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THE PHOTOCHEMISTRY OF CITRAL

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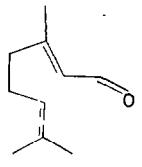
Abstract—Citral (I) is cyclized by UV irradiation[1] to 2-isopropenyl-5-methylcyclopentane-carboxaldehyde (II), containing the carbon skeleton of the monoterpenes of ants and catmint. 1,6,6-Trimethylbicyclo[2,1,1]hexane-2α-carboxaldehyde (XII, R = H), produced in lesser amount at the same time, was synthesized from camphor. The two photocitrals may, perhaps, come from a common intermediate containing the cyclopentane ring.

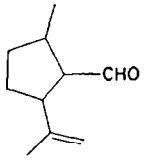
WHEN light from a medium-pressure mercury arc shone through citral*(I) the UV absorption at 238 mμ faded and the band in the IR spectrum at 1680 cm^{-1} was gradually replaced by one at 1720 cm^{-1} indicating that the conjugation was being destroyed. The product, after removal of unchanged citral as its bisulphite adduct, was mainly a mixture of two isomers roughly in the proportion of 2:1. The less abundant isomer, which came through a gas chromatogram rather later, proved to be a saturated, bicyclic aldehyde: its structure will be considered later.

Photocitral-A

The more abundant isomer, which we call photocitral-A, could be isolated in a fairly pure state (ca. 90%) by fractional distillation. It formed a yellow 2,4-dinitrophenylhydrazone. Chemical tests and the IR bands at 2715 and 1720 cm^{-1} showed



I



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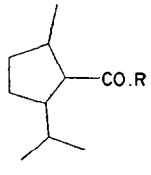

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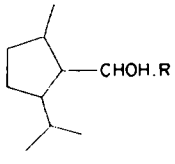

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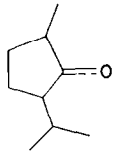

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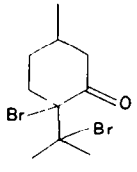

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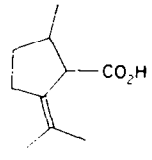


VII

* The sample used was a 1:1 mixture of *cis* and *trans* isomers: the interconversion of the geometrical isomers is probably faster than cyclization.

[1] R. C. Cookson, J. Hudec, S. A. Knight and B. R. D. Whitear, *Tetrahedron Letters* 79 (1962). A full account appears in B. R. D. Whitear's Ph.D. Thesis, Southampton, 1962.

that the aldehyde group was still intact, while the strong band at 890 cm^{-1} suggested that the unsaturation also present was in the form of a methylene group, which also accounted for the bands at 1640 and 3070 cm^{-1}. It took up one mole of hydrogen over platinum to give a saturated aldehyde, $C_{10}H_{18}O$, which must therefore contain one ring.

Initial attempts (some of which are described in the Experimental section) to degrade dihydrophotocitral-A by oxidation of the derived styrene or diphenylethylene were not very productive. A more successful sequence involved addition of methylmagnesium iodide to the aldehyde, and oxidation of the resulting alcohol (IV, R = Me) to the ketone (III, R = Me), which was subjected to Baeyer-Villiger oxidation with perbenzoic acid. The resulting esters (mostly benzoate) were hydrolysed and the alcohol produced was again oxidized. It was reassuring to find that this ketone, $C_9H_{16}O$, as expected, was a cyclopentanone (ν_{max} 1745 cm^{-1}). Comparison of crystalline derivatives identified it as *trans*-2-isopropyl-5-methylcyclopentanone[2] (V).

The structure (II) for photocitral-A was confirmed by its proton magnetic resonance spectrum (40 Mc/s in CS_2 containing $SiMe_4$), which had a doublet at 8·98τ (J = 6·4 c/s) — (CH_3—CH), singlets at 8·34τ (CH_3—C=) and 5·31τ (CH_2=C), and another doublet at 0·36τ (J = 2·2 c/s) (CHO—CH).

2-Isopropyl-5-methylcyclopentanecarboxylic acid (III, R = OH), made by hydrogenation of the product (VII) of Favorskii rearrangement[3] of pulegone dibromide (VI), was reduced *via* the ester to the alcohol (IV, R = H), oxidation of which with chromic oxide in pyridine yielded the aldehyde. This synthetic aldehyde had an infrared spectrum identical with that of dihydrophotocitral-A. Although the 2,4-dinitrophenylhydrazones derived from the photo- and synthetic aldehydes also had indistinguishable spectra, they crystallized in different forms and melted 15° apart: mixtures of the two melted at intermediate temperatures. Photocitral-A must be the racemic form of the optically active aldehyde from pulegone.

This photochemical change exhibits several points of interest—not the least remarkable being the conversion in one step of an acyclic terpene into a structure with the carbon skeleton of the terpenes of ants[4a] and of catmint,[4b] and carrying functional groups on the two carbon atoms that are oxygenated in the natural products.

An incidental observation worth mention concerns the stoichiometry of oxidation of alcohols with chromic oxide in pyridine. It is customary, and often not objectionable, to use a large excess of oxidant, but sometimes an excess should be avoided and knowledge of the theoretical requirement would be useful. In oxidation of the alcohols (IV, R = H, Me or Ph) to the respective carbonyl compounds (III, R = H, Me or Ph) an almost quantitative yield was obtained only when two moles of CrO_3 were used for each mole of alcohol. Unlike the reduction by alcohols in acid or neutral solution[5] of Cr (VI) through Cr (IV) to Cr (III), the reaction in pyridine seems thus to involve the reduction of Cr (VI) to Cr (V).

