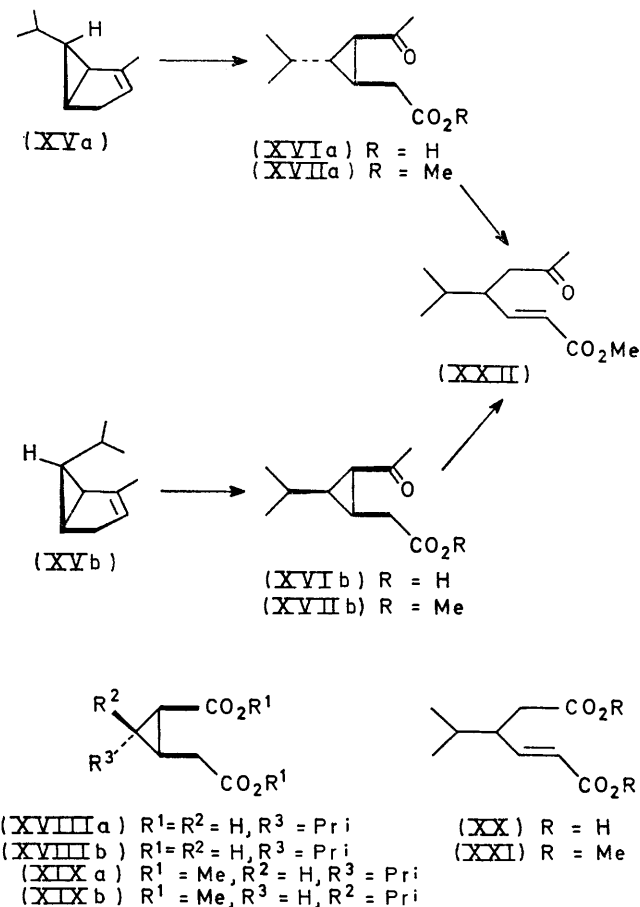
[14] J. J. Beereboom, J. Amer. Chem. Soc., 1963, 85, 3525.

[15] D. J. Cram, M. R. V. Sahyun, and G. R. Knox, J. Amer. Chem. Soc., 1962, 84, 1734.

[16] Huang-Minlon, J. Amer. Chem. Soc., 1946, 68, 2487.

[17] A. Padwa and S. Clough, J. Amer. Chem. Soc., 1970, 92, 5803, and references cited therein.

[18] L. Crombie, J. Crossley, and D. A. Mitchard, J. Chem. Soc., 1963, 4957.

[19] J. W. Cornforth, I. Y. Gore, and G. Popjak, Biochem. J., 1957, 65, 94; cf. L. F. Fieser and M. Fieser, ' Advanced Organic Chemistry,' Reinhold, New York, 1961, p. 477.

[20] A. T. Nielsen, J. Org. Chem., 1957, 22, 1539.

thesis of the *cis*-isomer of this diester has been described.[21] Ozonolysis of the acid (XX) gave isopropylsuccinic acid and hydrogenation gave 3-isopropyladipic acid. This confirms the structure (XX) and thus the structure (XVIII). The latter in conjunction with (IV) leads to structure (XVa) for the main photoproduct: its stereochemistry is discussed below.

Apart from photodimers [22] and the trienes (II), several minor photoproducts were obtained during the preparation of (XVa). The α-phellandrene contained 20—25% impurities, chiefly *p*-cymene, mycreme, and an unidentified component, probably β-phellandrene, but none of these should be rapidly isomerized by light of wavelength >255 nm. To confirm this a small sample of α-phellandrene, purified (>96%) by g.l.c., was irradiated and found to give the same pattern of photoproducts as the large-scale irradiations. Furthermore, irradiation of ethereal solutions of the terpene in the presence of excess of *p*-cymene, which might act as a sensitizer,[23] and, in other experiments, of copper(I) chloride [24] and silver nitrate, gave the usual product pattern.

Only one of the minor photoproducts was isolated in sufficient quantity and purity to permit an extensive examination. It is also isomeric with α-phellandrene, and its n.m.r. spectrum has broad singlets at δ 1·76 (3H) and 5·04 (1H) (–CH=CMe–) and 0·95 (CHMe$_2$). Its u.v. maximum at 207·5 nm (ε 4000) suggests the same type of conjugation as in the main photoproduct, and it seemed feasible that the two compounds differ only in their stereochemistry. This was proven by the following correlation.

The minor photoproduct (XVb) * was treated with the permanganate–periodate reagent,[25] affording the corresponding keto-acid (XVIb). Its methyl ester (XVIIb) has λ 215 nm (ε 2200), i.r. maxima at 5·74 (saturated ester) and 5·90 μm (cyclopropylketone),[26] and no i.r. or n.m.r. peaks indicative of unsaturation. The ester appears homogeneous on g.l.c. at 125°, but as the temperature of the injection block is raised, the formation of two new products (6 : 1) is observed. The major pyrolysis product has λ 215 nm (ε 11,000) and i.r. maxima at 5·81 μm (saturated ketone and αβ-unsaturated ester) and 6·02 μm (C=C). Its n.m.r. spectrum confirmed the presence of the methyl ketone [δ 2·04 (3H)], methyl [δ 3·56 (3H)], and isopropyl groups [δ 0·9 (6H, *J* 6·5 Hz with additional fine splitting)] while the close similarity of its two-proton olefinic splitting pattern [δ 5·71 (d, *J* 16 Hz) and 6·71 (dd, *J* 16 and 8 Hz)] to that of ethyl 4-methylpent-2-enoate (XXVI) indicated the presence of the *trans* olefinic system –CH=CH–CO$_2$R. The struc-

ture (XXII) was thus assigned to the compound, and confirmed by its preparation from the major photoproduct (XVa).

The latter could not be obtained pure, but gave the crude keto-acid (XVIa) in good yield. This did not crystallize, nor could the corresponding ester (XVIIa) be purified by g.l.c. owing to its thermal instability. However, the semicarbazone of (XVIIa) was cleaved without rearrangement by distillation from dilute aqueous oxalic acid. The resulting pure (>99%) keto-ester gave an i.r. spectrum similar to that of the crude ester mixture and different from that of the ester (XVIIb). On g.l.c. pyrolysis as before, it yielded a mixture of two products (7 : 1), the major component giving i.r. and n.m.r. spectra identical with those of (XXII). Thus the two unpyrolysed esters (XVII) can differ only in stereochemistry, and the same should be true of the parent photoproducts. These therefore differ either at the ring junction or in the orientation of the isopropyl group.

A *trans* fused bicyclo[3.1.0]hexene should be highly unstable. Both photoproducts are more stable to pyrolysis than is α-phellandrene, and both must have a *cis* ring fusion. Furthermore, both have been oxidized to their respective dicarboxylic acids (XVIII) and these give anhydrides which can be hydrolysed to the original acids by hot water. The n.m.r. spectra are in accord with these stereochemistries. The minor photoproduct (XVb) has no resonance at higher field than δ 0·5, while (XVa) gives a broad one-proton singlet at δ —0·08.† This can be attributed to the C(6) cyclopropyl proton lying above the plane of the double bond, which must have a marked shielding effect.[27]

The ready thermal ring-opening of the *cis*-fused 1-acyl-2-alkylcyclopropanes is well known.[28,29] The fact that both keto-esters (XVII) readily undergo this ring cleavage suggests the *cis* configurations (XVIIa) and (XVIIb). In accord with its crowded, all-*cis* nature, the keto-ester (XVIIb) is proylysed about twice as fast as is (XVIIa).

The results of hydroboration experiments are in agreement with the proposed stereochemistry. The ketone

(XXIV) (XXIII)
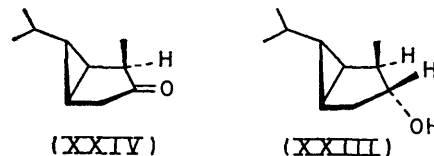
(XXIV) resulting from (XVa) by treatment with diborane, followed by chromic acid,[8] was also formed in

* This terminology is also applied to the related compounds, so that, for the diacid (XVIII) for example, (XVIIIa) has both carboxy-groups *trans* to the isopropyl group, while (XVIIIb) has all three groups *cis*: the suffix c [for example in (XXVIIc)] is used to indicate that the two carboxy-groups are *trans*.

† This resonance is masked by tetramethylsilane, and its presence was not noted in the original report.[4]

[21] N. Schamp, *Bull. Soc. chim. belges*, 1967, **76**, 400.
[22] J. E. Baldwin and J. P. Nelson, *J. Org. Chem.*, 1966, **31**, 336; G. O. Schenck and R. Steinmetz, *Bull. Soc. chim. belges*, 1962, **71**, 781.
[23] M. W. Schmidt and E. K. C. Lee, *J. Amer. Chem. Soc.*, 1970, **92**, 3579 and references cited therein.
[24] R. Srinivasan, *J. Amer. Chem. Soc.*, 1963, **85**, 3048.
[25] R. U. Lemieux and E. v. Rudloff, *Canad. J. Chem.*, 1955, **33**, 1701.
[26] K. Nakanishi, ' Infrared Absorption Spectroscopy,' Holden Day Inc., San Francisco, 1962, p. 62.
[27] Ref. 13, p. 98.
[28] R. M. Roberts and R. G. Landolt, *J. Amer. Chem. Soc.*, 1965, **87**, 2281.
[29] D. E. McGreer, N. W. K. Chiu, and R. S. McDaniel, *Proc. Chem. Soc.*, 1964, 415; G. Ohloff, *Tetrahedron Letters*, 1965, 3795.

non-acidic medium; treatment of the intermediate borane with alkaline hydrogen peroxide [30] gave the alcohol (XXIII) which was oxidized with the Sarett reagent [31] to (XXIV), confirming the illustrated configuration. The same hydroboration–chromic acid oxidation treatment of (XVb) yielded no satisfactory product; the intermediate organoborane would be very hindered.

Finally, the stereochemistry of the main photoproduct was confirmed by the synthesis of its degradation product, the diester (XIXa). This involved the synthesis of the diacid (XXVIIa), and homologation of this at either of the two carboxy-groups by the Arndt–Eistert sequence (Scheme 2). The Wolff rearrangement which is the final

somewhat extends the range reported [33] for such anhydrides. A minor product (1·4%) formed during the condensation may have been the all-*cis* diester, as it appeared to isomerize during saponification.[35]

Several unsuccessful attempts were made to convert the anhydride of the acid (XXVIIa) into the half-ester by heating with anhydrous methanol; [36] however, treatment of the anhydride with sodium methoxide [37] gave the half-ester without difficulty. On treatment with oxalyl chloride [38] this yielded a distillate with i.r. maxima corresponding to the acid chloride (5·57 µm) and ester (5·73 µm) groups, and diazomethane gave the corresponding diazo-ketone with an appropriate n.m.r. spectrum.
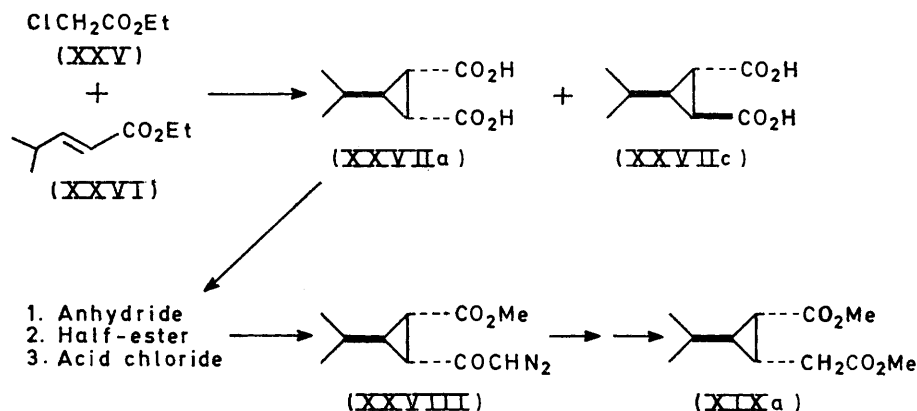
SCHEME 2

step of this is known to proceed with retention of configuration.[32]

Following the procedure for the synthesis of 3-methyl-cyclopropane-1,2-dicarboxylic acid,[33] we condensed ethyl chloroacetate (XXV) with ethyl 4-methylpent-2-enoate (XXVI). This gave two major products (16·9 and 6·3%), the diethyl esters of the acids (XXVIIa) and (XXVIIc). The derived acid mixture was treated with acetic anhydride and the resulting anhydride of the *cis*-acid distilled. With boiling water this yielded the acid (XXVIIa), which gave a liquid dimethyl ester, homogeneous on g.l.c. The non-volatile anhydride fraction yielded the *trans*-acid (XXVIIc), the methyl ester of which was also homogeneous on g.l.c. Vigorous treatment of the *trans*-acid (XXVIIc) with acetic anhydride resulted in conversion into the *cis*-acid (XXVIIa).[34] The n.m.r. spectra of these acids and esters are in good agreement with the assigned structures. The anhydride of (XXVIIa) has i.r. maxima at 5·36 and 5·58 µm, which

Attempts to bring about the Wolff rearrangement of the diazo-ketone using the silver oxide–dioxan [39] and the silver benzoate–methanol [40] methods were unsuccessful. Each gave a mixture of about eight components, few of which were common to both, and none of which was the desired product. However, on irradiation of the diazo-ketone in aqueous dioxan, followed by esterification of the acidic product, g.l.c. showed three components (55, 23, and 22%), the chief of which was not separated from the diester (XIXa), and gave the same i.r. and mass spectra.

The isopropyl n.m.r. signals obtained varied from double doublets to broad singlets, with only very few examples of the ' normal ' isopropyl doublet.

The predictions of Woodward and Hoffmann [10] regarding the stereochemical course of electrocyclic rearrangements can be satisfactorily applied to our results. Since α-phellandrene is optically active, while the photoproduct

[30] H. C. Brown and B. C. Subba Rao, *J. Amer. Chem. Soc.*, 1956, **78**, 5694.

[31] G. I. Poos. G. E. Arth, R. E. Beyler, and L. H. Sarett, *J. Amer. Chem. Soc.*, 1953, **75**, 422.

[32] J. F. Lane and E. S. Wallis, *J. Amer. Chem. Soc.*, 1941, **63**, 1674; *cf.* K.-P. Zeller, H. Meier, H. Kolshorn, and E. Müller, *Chem. Ber.*, 1972, **105**, 1875.

[33] L. L. McCoy, *J. Amer. Chem. Soc.*, 1958, **80**, 6568.