[2] J. Meinwald, *J. Amer. Chem. Soc.* **76**, 4571 (1954).

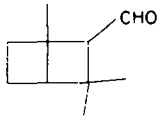
[3] G. Sauey, L. H. Chopard-dit-Jean, W. Guex, G. Ryser and O. Isler, *Helv. Chim. Acta.* **41**, 160 (1958).

[4] [a] G. W. K. Cavill and H. Hinterberger, *Austr. J. Chem.* **14**, 143 (1961), and earlier papers.
[b] S. M. McElwain and E. J. Eisenbraun, *J. Amer. Chem. Soc.* **77**, 1599 (1955).

[5] F. H. Westheimer, *Chem. Rev.* **45**, 419 (1949).

Photocitral—B

Since the second main component in irradiated citral, photocitral-B, was obtained pure only in small amount by gas chromatography, and rapidly autoxidized in air, we decided to synthesize its likely structure rather than to attempt its systematic degradation. It was a saturated aldehyde isomeric with citral (Mass No. 152), and therefore bicyclic. There was no chemical or spectroscopic evidence of a cyclopropane ring, so that the most likely isomerization of citral to have produced it seemed to be a straightforward addition of the two double bonds to form a cyclobutane ring. According to which way round the two double bonds joined together either structure VIII or IX might be produced. The latter looked stereochemically more probable, and could be imagined even arising from the same intermediate as photocitral-A (see later). We, therefore, undertook the synthesis of the epimeric formyl-trimethyl-bicyclo[2,1,1]hexanes (IX) and their derivatives.



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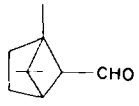

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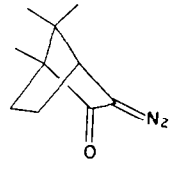

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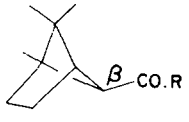

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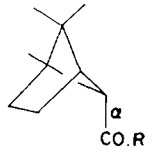

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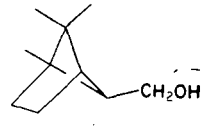

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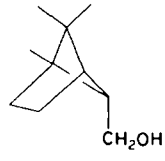


XIV

Horner and Spietschka[6] described the photochemical Wolff rearrangement of diazocamphor (X)* to the acid XI (R = OH),* the stereochemistry of which was later established by Meinwald *et al.*,[7] who also made the more stable epimer XII (R = OH).* The previous investigators have implied that only the β-epimer XI

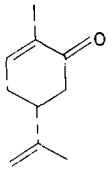
* These formulae represent the compounds derived from *d*-camphor: photocitral-A and B are, of course, racemic.

[6] L. Horner and E. Spietscha, *Chem. Ber.* **88**, 934 (1955).

[7] J. Meinwald, A. Lewis and P. G. Gassman, *J. Amer. Chem. Soc.* **84**, 977 (1962).

(R = OH) was formed in the photolysis, but our crude photo-acid was a mixture of both, containing about a quarter of the α-epimer XII (R = OH).

Since photocitral-B was so unstable in air preliminary comparisons were made on more manageable derivatives. Pure photocitral-A was reduced to the alcohol which was converted to the 3,5-dinitrobenzoate. The bicyclic epimeric esters XI (R = OMe) and XII (R = OMe) were separately reduced to the alcohols XIII and XIV, which were also converted to the crystalline 3,5-dinitrobenzoates. All three esters had conspicuously different IR spectra. A sample of mixed photocitrals, containing about 40% of B, was then reduced and esterified in the same way. The IR spectrum of the mixed esters could be interpreted as a superimposition of the spectra of the dinitrobenzoate from photocitral-A and the α-alcohol XIV, but not the β-alcohol XIII. With this encouragement the synthesis of the α-aldehyde XII (R = H) was undertaken.



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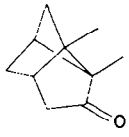
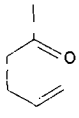
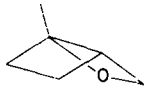


XVI



XVII



XVIII

XIX

After several attempts the alcohol was oxidized in low yield to the aldehyde XII (R = H), which was thus obtained in nine stages from (+)-camphor. Its IR and PMR spectra were identical with those of photocitral-B purified by gas chromatography. It quickly absorbed oxygen from the air, but its crystalline 2,4-dinitrophenylhydrazone was stable (m.p. 141°). Eventually, by careful "seeding" with crystals of photocitral-A 2,4-dinitrophenylhydrazone of a solution of the mixed 2,4-dinitrophenylhydrazones made from crude photocitral, followed by fractional crystallization of the residue, the pure derivative of photocitral-B was separated, m.p. 115–117°. Mixtures of this racemate and the optically active dinitrophenylhydrazone from (+)-camphor melted at temperatures between the melting points of the two components, which had the same IR spectrum.

The photo-isomerization, by formation of a bicyclo[2,1,1]hexane from a 2,6-dien-1-one, of citral (I) to photocitral-B (XII, R = H) exactly corresponds with the conversion of carvone (XV) to carvone-camphor[8] (XVI). On the other hand the hexenone (XVII) is reported[9] to cyclize to XVIII rather than XIX.