[34] T. W. D. Gregory and W. H. Perkin, jun., *J. Chem. Soc.*, 1903, **83**, 780; *cf.* M. Mousseron, R. Fraise, R. Jacquier, and G. Bonavent, *Compt. rend.*, 1959, **248**, 1465.

[35] *Cf.* L. L. McCoy, *J. Org. Chem.*, 1964, **29**, 240.

[36] *E.g.* G. D. Gutsche, M. W. Wendt, and K. L. Seligman, *J. Amer. Chem. Soc.*, 1958, **80**, 3711; A. Zilkha and M. D. Bachi, *J. Org. Chem.*, 1959, **24**, 1096.

[37] P. C. Guha and M. S. Muthanna, *J. Indian Inst. Sci.*, 1939, **22A**, 278 (*Chem. Abs.*, 1940, **34**, 3256).

[38] R. Adams and L. H. Ulich, *J. Amer. Chem. Soc.*, 1920, **42**, 599; A. L. Wilds and C. H. Shunk, *ibid.*, 1948, **70**, 2427.

[39] W. P. Campbell and M. D. Soffer, *J. Amer. Chem. Soc.*, 1942, **64**, 417.

[40] M. S. Newman and P. F. Beal, *J. Amer. Chem. Soc.*, 1950, **72**, 5163.

(XVa) is not, the ring-opened triene (II) is evidently an intermediate. The 3-*cis*-5-*trans*-isomer of this triene should photocyclize in its first excited state to the principal photoproduct (XVa).[41] The more hindered, and therefore less stable, 3-*cis*-5-*cis* isomer should similarly give rise, through its first excited state, to the minor photoproduct (XVb). The 1 : 5 ratio of (XVb) to (XVa) is to be expected in view of the 1 : 3 ratio [2] of their respective precursors, and of the greater steric hindrance in the cyclization of the 3-*cis*-5-*cis* triene.

EXPERIMENTAL

Unless otherwise stated melting points were taken on a Kofler hot-stage apparatus, i.r. spectra with a Perkin-Elmer Infracord, and u.v. spectra with a Cary model 14 recording spectrophotometer; for the spectra of the photoproducts (XVa) and (XVb) this instrument was flushed with Matheson prepurified nitrogen for 4 h before use. When not specified, i.r. spectra of liquids were obtained neat, and of solids as potassium chloride discs, and 2,2,4-trimethylpentane was used as solvent for u.v. spectral determinations. N.m.r. spectra were obtained at 60 MHz with a Varian A-60 spectrometer, using carbon tetrachloride as solvent and tetramethylsilane as internal standard. An Aerograph model 660 was used for most of the gas chromatographic (g.l.c.) separations (with 6 ft × 1/8 in columns) but some results were obtained with a Perkin-Elmer model 154-D Vapor Fractometer; separations termed 'preparative' were done with a modified Beckman GC 2 apparatus on 10 ft × 3/8 in columns.

For preparative scale irradiations a 450 W Hanovia lamp, No. 679A-36 in a standard Hanovia water-cooled immersion well of Vycor glass was used, with a filter sleeve of Corex glass, and Matheson, Coleman, and Bell A.C.S. analysed ether as solvent.

α-Phellandrene purified by careful fractional distillation through a 36 in spinning band column, had b.p. 70° at 20 mmHg; its major contaminants were collected by g.l.c. and identified by their i.r. and n.m.r. spectra as myrcene (*ca.* 10%) and *p*-cymene (*ca.* 5%). The main unidentified contaminant (*ca.* 3%) may have been β-phellandrene as it had $\lambda_{max.}$ 229 nm (ε *ca.* 6000) [lit.,[42] $\lambda_{max.}$ 231 nm (ε 9120)], and δ 4·72 (2H, s, C=CH$_2$), 5·73 and 6·16 (2H, ABq, *J* 10 Hz, *cis* CH=CH), and 0·9 (6H, d, *J* 7 Hz, ¬CHMe$_2$); its i.r. spectrum differed appreciably from that published for β-phellandrene.[43]

Irradiation of α-Phellandrene.—This terpene (17 g; 75—80% pure) in ether (500 ml) was irradiated at 25—30° for 137 h, during which period five samples (5 ml each) were withdrawn. The irradiated solution (475 ml) was distilled to give a monomeric distillate, b.p. 51—71° at 22 mmHg (9·82 g), a dimeric distillate, b.p. 108—121° at 0·9 mmHg (2·9 g), and a residue (2·6 g). G.l.c. of the first fraction indicated yields,* based on α-phellandrene, of 56% (XVa) and 11% (XVb). Unchanged myrcene and *p*-cymene (g.l.c. and i.r.) were recovered by g.l.c.

The main photoproduct, exo-6-*isopropyl-2-methylbicyclo*-[3.1.0]*hex-2-ene* (XVa), had b.p. 66·3—66·5° at 36 mmHg, n_D^{21} 1·4543, [α]$_D^{22}$ ± 0° (5 cm tube; no solvent). After

purification by g.l.c. (30% cyano-silicone, 60°) it had $\lambda_{max.}$ 205·5 nm (ε 5200) (slit width <1 mm down to 194 nm, at which point ε = 4000), i.r. $\lambda_{max.}$ 3·3, 3·4—3·52s, 6·1, 6·8s, 6·89s, 7·2s, 7·31s, 7·43, 7·51, 7·75w, 8·3, 8·41, 8·61, 9·53, 9·71, 10·21, 10·72, 11·31w, 12·14, 12·27, and 12·84 μm, δ 4·87 (1H), 2·3—2·5 (2H), 1·3—1·5 (2H), and 0·95 (7H) (all m), 1·76 (3H, q, *J* 1·8 Hz); with external tetramethyl-silane δ − 0·08 br (1H, s) was observed (Found: C, 88·1; H, 11·7. C$_{10}$H$_{16}$ requires C, 88·2; H, 11·8%).

The second photoproduct, endo-6-*isopropyl-2-methyl-bicyclo*[3.1.0]*hex-2-ene* (XVb), had b.p. 73—76° at 36 mmHg; after purification by g.l.c. and distillation in a bulb-tube the *olefin* had $\lambda_{max.}$ 207·5 nm (ε 4000) (slit width <1 mm down to 194 nm, at which point ε = 3400), i.r. $\lambda_{max.}$ 3·3, 3·41—3·5s, 6·09w, 6·91s, 7·26s, 7·33, 7·74w, 8·2, 8·68, 9·0, 9·3w, 9·52, 9·75, 10·3w, 10·75, 11·55w, 11·82, 12·75s, 13·25s, and 14·1 μm, δ 5·04 (1H), 2·0—2·3 (2H), 1·76 (3H), and 0·95 (7H) (all m), 0·5—2·0 (3H, complex) (Found: C, 88·3; H, 11·7%).

Photoaddition of Isobutylene to Cyclopentenone.—The method used was that of Corey and his co-workers [12] except that the reaction temperature was maintained at 0° rather than −80°; at the lower temperature the cyclopentenone crystallized from the solution and was recovered unchanged.

The reaction vessel was charged with pentane (spectral grade; 300 ml) and freshly distilled cyclo-pentenone (20·0 g) and was immersed in an ice–salt bath and alternatively evacuated and filled with nitrogen five times. Isobutylene (400 ml) was introduced and at 4 h intervals further portions (200 ml) were added. After 12 h the solution was concentrated and the residue distilled, giving unchanged cyclopentenone (4·0 g), a non-volatile residue (12·5 g), and a mixture of products, b.p. 87° at 45 mmHg to 78° at 10 mmHg (3·71 g), which was separated by g.l.c. (30% Carbowax 20 M, 160°). The two main products were the expected ketones (X) (1·8 g. 5·4%), and (XI) (0·6 g, 1·8%). The former showed i.r. $\lambda_{max.}$ 5·77, 7·24, 7·32, and 8·60 μm, δ 1·03 (3H) and 1·20 (3H) (both s) and 1·50—2·80 (8H, complex), and the latter i.r. $\lambda_{max.}$ 5·75, 7·20, 7·29, and 8·60 μm, δ 0·84 (3H) and 1·20 (3H) (both s) and 1·50—3·20 (8H, complex).

2,6,6-*Trimethylbicyclo*[3.2.0]*heptan-2-ol* (XII).—Methyl-lithium was prepared from methyl iodide (2·5 g) and lithium (0·27 g) in ether. 6,6-Dimethylbicyclo[3.2.0]heptan-2-one (1·2 g) was added with stirring at room temperature. After 2 h water was added, and ether extraction yielded a crystalline solid, sublimation of which afforded pure *alcohol* (XII) (1·3 g), m.p. 70—70·5°, i.r. $\lambda_{max.}$ 3·12, 8·62, 9·04, and 10·25 μm, δ 0·95 (3H), 1·22 and 1·25 (6H) (all s), and 1·6—2·5 (9H, complex) (Found: C, 77·5; H, 11·7. C$_{10}$H$_{18}$O requires C, 77·9; H, 11·8%).

2,7,7-*Trimethylbicyclo*[3.2.0]*heptan-2-ol* (XIII).—Methyl-lithium was prepared from methyl iodide (0·3 g) and lithium (0·15 g) and 7,7-dimethylbicyclo[3.2.0]heptan-2-one (0·1 g) was added. Work-up and sublimation as for (XII) at 30° and 2 mmHg gave stout needles, m.p. 63—64° (0·11 g). Repeated sublimation afforded the pure *alcohol* (XIII), m.p. 63·5—64°, i.r. $\lambda_{max.}$ 3·00, 8·50—8·89, 9·11, and 10·22 μm, δ 1·28 and 1·30 (9H) (both s) and 1·4—2·8 (9H, complex) (Found: C, 78·0; H, 11·7. C$_{10}$H$_{18}$O requires C, 77·9; H, 11·8%).

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* These yields are obtained when light of wavelength less than *ca.* 255 nm was filtered out with a Corex glass filter; when a Vycor glass filter was used (*i.e.* λ *ca.* 220 nm) both the irradiation time and the yield of photoisomers were reduced; with a quartz well mainly polymeric products were obtained.

[41] K. J. Crowley, *Photochem. Photobiol.*, 1968, **7**, 775.
[42] H. Booker, L. K. Evans, and A. E. Gillam, *J. Chem. Soc.*, 1940, 1453.
[43] G. G. Acheson and T. F. West, *J. Chem. Soc.*, 1949, 812.

2,6,6-Trimethylbicyclo[3.2.0]*hept-2-ene* (VII).—2,6,6-Trimethylbicyclo[3.2.0]heptan-2-ol (1·0 g) was dissolved in pyridine and the solution was cooled in an ice-bath. With vigorous stirring, phosphoryl chloride (2·0 g) was added dropwise. The mixture was stirred in ice for 4 h, left at 0° for 40 h, cautiously decomposed with ice, and extracted with ether. The extract was washed with water, dilute acid, sodium carbonate solution, and saturated brine and yielded two hydrocarbons (4 : 1), b.p. 60° at 20 mmHg (0·5 g). The distillation residue afforded unchanged alcohol (0·1 g). Preparative g.l.c. (20% tricresyl phosphate, 100°) gave samples of each hydrocarbon. The major component, 2,6,6-*trimethylbicyclo*[3.2.0]*hept-2-ene* (VII), had i.r. $\lambda_{max.}$ 3·29, 6·06, 7·27, 7·34, and 12·43 μm, δ 0·94 (3H) and 1·08 (3H) (both s) and 1·25—3·10 (10H, complex) (Found: C, 88·4; H, 11·8. $C_{10}H_{16}$ requires C, 88·2; H, 11·8%).

The minor component, believed to be 6,6-dimethyl-2-methylenebicyclo[3.2.0]heptane, showed i.r. $\lambda_{max.}$ 3·28, 6·04, 7·27, 7·35, and 11·32 μm.

2,7,7-Trimethylbicyclo[3.2.0]*hept-2-ene* (VIII).—2,7,7-Trimethylbicyclo[3.2.0]heptan-2-ol (100 mg) was dissolved in pyridine and cooled in an ice-bath, phosphoryl chloride (0·25 g) was added dropwise, and the mixture was left at 0° for 48 h. Work-up as described above yielded a hydrocarbon distillate (70 mg) which showed only one single symmetrical peak on g.l.c. and had i.r. $\lambda_{max.}$ 3·25, 6·04, 7·24, 7·32, 11·35, and 12·61 μm, δ 0·80, 0·92, 1·20, and 2·08 (all s), 1·40—1·9 and 2·2—2·9 (both m), 4·78br (d), and 5·33 (m). The proton ratios indicated that the mixture consisted of *ca.* 80% 2,7,7-trimethylbicyclo[3.2.0]hept-2-ene (VIII) and 20% 7,7-dimethyl-2-methylenebicyclo[3.2.0]heptane.

Wolff–Kishner Reduction of 2,6,6-Trimethylbicyclo[3.2.0]-*hept-2-en-7-one* (XIV).—A mixture of ethylene glycol (10 ml) and potassium hydroxide (0·90 g) was stirred and heated slowly until solution occurred, after which the ketone (XIV) (1·0 g) and 85% hydrazine hydrate (1 ml) were added. The mixture was refluxed for 1 h, the temperature increased by distillation to 180°, and the mixture refluxed for 6 h. The usual work-up and distillation of the resulting yellow oil gave 2,6,6-trimethylbicyclo[3.2.0]hept-2-ene (VII) (i.r. and n.m.r.).

Oxidation of the Photoproduct (XVa).—A fraction, b.p. 82·5° at 72 mmHg, of the main photoproduct [4·91 g; 90% with 8% of (XVb) by g.l.c.] was dissolved in a mixture of methanol (30 ml) and chloroform (30 ml) and treated at −80° with ozonized air for 18 h. The solution was evaporated under reduced pressure, and formic acid (20 ml) and 30% hydrogen peroxide (20 ml) were added. The solution was heated to start the reaction and then cooled with ice–water as necessary to moderate it. After 10 min, external heating was resumed, so that reflux continued for a further 20 min. Next day the solution was concentrated by evaporation (40° at 5 mmHg) and the residual brown oil (4·7 g) was taken up in ether. The acidic components were rapidly extracted with ice-cold dilute aqueous sodium hydroxide, which was acidified, and twice extracted with ether. This yielded the crude acid (XVIa) as a dark brown oil (3·3 g, 47%).

The whole acid fraction, on treatment with excess of ethereal diazomethane, gave the crude ester (XVIIa). The same compound was obtained in *ca.* 63% yield on oxidation of (XVa) with permanganate–periodate according to the method described below for the oxidation of (XVb). The ester yielded a semicarbazone, which, after being twice recrystallized from aqueous ethanol, had m.p. 164—166°.