[8] G. Büchi and I. M. Goldman, *J. Amer. Chem. Soc.* **79**, 4741 (1957).
[9] R. Srinivasan, *J. Amer. Chem. Soc.* **82**, 755 (1960).

Proton magnetic resonance spectra of photocitral-B and its relatives

The spectra of photocitral-B and of the epimeric acids XI and XII (R = OH) and alcohols XIII and XIV are shown in Figs. 1–5, with the assignments in the accompanying tables. The spectra (Fig. 1) of photocitral-B and of the α-aldehyde XII

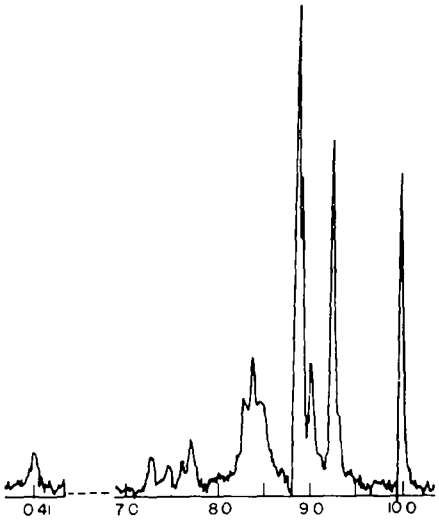


FIG. 1. Photocitral-B (from gas chromatography) and synthetic α-aldehyde
75 Mc/s, CS_2 solution

p.p.m. from $SiMe_4$ at 10.	Assignment
9·27	CH_3—C
8·9	$(CH_3)_2C$
8·44 (multiplet)	CH_2—CH_2
7·80, 7·70	Bridgehead CH
7·45, 7·37	*CH*—CHO
0·42 (unresolved)	CHO

The band at 9·05 may be due to an impurity.

(R = H), which were identical, had to be obtained as fast as possible, for they both oxidized in air in a matter of minutes.

Acids

In the spectra of both of the acids (Figs. 2 and 3) two of the methyl groups in each molecule appear at the same field strength, although in the α-acid XII (R = OH) the peak is just resolved into two. The peaks at 9·27 and 8·88τ may not characterize the same methyl groups in each epimer.

The peaks from the 2- and 3-protons in the β-acid XI (R = OH: Fig. 3) are sharp compared with those in the α-acid's spectrum (Fig. 2). Looking down the C2—C3 bond in models of the acids XI and XII one sees that the bonds C2—H and C3—H are inclined at about 45° in the α-acid and about 90° in the β-acid. Broadening by spin coupling would therefore be expected[10] in these resonances in the α-acid, but not in the β. The rather surprising absence of coupling between H3 and the two protons

[10] M. Karplus, *J. Chem. Phys.* **30**, 11 (1959); H. Conroy *Advances in Org. Chem.* Vol. 2 p. 311. Interscience, New York (1961).

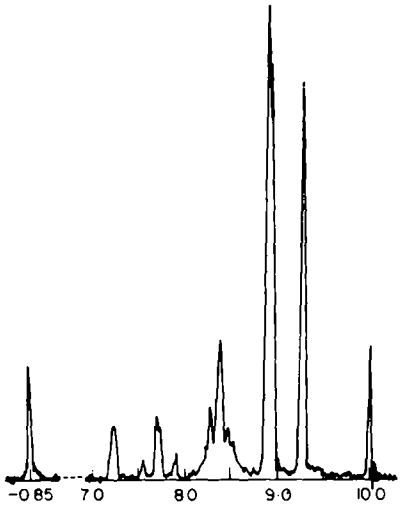


FIG. 2. *α-Acid*

75 Mc/s, $CHCl_3$ solution

p.p.m.	Assignment
9·27	CH_3—C
8·90	$(CH_3)_2C$
8·4 (multiplet)	CH_2—CH_2
7·71	Bridgehead CH
7·24	C*H*—CO_2H
−0·85	CO_2H

Bands at 7·90 and 7·56 are probably due to traces of *β*-acid.

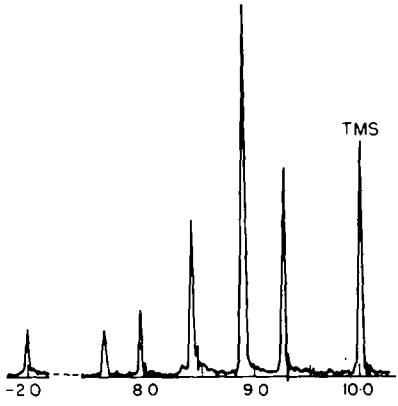


FIG. 3. *β-Acid*

75 Mc/s in $CHCl_3$ solution

p.p.m.	Assignment
9·28	CH_3—C
8·88	$(CH_3)_2C$
8·40	CH_2—CH_2
7·90	Bridgehead
7·55	C*H*—CO_2H
−2·0	CO_2H