After four further recrystallizations, from ethyl acetate, the *derivative* (0·55 g) had m.p. 174—174·5° (Found: C, 56·5; H, 8·1; N, 16·5. $C_{12}H_{21}N_3O_3$ requires C, 56·4; H, 8·3; N, 16·5%).

The semicarbazone (295 mg) was added to 1% aqueous oxalic acid (50 ml), and the mixture was slowly distilled until 25 ml of distillate had been collected. This was extracted with ether (15 ml) which was then washed with saturated brine, and dried (MgSO₄). On evaporation (30° at 3 mmHg), this left the ester (XVIIa) as an oil (186 mg), i.r. $\lambda_{max.}$ 3·36, 3·42, 5·73s, 5·89s, 6·8, 6·95, 7·25, 7·36, 7·52, 8·0w, 8·4, 8·52s, 9·75w, and 10·2 μm, δ 3·58 (3H) and 0·97br (both s). On g.l.c. at 125° the ester appeared to be >99% pure, but when the injector temperature was raised two products were formed in a ratio (*ca.* 6 : 1) independent of the temperature (see below).

c-2-Carboxymethyl-t-3-isopropylcyclopropane-r-1-carboxylic Acid (XVIIIa).—The crude keto-acid (XVIa), prepared as above from the photoproduct (2·4 g, 78% pure), was dissolved in a little aqueous sodium hydroxide, cooled to −10°, and a solution (140 ml) of sodium hypobromite [from bromine (7 ml) and sodium hydroxide (20 g)] was added during 0·5 h. The mixture was maintained at 50° for 10 min, then decolourized with sodium metabisulphite. After being washed with ethyl acetate the solution was acidified, and twice extracted with the same solvent. The combined acidic extracts yielded a gum which, from ether–hexane, gave the *acid* (XVIIIa) (0·77 g, 36%) [30% yield based on (XVa)], m.p. 133° (from chloroform–hexane), i.r. $\lambda_{max.}$ 5·88s, 6·78, 7·04, 7·21, 7·29, 7·40, 7·52, 7·63, 7·82, 8·06s, 8·43, 9·2, 9·4, 9·84, 10·05, 10·4, 10·65, 11·35, 11·96, 14·52w, and 14·86w μm, δ (CDCl₃) 2·82 (2H, d, *J* 6 Hz), 1·04br (7H, s, $W_{\frac{1}{2}}$ 5·3 Hz), and 1·2—2·3 (3H) [Found: C, 58·5; H, 7·6%; equiv. wt. 97. $C_7H_{12}(CO_2H)_2$ requires C, 58·0; H, 7·6%; neut. equiv. 93]. The acid (XVIIIa) was obtained in 49% yield from (XVa) by treatment with periodate–permanganate followed by hypobromite, as described below for the oxidation of (XVb) to (XVIIIb).

Treatment of the acid, in methanol, with excess of ethereal diazomethane gave *dimethyl t-3-isopropylcyclopropane-r-1,c-2-dicarboxylate* (XIXa), n_D^{22} 1·4423, i.r. $\lambda_{max.}$ 3·38, 3·47, 5·76s, 6·94, 7·25, 7·38, 7·5, 7·9, 8·4s, 9·08, 9·2, 9·4, 9·78, 10·03, 10·33w, 10·5w, 10·76w, 11·41, 11·9, 13·1w, and 14·4w μm, δ 3·67 (6H, s), 1·57 (2H, d, *J* 5 Hz), and 1·04br (*ca.* 7H, s, $W_{\frac{1}{2}}$ 3 Hz) (Found: C, 61·7; H, 8·7. $C_{11}H_{18}O$ requires C, 61·7; H, 8·5%).

The anhydride of acid (XVIIIa) was obtained by refluxing the acid (0·3 g) for 30 min with acetic anhydride (10 ml) and evaporating to dryness under reduced pressure; *t-3-isopropylcyclopropane-r-1,c-2-dicarboxylic anhydride* had m.p. 40—40·5° (from ether–hexane), i.r. $\lambda_{max.}$ 3·38—3·48, 5·54s, 5·68s, 6·8, 7·03, 7·19, 7·29, 7·38, 7·49, 7·62, 7·86s, 8·32, 8·46, 8·63s, 9·07s, 9·52, 9·78, 10·03, 10·28s, 10·44, 10·9, 11·03, 12·1, 12·48w, 13·87w, and 15·05 μm, δ (CDCl₃) 3·06 (2H, d) and 1·06 (*ca.* 7H, d) (Found: C, 64·3; H, 7·2. $C_9H_{12}O_3$ requires C, 64·3; H, 7·2%). When this anhydride was left for 1 h on a steam-bath with a little water it yielded crystals, m.p. 133—134·5°, undepressed on admixture with the authentic diacid (XVIIIa).

Ring-opening of the Diester (XIXa).—The ester (98% pure by g.l.c.) from crude acid (XVIIIa) (0·95 g) was refluxed during 3 h with 10% methanolic potassium hydroxide (30 ml). Most of the solvent was removed under reduced pressure, and the residue acidified with ice-cold dilute sulphuric acid (30 ml). The acid was extracted with ether

(2 × 30 ml) and the combined extracts were washed with saturated brine (2 × 10 ml), dried, and evaporated. The residue, re-esterified with diazomethane, contained starting material (38%), one principal product (58%), and several minor components. It was re-saponified as before; esterification followed by g.l.c. of a small amount of the resulting solid fraction (0·89 g) showed starting material (8%), the main product (86%), and two minor products. Crystallization from methanol–chloroform–hexane, yielded 4-*isopropylhex-2-enedioic acid* (XX) (0·501 g 53%,), m.p. 156—157°, $\lambda_{max.}$ 206 nm (ε 15,000) (in 95% ethanol on a Unicam SP 500 instrument), i.r. $\lambda_{max.}$ 5·84s, 5·92s, 6·05s, 7·04, 7·18, 7·28, 7·6s, 7·8s, 8·27, 8·48, 8·7, 9·0, 9·43w, 9·92, 10·5, 11·1, 11·4, 13·5w, 13·75w, and 14·3w μm (Found: C, 58·2; H, 7·4. $C_9H_{14}O_4$ requires C, 58·0; H, 7·6%).

Dimethyl 4-isopropylhex-2-enedioate (XXI), prepared from (XX) with diazomethane, had $\lambda_{max.}$ 207 nm (ε 13,800) i.r. $\lambda_{max.}$ 3·38, 3·48, 5·7s, 5·8s, 6·02, 6·81, 6·93, 7·18, 7·28, 7·35, 7·55, 7·87s, 8·32, 8·6, 9·0, 9·25w, 9·62, 10·02, 10·9w, 11·3w, 11·5, 12·2w, and 13·8 μm, δ 6·65 (1H, dd, *J* 15 and 8 Hz), 5·72 (1H, d, *J* 15 Hz), 3·67 and 3·60 (total 6H, each s), 2·39br (2H, s), and 0·84 (6H, d, *J* 8 Hz, with fine splitting) (Found: C, 61·7; H, 8·5. $C_{11}H_{18}O_4$ requires C, 61·7; H, 8·5%).

The anhydride of the diacid (XX) was prepared as usual; it distilled at 1 mmHg as an oil (100° block temp.) which did not crystallize at −80°, but showed strong i.r. maxima at 5·57 and 5·75 μm.

When the ester (XIXa) (60 mg) in iso-octane (1·0 ml) was maintained at 270—280° for 20 h in a sealed glass tube, g.l.c. showed starting material (14%), the ester (XXI) (75%), and four other compounds (1·8—3·3%).

Oxidation of the Acid (XX).—A solution of the acid (88 mg) in methanol (10 ml) and chloroform (10 ml) was cooled to −80°, and treated with ozone until deep blue. After removal of the excess of ozone and evaporation of the solvents, 30% hydrogen peroxide (4 ml) was added. The mixture was heated for 1 h on a steam-bath, aqueous 10% sodium carbonate (2 ml) was added and the solution was evaporated to dryness. Dilute sulphuric acid (10 ml) was added to pH 3, and the solution distilled. The distillate (5 ml) showed (g.l.c.) only traces of volatile acids; the residue, when continuously extracted with ether, yielded isopropylsuccinic acid (34 mg, 45%), m.p. 116—117·5° (identified by i.r. and mixed m.p. with an authentic specimen [44]).

Degradation of the Diester (XIXa) *to 3-Isopropyladipic Acid.*—The diester (XIXa) (*ca.* 70 mg) was refluxed for 6 h with methanolic sodium hydroxide, and the acidic products were extracted, dissolved in methanol, and hydrogenated. Treatment with diazomethane gave the diester (XIXa), and chiefly dimethyl 3-isopropyladipate (g.l.c., i.r.). The latter was hydrolyzed by refluxing with methanolic 10% potassium hydroxide for 4 h. The acidic product was recrystallized three times from ether–pentane to give 3-isopropyladipic acid (mixed m.p., i.r.). Authentic β-isopropyladipic acid, m.p. 80·5—81·5°, was synthesized as described.[45]

Dehydrogenation of the Photoproduct (XVa).—The photoproduct (XVa) (0·122 g; purified by preparative g.l.c., and apparently 96% pure with no single major contaminant) and 5% platinized charcoal (68 mg) were heated together in a sealed tube at 240° for 5 h. Extraction with pentane yielded a brown oil (71 mg) found by g.l.c. (internal standard)

to contain *m*-cymene (9·7 mg) and *p*-cymene (6·5 mg) [confirmed by g.l.c. and i.r. of the distilled oil (19 mg)].

Oxidation of the Photoproduct (XVb) *to* c-2-*Acetyl*-c-3-*isopropylcyclopropane*-r-1-*acetic Acid* (XVIb).—The hydrocarbon (XVb) (143 mg; 98%) in t-butyl alcohol (40 ml) was added to a solution of potassium permanganate (39 mg) and potassium periodate (1·46 g) in water (180 ml) and the pH of the solution was adjusted to 8·5 using dilute aqueous potassium carbonate. After being stirred for 40 h, the solution was continuously extracted with ether for 12 h, brought to pH 1, and extracted with fresh ether for 15 h. The acid extract was concentrated, washed with aqueous sodium thiosulphate, then with brine, and dried. Evaporation (50° at 2 mmHg) left a pale yellow oil (129 mg) which slowly crystallized. After being twice recrystallized from hexane, the *acid* (XVIb) (49%) had m.p. 68—69°, δ 2·21 (3H, s), 0·94 (3H, d, *J* 6·5 Hz), 0·8 (3H, d, *J* 6·5 Hz), and 0·5—3·5 (9H) (Found: C, 64·5; H, 9·0. $C_{10}H_{16}O_3$ requires C, 65·2; H, 8·7%).

The corresponding keto-ester (XVIIb) (prepared using diazomethane) had λ (MeOH) 215 (ε 2200) and 205 nm (5200), i.r. $\lambda_{max.}$ 3·37, 5·74s, 5·91s, 6·85, 6·98, 7·21, 7·33, 7·42, 7·53, 7·98, 8·38, 8·56s, 8·9w, 9·15, 9·8, 10·24, 11·05w, 11·34w, 12·2w, and 12·8w μm, δ 3·63 (3H) and 2·22 (3H) (both s) 0·91 (3H, d, *J* 6·7 Hz), 0·8 (3H, d, *J* 6·4 Hz), and 1·0—3·0 (6H, complex), g.l.c. (5% silicone, 125°) showed this ester to be 99% pure.

Pyrolysis of the Keto-esters (XVIIa) *and* (XVIIb).—During g.l.c. of both esters, as the temperature of the injection block was raised, the formation of two products (*ca.* 85 and 15%) could be observed, and at 360° no starting material could be detected in either case. The *cis-cis*-ester (XVIIb) was thus isomerized in small portions (12 × 5 mg) and the two products were separated at the same time (10% Carbowax, 200°). The minor product was eluted first from Carbowax, but after the major product on a silicone oil column. The major product, *methyl 4-isopropyl-6-oxohept-2-enoate* (XXII) was *ca.* 99% pure (g.l.c.), λ 225 (ε 5800), 215 (11,100), and 205 nm (13,200), i.r. $\lambda_{max.}$ 3·37, 5·81s, 6·02, 6·83, 8·74, 9·63w, 9·87w, 10·12, 11·05w, and 11·48w μm, for n.m.r. spectrum see Discussion section (Found: C, 66·8; H, 9·1. $C_{11}H_{18}O_3$ requires C, 66·6; H, 9·1%). On admixture of (XVIIb) with the isomeric cyclopropane keto-ester (XVIIa), g.l.c. showed two well-defined peaks (15% butanediyl succinate, 130°); under these conditions (t_R *ca.* 20 min.) some ring-opening occurred, particularly of the all-*cis*-compound (XVIIb).

The *trans-cis*-ester (XVIIa) was injected similarly (15 × 5 mg) into the gas chromatograph (injector block temp. 330°) and the two pyrolysis products were collected. The main product (38·9 mg) had i.r. and n.m.r. spectra identical with those of the unsaturated keto-ester (XXII) obtained from the minor photoproduct (XVb). The minor pyrolysis product from (XVIIa) (5·4 mg) gave an i.r. spectrum resembling that of the minor pyrolysis product from (XVIIb).

Hypobromite Oxidation of the Keto-acid (XVIb).—The crude keto-acid from the oxidation of (XVb) was dissolved in aqueous 10% sodium hydroxide (2 ml.) To this, cooled in ice, was added a cold solution of sodium hypobromite prepared from bromine (*ca.* 110 mg) and aqueous 10% sodium hydroxide (4 ml). After 15 min the solution was allowed to warm to room temperature during 25 min. It

[44] P. A. S. Smith and J. P. Horwitz, *J. Amer. Chem. Soc.*, 1949, **71**, 3418.

[45] C. G. Overberger, A. Fischman, C. W. Roberts, L. H. Arond, and J. Lal, *J. Amer. Chem. Soc.*, 1951, **73**, 2540.

was washed with ether, acidified to pH 1, and twice extracted with ether. The combined extracts were washed three times with small quantities of brine, and dried. Evaporation of the ether left a glass (46·2 mg). On treatment with ether–hexane, this yielded c-3-*isopropylcyclopropane*-r-1,c-2-*dicarboxylic acid* (XVIIIb) (19 mg, 31%), m.p. 134—136° (from ether–hexane), i.r. $\lambda_{max.}$ (Nujol) 5·83s, 5·95s, 8·2s, 8·55, 9·15, 12·15w, 13·0, and 14·1 μm, δ (CDCl₃) 2·8 (2H, m) and 0·97 (ca. 6H, d, J 6 Hz).