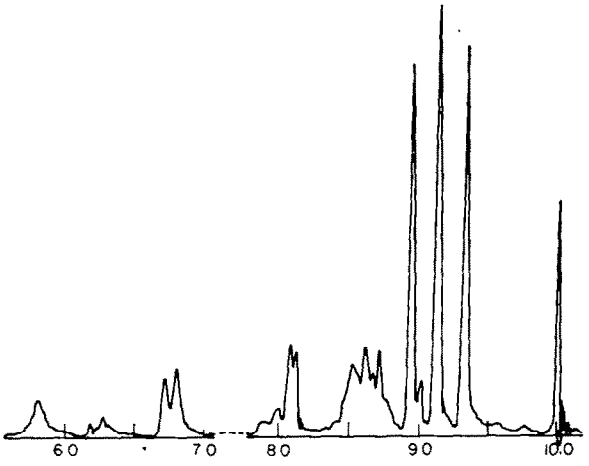


FIG. 4. *α-Alcohol*

75 Mc/s in $CHCl_3$ solution

p.p.m.	Assignment
9·32	CH_3—C
9·13	CH_3—C
8·94	CH_3—C
8·6 (multiplet)	CH_2—CH_2
8·11, 8·06	Bridgehead CH
7·87	C*H*—CH_2OH. Part of triplet, J = 5·1 c/s
6·77	CH—C*H*$_2$OH. Doublet J = 5.1 c/s
5·74	OH

Bands at 9·02, 6·28 and 6·18 are probably due to traces of *β*-alcohol.

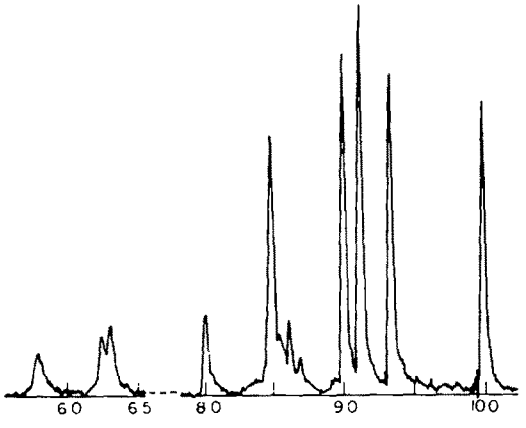


FIG. 5. *β-Alcohol*

75 Mc/s in $CHCl_3$

p·p.m.	Assignment
9·34	CH_3—C
9·12	CH_3—C
9·00	CH_3—C
8·65	C*H*—CH_2OH. Triplet, J = 5·1 c/s
8·50	CH_2—CH_2
8·04	Bridgehead CH
6·29	CH—C*H*$_2$OH. Doublet, J = 5·1 c/s
5·80	OH

on the adjacent C4 methylene group has been noticed by Meinwald and Lewis[11] in the unmethylated ring-system.

In the α-configuration the carboxyl group slightly unshields the two α-hydrogen atoms on C4 and C5, increasing the chemical shift between them and the two β-hydrogen atoms. Thus the band from these two methylene groups is broader and shows more structure in the spectrum of the α-acid (Fig. 2) than of the β (Fig. 3). The same feature is conspicuous in the spectra of the alcohols (Figs. 4 and 5).

The negligible coupling between any protons in the β-acid produces a strikingly simple spectrum (Fig. 3).

Alcohols

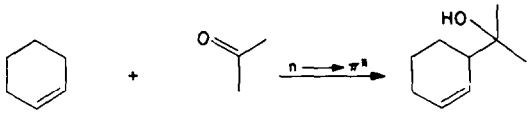
The absorption from H2 now appears at higher field, since it is no longer unshielded by an aldehyde or carboxyl group. It is easily identified in each epimer by its triplet structure, due to coupling with —CH_2—O. The H3 band remains at about 8·0τ, and is a singlet in the β-alcohol's spectrum (Fig. 5) but a doublet in the α-alcohol's because of coupling with H2. The four methylene protons again have the same chemical shift in the β-epimer, but not in the α, where there is a broad multiplet near 8·6τ.

Reverting now to the spectrum of photocitral-B (Fig. 1), it clearly has all the features of the α-series, and indeed is very similar to that of the α-acid.

Discussion

The overall change in formation of photocitral-A is the photochemical, intramolecular analogue of Alder's thermal "ene reaction" or "substituting addition",[12] which certainly in some cases,[13] and probably in most, passes through a cyclic transition state:

In a formal sense the reaction can also be regarded as the vinylogue of the photochemical addition of an olefin to a ketone[14]



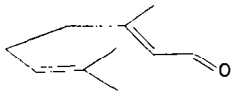
the allylic hydrogen atom in citral adding to the β-carbon atom instead of the carbonyl carbon.

The latter reaction[14] probably proceeds *via* transition of the π^* singlet to the triplet, the oxygen atom of which abstracts the allylic hydrogen to form radicals that subsequently couple.[15] Application of such a process to *cis*-citral (H and Me *cis*)

[11] J. Meinwald and A. Lewis, *J. Amer. Chem. Soc.* **83**, 2769 (1961).
[12] K. Alder, *Experientia Supplementum* II p. 106. Birkhaüser, Basel (1955).
[13] R. Huisgen and H. Pohl, *Chem. Ber.* **93**, 527 (1960).
[14] P. de Mayo, J. B. Stothers and W. Templeton, *Proc. Chem. Soc.* 72 (1960); P. de Mayo, *Advances in Org. Chem.* Vol. 2, p. 367. Interscience, New York (1960).
[15] G. S. Hammond, W. P. Baker and W. H. Moore, *J. Amer. Chem. Soc.* **83**, 2795 (1961).

would yield isopiperitenol (XXIII), of which there was no sign in the product, although, interestingly enough, it is produced from *cis*-citral at 205° in the dark.[16]

One possibility is that the formation of photocitral-A proceeds by isomerization of a molecule in the electronic ground-state with a large excess of vibrational energy, produced by relapse of an electronically excited state with a suitable conformation (XX) for an intramolecular ene reaction. However, the absence from the product of any XXIII, which might have arisen from such a vibrationally excited molecule of *cis*-citral, tends to discount this possibility.