When treated for 15 min with excess of boiling acetic anhydride which was then evaporated off (40° at 1 mmHg), this acid (ca. 10 mg) yielded a liquid anhydride; the i.r. spectrum of this indicated virtually complete absence of acetic anhydride, but had $\lambda_{max.}$ 5·56 and 5·68 μm. The anhydride was kept at 100° for 1 h with aqueous acetone and gave the acid (XVIIIb) (m.p. and mixed m.p. and i.r. spectrum) on work-up.

Hydroboration and Oxidation of the Photoproduct (XVa) *to give the Ketone* (XXIV).—To a solution of the photo-product (XVa) (0·396 g; purified by g.l.c.) in dry ether (5 ml) at 20° was added a solution of diborane (4 mmol) in tetrahydrofuran (4 ml) during 25 min. Stirring was continued at room temperature for 2·5 h, and excess of diborane was destroyed by adding water (2 ml). A solution of sodium dichromate (0·635 g) in conc. sulphuric acid (0·47 ml) and water (2·65 ml) was slowly added and the dark mixture was then refluxed for 2 h. The usual work-up, followed by distillation at 3·5 mmHg (bath temp. 52—54°) afforded 6-exo-*isopropyl*-2-endo-*methylbicyclo*[3.1.0]*hexan-3-one* (XXIV) (0·277 g, 64%) (95% pure by g.l.c.), i.r. $\lambda_{max.}$ 3·38s, 5·74s, 6·83, 6·9, 7·1, 7·25, 7·32, 7·5w, 7·66, 7·77, 7·96, 8·37, 8·57, 8·73, 9·33, 9·44, 9·95, 10·2, 10·7w, 11·48, 12·04, and 12·7 μm, δ (external standard) 2·2br and 0·01br (both 1H, s), 1·25—1·6 (2H, m) 2·6—2·8 (2H, m), and 1·01 (s) and 1·05 (d, J 6·5 Hz) (total 10H) (Found: C, 78·7; H, 10·6. $C_{10}H_{16}O$ requires C, 78·9; H, 10·6%). Similar treatment of the minor photoproduct (XVb) gave a very small yield of an acidic fraction, and one main neutral product (ca. 40%), the i.r. spectrum of which rapidly changed when the sample was left in the air at room temperature. The principal change was the disappearance of a strong maximum at 5·74 μm, with the concomitant growth of another at 5·86 μm. This reaction was not investigated further.

Condensation of the Ketone (XXIV) *with Benzaldehyde.*—One drop of aqueous 30% sodium hydroxide followed by a solution of benzaldehyde (33 mg) in methanol (2 ml) were added to an ice-cold solution of the ketone (XXIV) (57 mg) in methanol (1 ml). The mixture was stored under nitrogen for 24 h at 0°, and then for 7·5 h at room temperature. The solvent was evaporated under reduced pressure, and the residue was dissolved in water (5 ml) and extracted with ether (2 × 5 ml). Evaporation of the solvent and crystallization of the residue from 60% aqueous methanol at −20° afforded needles (51 mg, 72%), m.p. 70—71·5°. After two recrystallizations the product, 4-*benzylidene*-6-exo-*isopropyl*-2-endo-*methylbicyclo*[3.1.0]*hexan-3-one*, had m.p. 73—74°, i.r. $\lambda_{max.}$ (CHCl₃) 5·83s and 6·23s μm, δ 7·25 (1H, s), 7·4—7·8 (5H, m), 1·65—1·94 (1H, m), 0·67 (1H, m), 2·44 (1H, q), 2·74 (1H, t, J 6·8 Hz), and 1·28 (10H, d, J 7 Hz), $\lambda_{max.}$ (MeOH) 311 (ε 13,000) and 227·8 nm (6300) (Found: C, 85·0; H, 8·3. $C_{17}H_{20}O$ requires C, 85·0; H, 8·4%).

Hydroboration and Oxidation of the Photoproduct (XVa) *to give* 6-exo-*Isopropyl*-2-endo-*methylbicyclo*[3.1.0]*hexan-3-exo-ol* (XXIII).—Diborane solution (8 ml; M) was added during 20 min to a stirred solution of (XVa) (0·939 g; 78% pure)

in ether (10 ml) under nitrogen. After stirring at room temperature for 1 h, excess of diborane was destroyed by adding water (1·5 ml). The mixture was warmed to 40—45°, 3N-aqueous sodium hydroxide (0·55 ml) was slowly added, followed by 30% hydrogen peroxide (0·7 ml). To avoid a heterogeneous system tetrahydrofuran and bis-(2-methoxyethyl) ether (10 ml of each) were added and the mixture was stirred at 40—50° for 2 h. The cold solution was diluted with ether (75 ml) and the organic layer was washed with ice–water (5 × 20 ml), dried, and evaporated. Distillation of the pale yellow residual oil at 60—65° and 1 mmHg afforded an oil (0·39 g; 80% pure by g.l.c.; 39% yield). When treated with phthalic anhydride in pyridine, this alcohol (XXIII) yielded a *monophthalate*, m.p. 116—117° (from ether–pentane) (Found: C, 71·6; H, 7·3. $C_{18}H_{22}O$ requires C, 71·5; H, 7·3%).

Oxidation of the Alcohol (XXIII) *to the Ketone* (XXIV).—A solution of the alcohol (XXIII) (0·197 g; 80% pure) in pyridine (1 ml) was added to the slurry prepared [21] from chromium trioxide (0·45 g) and pyridine (2·5 ml). The yellow complex dissolved within 5 min, and the solution became black. After stirring at room temperature for 20 h the solution was diluted with water (25 ml) and extracted four times with ether. The combined extracts (85 ml) were washed with water (20 ml), 2N-sulphuric acid (50 ml), water (10 ml), and dried. Evaporation and distillation at 55° (bath temp.) and 1·7 mmHg afforded a liquid (0·105 g) which appeared, by g.l.c., to contain 75—80% of (XXIV) (yield 50—54%). Preparative g.l.c. (30% Carbowax 20 M at 130°) yielded the main product (57 mg) shown by its i.r. and n.m.r. spectrum to be the ketone (XXIV).

3-*Isopropylcyclopropane*-1,2-*dicarboxylic Acids* (XXVIIa) *and* (XXVIIc).—4-Methylpent-2-enoic acid, b.p. 107—108° at 12 mmHg, was obtained as reported,[46] in 42% yield, from malonic acid, pyridine, and isobutyraldehyde. Its ethyl ester (XXVI) had b.p. 93—97° at 57 mmHg, δ (neat) 6·29 (2H, ABq with fine splitting, J 16 Hz, CH=CH), 4·1 (2H, J 7 Hz, CH₃CH₂-), 2·4—1·3 (1H, m), 1·19 (3H, t, J 7·1 Hz, CH₃CH₂-), and 1·02 [6H, d, J 6·9 Hz, CH(CH₃)₂]. This ester (71 g) and redistilled ethyl chloroacetate (68 g) were mixed and added dropwise to a stirred suspension of sodium hydride (24 g; 53% mineral oil dispersion) in dry toluene. After 10 min the mixture rapidly warmed to 42°, and during the rest of the addition (50 min) it was cooled with ice to maintain the temperature at 35—40°. Stirring was continued for a further 2 h without external cooling, and methanol was added to decompose the excess of hydride. The usual work-up gave starting material (31·6 g), and a fraction b.p. 99—105° at 2·0 mmHg containing three main compounds (g.l.c.) (yields 1·4, 16·9, and 6·3%). Redistillation through a 24 in spinning band column gave a fraction, b.p. 94—95° at 1·1 mmHg, containing ca. 80% of the major product. On saponification this gave a mixture of acids, which, after being twice crystallized from ether–hexane and once from nitromethane, yielded c-3-*isopropylcyclopropane*-r-1,t-2-*dicarboxylic acid* (XXVIIc), m.p. 163—164°, i.r. $\lambda_{max.}$ (Nujol) 5·91s, 7·0, 7·52, 7·81, 8·51s, 8·4, 8·55, 8·89w, 9·35w, 9·85w, 10·35, 10·5, 11·0, 11·2, 12·5w, 14·3w, and 14·6w μm [Found: C, 55·8; H, 7·1%; equiv. wt., 86. $C_6H_{10}(CO_2H)_2$ requires C, 55·8; H, 7·0%; neut. equiv., 86].

Dimethyl c-3-*isopropylcyclopropane*-r-1,t-2-*dicarboxylate* was obtained by treatment of a methanolic solution of the acid (XXVIIc) with ethereal diazomethane. After crystallization from pentane at −15° it had m.p. 64·5—65·5°,

[46] K. v. Auwers, *Annalen*, 1923, **432**, 46.

i.r. $\lambda_{max.}$ (CCl$_4$) 3·38, 5·8s, 6·82, 6·9, 7·0, 7·28, 7·34, 7·52s, 7·88, 8·3—8·7s, 8·92, 9·15w, 9·4, 9·72, 10·45w, 11·0, 11·2, 11·6, and 12·6—13·3s μm, δ 3·65 (6H, s) and 0·98 (6H, dd, J 9 and 6 Hz) (Found: C, 60·2; H, 8·2. $C_{10}H_{16}O_4$ requires C, 60·0; H, 8·0%).

The least volatile fractions of the ester mixture were saponified, and the crude acid mixture was refluxed for 30 min with acetic anhydride. Distillation through a 5 cm Vigreux column yielded an anhydride, b.p. 66—68° at 1·7 mmHg, which was heated overnight with water. The product was crystallized from ether–hexane, then from nitromethane, and yielded t-3-*isopropylcyclopropane*-r-1,c-2-*dicarboxylic acid* (XXVIIa), m.p. 190—191°, i.r. $\lambda_{max.}$ (Nujol) 5·82s, 7·48, 7·86, 8·1s, 8·22s, 8·47w, 8·65w, 11·3, 11·9, and 13·9w μm [Found: C, 56·0; H, 7·2%, neut. equiv., 88. $C_8H_{10}(CO_2H)_2$ requires C, 55·8; H, 7·0%; neut. equiv., 86]. The dimethyl ester of (XXVIIa) was obtained (diazomethane) as an oil, i.r. $\lambda_{max.}$ 5·72s, 5·77s, 6·92, 6·99, 7·32, 7·38, 7·9, 8·3s, 8·6s, 9·22w, 9·38w, 9·75, 10·1w, 10·42w, 10·6w, 10·96w, 11·2, 11·87, 12·15w, 12·7, and 13·2w μm, δ 3·59 (6H, s), and 1·76 (3H) and 1·02 (7H) (both finely split m). The non-volatile product from the above anhydride preparation was heated overnight with water. The product, after six crystallizations from nitromethane, was the acid (XXVIIc).

Isomerization of the Diacid (XXVIIc) *to the Diacid* (XXVIIa).—The acid (XXVIIc) (78 mg) was dissolved in acetic anhydride (1·0 ml) and the solution sealed in a glass ampoule and heated at 160—170° for 65 h. The mixture was distilled (maximum bath temp. 130°) at 1 mmHg and the distillate was heated for 3 h in a steam-bath with water. The solution was evaporated to dryness and the residue twice crystallized from ether–hexane. This yielded the diacid (XXVIIa) (21 mg), m.p. 191—192°, undepressed on admixture with an authentic sample.

Preparation of the Diazoketone (XXVIII).—The diacid (XXVIIa) (0·465 g) and acetic anhydride (2·0 ml) were refluxed for 30 min, then evaporated. When the resultant pale yellow oil (0·44 g) was treated with 1 equiv. of sodium methoxide in methanol (5·5 ml), there was an immediate exothermic reaction. The methanol was evaporated off under reduced pressure, and the residual white powder was suspended in dry benzene (10 ml) containing three drops of pyridine. Dry nitrogen was bubbled through the solution, which was cooled in ice while oxalyl chloride (2 ml; Matheson, Coleman, and Bell) was added. The initial frothing rapidly subsided, and after 5 min the solution was evaporated under reduced pressure. The residue was distilled at 7 mmHg

(max bath temp. 160°). The resultant acid chloride (i.r. $\lambda_{max.}$ 5·57 and 5·73 μm in CCl$_4$) was dissolved in ether, and added, during 1 min, to ethereal diazomethane [prepared from *p*-tolylsulphonylmethylnitrosamide (35 g) using 2-methoxyethanol rather than ethanol; [47] the solution of diazomethane was dried over KOH, redistilled, re-dried over KOH and then over Na ribbon] which was cooled to −15°. The solution was kept at −15° for 30 min, then evaporated. The residue (two phases) was separated into a pentane-soluble, acetone-insoluble oil (88 mg) which was discarded, and the pentane-insoluble, acetone-soluble diazoketone (0·53 g) which was obtained as a yellow oil. This product was not obtained pure, but showed i.r. $\lambda_{max.}$ (CCl$_4$) 3·38, 4·71, 5·75, 7·3, and 8·31 μm, δ 5·66 (0·6H) and 3·61 (3H) (both s), 1·9 (2H) and 1·02 (7H) (both m), and continuous background at 0·7—2·2. The diazoketone slowly crystallized, but the resulting solid, m.p. *ca.* 55°, gave an n.m.r. spectrum which also indicated about 40% of impurities.

Photochemical Wolff Rearrangement.—The crystalline diazoketone (54 mg) in water (8 ml) and dioxan (8 ml; distilled from sodium) was irradiated at *ca.* 50° for 16 h in a Pyrex flask using a 100 W Hanovia Utility Quartz lamp, while purified nitrogen was bubbled through the solution. Evaporation left a yellow gum which was dissolved in ether, washed with water, and then extracted with aqueous 1% sodium carbonate (10 ml). The latter was acidified with 3% sulphuric acid (4 ml) and twice extracted with ether, which was washed three times with brine, and dried. The resultant glass (24·8 mg) was treated with excess of dry ethereal diazomethane. Gas chromatography showed three components (55, 23, and 22%, in order of elution from a 15% butanediyl succinate column at 165°). The major product was not separated from the diester (XIXa) under these g.l.c. conditions, and, when collected, gave i.r. and mass spectra virtually identical with those of the diester from (XVa).

[47] L. F. Fieser and M. Fieser, ' Reagents for Organic Synthesis,' J. Wiley and Sons Inc., New York, Vol. 1, 1967, p. 192.