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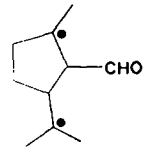
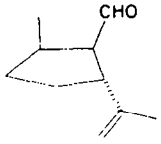
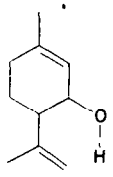


XXI



XXII



XXIII

Since the photochemical reaction was carried out in a Pyrex vessel that is opaque below 300 mμ, it must be initiated by the n $\rightarrow \pi^*$ transition, the only one that absorbs significantly at such long wavelengths† (λ_{max} 325 mμ, ϵ 72). Any mechanism for conversion of citral into the photocitrals by promotion of an electron localized in the oxygen *p*-orbital to the enone π^* orbital must obviously involve the eventual return of an electron to the *p*-orbital. During this time one or both new bonds may be formed. However, in the average conformation of citral the electron promoted is probably not entirely localized on the oxygen atom: the slight but distinct enhancement of intensity of the n $\rightarrow \pi^*$ transition of citral (ϵ 72) over that of β-methacrolein[17] (ϵ 25) indicates some mixing of the pure localized n $\rightarrow \pi^*$ transition with a charge-transfer transition to the same anti-bonding π^* orbital, probably from the unconjugated double bond, which then overlaps both the oxygen *p*-orbital and the enone π^* orbital.[18] The π^* state thus contains a small contribution from a structure in which the oxygen atom has its two electron pairs fully occupied, but the $C_{(6)}$—$C_{(7)}$ π-bond has only one electron (and therefore a positive charge), the other occupying the enone π^* orbital. (The same state could be reached, of course, by rotation into the same conformation of the π^* excited state of a molecule initially excited in a conformation in which the $C_{(6)}$—$C_{(7)}$ double bond was not near the enone group.

† Other transitions that might occur very weakly, though they were not observed in the absorption spectrum, are the triplet version of the n $\rightarrow \pi^*$ transition, and perhaps even the triplet charge-transfer transition from either double bond to the π^* orbital.

[16] G. Ohloff, *Tetrahedron Letters* No 11, 10 (1960).

[17] B. D. Saksena and R. E. Kagarise, *J. Chem. Phys.* **19**, 994 (1951).

[18] H. Labhart and G. Wagniere, *Helv. Chim. Acta* **42**, 2219 (1959). R. C. Cookson and J. Hudec, *J. Chem. Soc.* 429 (1962). S. F. Mason, *Quart. Rev.* **15**, 310 (1961).

but such a route would be less likely because of the molecule's lower ϵ). Which new bond would be formed first is uncertain, but an attractive possibility is that the five-membered ring is first closed to give the singlet (XXI) or the corresponding zwitterion, which can then either form a second C—C bond to give photocitral-B (XII) or transfer a hydrogen atom to give photocitral-A (II). A likely alternative is that the spin of an electron is reversed in the excited state and that the diradical equivalent of one of the double bonds then attacks the other to give the triplet version[19] of XXI.

If the two steps are concerted, or go through the intermediate XXI, the methyl and isopropenyl groups in photocitral-A would be *trans*, as in the natural terpenes: *cis*-citral (H, Me) would yield the isomer XXII and *trans*-citral the epimeric aldehyde. (The degradation product was equilibrated before identification with *trans*-2-isopropyl-5-methylcyclopentanone, so the point has not been proved.) Similarly *trans*-citral would give the β-isomer of photocitral-B (XI) and *cis*-citral the isolated α-isomer. *If* the photocitrals are formed through a common intermediate XXI, then the configuration of photocitral-B (XII) implies configuration XXII for the isomer A. There is the further doubt, though, that the isomer B may be photochemically equilibrated after it is formed, or that the *cis* and *trans* citrals may be partitioned differently amongst the two routes of reaction.

EXPERIMENTAL

Irradiation of Citral. Citral (200 g) was dissolved in cyclohexane (400 ml) and the solution irradiated with two 125 W mercury arc lamps through a pyrex glass filter for 15 days. The solvent was evaporated under vacuum and the residual oil was stirred for 4 hr with a solution of sodium sulphite, $7H_2O$ (850 g) and sodium hydrogen carbonate (320 g) in water (2 l.). The reaction mixture was filtered and the filtrate was extracted with light petroleum (4 × 250 ml) and dried over sodium sulphate. The solvent was evaporated, giving a liquid (yield 50–60 g) which was fractionally distilled. The first fraction (35 g) was a 1:1 azeotrope of Photocitrals A and B and the second fraction (20 g) was *Photocitral* A, b.p. 85°C/15 mm. (Found: C, 78·45; H, 10·1. $C_{10}H_{16}O$ requires: C, 78·95; H, 10·5%). The *2,4-dinitrophenylhydrazone*, m.p. 115–116° (from isopropanol as needles) (Found: C, 57·6; H, 5·9; N, 16·7. $C_{16}H_{20}N_4O_4$ requires: C, 57·85; H, 6·0; N, 16·9%).

2-Isopropyl-5-methylcyclopentan-1-aldehyde (III, R = H). 2-Isopropenyl-5-methylcyclopentan-1-aldehyde (5 g) was hydrogenated in ethyl acetate (75 ml) using Adams' catalyst. The solvent was evaporated and the residue distilled giving 2-isopropyl-5-methylcyclopentan-1-aldehyde as an oil, b.p. 194–196°. (Found: C, 77·8; H, 11·5. $C_{10}H_{18}O$ requires; C, 77·9; H, 11·7%).

2,4-Dinitrophenylhydrazone. (from methanol as orange needles), m.p. 150–151°. (Found: C, 57·75; H, 6.7; N, 16·8. $C_{16}H_{21}N_4O_4$ requires: C, 57·7; H, 6·3; N, 16·7%).

(2-Isopropyl-5-methylcyclopentyl)-phenylcarbinol (IV, R = Ph). 2-Isopropyl-5-methylcyclopentan-1-aldehyde (4·1 g) was dissolved in dry ether (20 ml) and added slowly to a solution of *phenyl magnesium* bromide [bromobenzene (6·0 g) and magnesium (1 g) in ether (50 ml)]. The mixture was refluxed for 1 hr, then cooled, hydrolysed with saturated solution of ammonium chloride. The aqueous layer was extracted with ether (3 × 50 ml) and the extracts dried over sodium sulphate. Evaporation of solvent gave an oily alcohol (5·3 g) which could not be obtained analytically pure and was used for the next step. ν_{max} 3400 cm^{-1} (strong), no C=O band.

2-Benzylidene-3-isopropylmethylcyclopentane. (2-Isopropyl-5-methylcyclo-pentyl)-phenyl carbinol (5·0 g) was dissolved in glacial acetic acid (15 ml), perchloric acid (60%–2 drops) added, the mixture heated on a steam bath for 20 min, and then poured into water. Extraction with light petroleum (4 × 20 ml) followed by sodium bicarbonate wash, drying and evaporation of the solvent gave a crude product which was purified by chromatography on silica gel using light petroleum as eluant. The product (1·4 g) had λ_{max} 253 mμ (2050). (Found: C, 89·85; H, 10·3. $C_{16}H_{22}$ requires: C, 89·7; H, 10·3%).

[19] G. S. Hammond and R. S. H. Liu, *J. Amer. Chem. Soc.* **85**, 477 (1963).

2-Benzoyl-3-isopropylmethylcyclopentane (III, R = Ph). A solution of chromic acid [chromium trioxide (2·6 g), water (5 ml) and acetic acid (10 ml)] was added with stirring to a solution of (*2-isopropyl-5-methyl-cyclopentyl)-phenyl carbinol* (7·0 g) in acetic acid (20 ml) the temp being kept below 25°. The reaction mixture was allowed to stand for 5 min, then poured into water and extracted with light petroleum (3 × 20 ml). The extract was washed with sodium bicarbonate solution and dried over sodium sulphate. Evaporation of the solvent gave the ketone as an oil, λ_{max} 241 mμ (11150). (Found: C, 83·8; H, 9·0. $C_{16}H_{22}O$ requires: C, 83·45; H, 9·5%).

Diphenyl-(2-isopropyl-5-methylcyclopentyl)-carbinol. 2-Benzoyl-3-isopropylmethylcyclopentane (4 g) was dissolved in ether (20 ml) and slowly added with stirring to a solution of phenyllithium [bromobenzene (4·0 g), lithium (0·2 g) in ether (50 ml)]. The reaction mixture was refluxed for 1 hr then decomposed with ammonium chloride solution and extracted with light petroleum. The extracts were dried and evaporated, leaving the product as a viscous oil (5·6 g) which was used for the next step. The crude diphenyl-(2-isopropyl-5-methylcyclopentyl)-carbinol (5·6 g) in glacial acetic acid (25 ml) and sulphuric acid (98%–2 drops) was heated on a steam bath for 30 min. The solution was poured into water and extracted with light petroleum, the extract washed with sodium bicarbonate solution, dried, and the solvent evaporated. The product thus obtained was a very viscous oil (4·4 g) λ_{max} 248 mμ (9300).

Treatment of 2-Isopropyl-5-methylcyclopentylidenediphenylmethane with osmium tetroxide. The solution of the above olefin in ether (50 ml) and osmium tetroxide (2 g) was allowed to stand for 7 days in darkness. The reaction mixture was poured into a solution of water (100 ml), ethanol (100 ml), mannitol (5 g), potassium hydroxide (0·5 g) and shaken for 1 hr. The mixture was extracted with ether (4 × 50 ml), the extract washed with water, dried and evaporated, leaving an oily product (0·7 g), m.p. 83–84° (after crystallization from methanol). (Found: C, 89·6; H, 8·9; O, 0·8. $C_{25}H_{26}$ requires C, 91·1; H, 8·9; O, 0·0%).

Ozonolysis of the crude olefin yielded no identifiable product.

Methyl-(2-isopropyl-5-methylcyclopentyl)-carbinol (IV, R = Me). 2-Isopropyl-5-methylcyclopentan-1-aldehyde (9·0 g) was slowly added to a solution of methyl magnesium iodide [magnesium (1·6 g), methyl iodide (10 g), ether (80 ml)] in ether with vigorous stirring. The reaction mixture was refluxed for 1 hr, decomposed with ammonium chloride solution and the oily product (9·0 g), b.p. 102°/15 mm isolated in the usual way. Although 3 specimens were prepared none of them analysed correctly (Found: C, 76·35; H, 11·8; O, 10·8. $C_{11}H_{22}O$ requires;· C, 77·7; H, 12·9; O, 9·4%).

2-Acetyl-3-isopropylmethylcyclopentane (III, R = Me). Methyl-(2-isopropyl-5-methylcyclopentyl-carbinol (11·5 g) in acetic acid (50 ml) was cooled to 10° and then chromic acid [chromium trioxide (5·0 g) in minimum amount of water to dissolve it and acetic acid (10 ml)] was slowly added with stirring and cooling (15°). The reaction mixture was allowed to stand for 10 min then poured into water and extracted with light petroleum. The ketone was a mobile liquid (9·4 g), b.p. 85–87°/14 mm. (Found: C, 78·6; H, 12·0. $C_{11}H_{20}O$ requires; C, 78·6; H, 11·9%). ν_{max} 1710 cm^{-1}.

Baeyer-Villiger Oxidation. 2-Acetyl-5-isopropylmethylcyclopentane (6·0 g) in chloroform (150 ml) was treated with a solution of perbenzoic acid (3 equivs) and allowed to stand in a refrigerator for 28 days. The solution was washed with sodium bicarbonate, ferrous sulphate solution, dried and solvent evaporated. The residue was a viscous oil (6·5 g) and its IR spectrum showed the presence of a large amount of benzoate ester.

2-Isopropyl-5-methylcyclopentanol. The ester (6·5 g) from Baeyer-Villiger oxidation was hydrolysed by heating under reflux for 3 hr in a solution of sodium hydroxide (4 g) in water (40 ml) and methanol (50 ml). The reaction mixture was poured into water and was extracted with light petroleum (4 × 30 ml). The extract was washed with dil. acetic acid, sodium hydrogen carbonate, then dried and solvent evaporated. The product (5·5 g) was an oil which was mainly polymeric.

Trans-2-isopropyl-5-methylcyclopentanone (V). The above crude alcohol (5·5 g) was dissolved in glacial acetic acid (30 ml) and then a solution of chromium trioxide [2·3 g in water (2 ml) and acetic acid (10 ml)] was slowly added. The reaction mixture was poured into water and extracted with petroleum ether giving 2 g of the ketone, ν_{max} 1745 cm^{-1}. The *2,4-dinitrophenylhydrazone* was purified by chromatography on silica gel and crystallized from pet ether as orange needles, m.p. 176–178°, undepressed on admixture with an authentic specimen (Found: C, 56·4; H, 6·3; N, 17·45. $C_{15}H_{20}N_4O_4$ requires; C, 56·25; H, 6·25; N, 17·5%).

The semicarbazone separated from pet ether as microcrystals, m.p. 198–200°, undepressed on admixture with an authentic specimen (Found: C, 61·0; H, 9·45; N, 22·0. $C_{10}H_{19}N_3O$ requires;

C, 60·9; H, 9·65; N, 21·3%). The IR spectra of the derivatives were identical with the corresponding authentic samples.

2-Methoxycarbonyl-3-isopropyl-methylcyclopentane. (III, R = OMe). The corresponding acid was prepared by the combined methods of Rupe and Schäfer and Isler *et al.*[8]; by reducing the product of Favorskii rearrangement of pulegone dibromide. The acid was esterified with diazomethane and the resultant methyl ester distilled, b.p. 85°/14 mm.

2-Hydroxymethyl-3-isopropylmethylcyclopentane. (IV, R = H). The ester described above (3·5 g) was reduced with lithium aluminium hydride (1·5 g) in dry ether (150 ml) by boiling for 17 hr. The product was isolated by extraction with pet ether after the excess of the reagent had been destroyed by methyl acetate followed by aqueous ammonium chloride solution. The alcohol was a colourless oil, b.p. 98°/15 mm, yield 3·0 g. The IR absorption was identical with that given by Isler[3].

2-Isopropyl-5-methylcyclopentanal. (III, R = H). Chromic oxide (4·0 g) was stirred into pyridine (40 ml), kept at 15°, so that a yellow-brown paste was obtained. The alcohol (3·0 g) in pyridine (10 ml) was added and the mixture warmed to 35°. The oxidation proceeded, the initial adduct dissolved and reduced chromium complex separated. The mixture was allowed to stand at 20° for 2 hr, then pet ether (50 ml) was added and the solids removed by filtration. The filtrate was washed free of pyridine and acid, then dried and the solvent evaporated. The aldehyde was obtained as a colourless oil, b.p. 87–90°/18 mm, yield 2·4 g. The IR absorption was identical with that of the dihydro-photocitral-A. The 2,4-*dinitrophenylhydrazone* crystallized from isopropanol as orange needles, m.p. 165°. (Found: C, 57·55; H, 6·6; N, 17·1. $C_{16}H_{21}N_4O_4$ requires; C, 57·65; H, 6·3; 16·7%). The IR spectrum was indistinguishable from that of the derivative of photocitral-A, which had a melting point of 151°. Mixed m.p. however, was 150–153° either because the compounds were stereoisomers or, more likely, the synthetic isomer was optically active as it was prepared from natural pulegone.

2-Acetyl-3-isopropenyl-methylcyclopentane. The ketone was prepared essentially as described for the phenyl derivative by oxidation of the corresponding alcohol. It was a mobile liquid which could not be distilled owing to uncontrollable foaming, ν_{max} 1710, 1640, 890 cm^{-1}.

D-*Camphor-quinone.* Selenium dioxide (75 g) and camphor (50 g) were heated under reflux for 20 hr in acetic anhydride (70 ml). The cooled solution was passed through a column of silica gel and eluted with benzene. The eluate was washed with sodium bicarbonate, dried and the solvent evaporated. The residue was crystallized from pet ether, yielding yellow prisms, m.p. 202°, yield 47 g.

D-*Camphor-quinone α and β monohydrazones.* The derivatives were prepared by the method of Forster and Zimmerli, (see ref. 3), α hydrazone m.p. 206°, β isomer m.p. 75°.

D-*Diazocamphor* (X). The monohydrazone (5 g) was dissolved in pyridine (40 ml) at 50° and a solution of mercuric oxide (6·5 g) in water (30 ml) containing acetamide was added. The mixture was left at room temp for 1 hr, the mercury filtered off and the filtrate diluted with water (100 ml) and extracted with pet. ether. The extract was washed with water dried, and the solvent evaporated leaving a golden yellow crystalline solid, m.p. 75°, yield 4·0 g.

The irradiation of D-*diazocamphor.* The diazocompound (8 g) was dissolved in a mixture of dioxan (100 ml) and water (25 ml) and irradiated with an 80 W. medium pressure mercury lamp through a quartz tube for 17 hr. A solution of sodium carbonate (5 g) in water was added and the solvents evaporated; the residual oils were removed by extraction with pet ether and the aqueous layer filtered and then acidified. The acid which separated was taken up in pet ether which was dried and evaporated yielding the mixed acids, yield 4·0 g.

D-1,6,6-*Trimethylbicyclo*[2,1,1]*hexan-5β-oic acid* (XI, R = OH). The crude acid mixture (4 g) was recrystallized from a solution of methanol and water and the product thus obtained was dried and then sublimed *in vacuo*. The sublimate was recrystallized from aqueous methanol yielding the acid as plates, m.p. 101°, yield 1·5–2·0 g. (Found: C, 71·3; H, 9·6. $C_{10}H_{16}O_2$ requires; C, 71·4; H, 9·6%) ν_{max} 1720, 1280, 1305 cm^{-1}. The acid (2·5 g) was esterified with diazomethane to give the methyl ester (2·4 g), b.p. 85°/15 mm.

D-5β-*Hydroxymethyl*-1,6,6-*trimethylbicyclo*[2,1,1]*hexane.* (XIII) The ester (2·4 g) was reduced with lithium aluminium hydride (1·0 g) in ether (75 ml) by refluxing for 20 hr. The excess of lithium aluminium hydride was decomposed with methyl acetate, ammonium chloride solution added and the solids were filtered and the filtrate extracted with pet. ether. The total filtrates were dried and the solvent evaporated leaving the alcohol as an oil which solidified, m.p. 70°, yield 2·0 g. (Found: C, 77·7; H, 11·5. $C_{10}H_{18}O$ requires; C. 77·91; H, 11·8%).

3,5-*Dinitrobenzoate ester of* D-5β-*hydroxymethyl*-1,6,6-*trimethylbicyclo*[2,1,1]*hexane*. A solution of the alcohol (0·4 g) in pyridine (5 ml) was added to a solution of 3,5-dinitrobenzoyl chloride (0·8 g) in pyridine (10 ml) and the solution let stand at room temp. for 4 hr and then poured into water (75 ml). The product separated was filtered off and crystallized from isopropanol, m.p. 98°. (Found: C, 58·8; H, 6·0; N, 7·9. $C_{17}H_{20}N_2O_6$ requires; C, 58·6; H, 5·8; N, 8·0%) ν_{max} 1740, 925, 930 cm^{-1}.

D-1,6,6-*Trimethylbicyclo*[2,1,1]*hexan*-5α-*oic acid* (XII, R = OH). The 5β-carboxylic acid, methyl ester (0·5 g) was suspended in a hot solution of potassium hydroxide (0·5 g) in water (3 ml) and dioxan (7 ml). 2-Methoxyethanol was added until a clear solution was obtained and the mixture was heated on a steam bath for 17 hr. The solvents were evaporated and the residue dissolved in water and acidified. The acid separated as an oil and was extracted with pet ether which was dried and evaporated off leaving the product which was sublimed, m.p. 38–40°, yield 0·3 g. (Found: C, 71·5; H, 9·5. $C_{10}H_{16}O_2$ requires; C, 71·4; H, 9·6%) ν_{max} 1710, 1285 cm^{-1}. Further quantities of the 5α acid could be obtained from the mother liquors of crystallization of the 5β acid. The methyl ester was obtained by esterification with diazomethane as a colourless oil, b.p. 85°/14 mm. (Found: C, 72·7; H, 9·95. $C_{11}H_{18}O_2$ requires: C, 72·5; H, 9·95%).

D-5α-*Hydroxymethyl*-1,6,6-*trimethylbicyclo*[2,1,1]*hexane* (XIV). The alcohol was prepared essentially as described for the β isomer. The product was obtained as an oil, b.p. 100°/15 mm. (Found: C, 76·8; H, 11·7. $C_{10}H_{18}O$ requires; C, 77·9; H, 11·75%). The 3,5-*dinitrobenzoate ester* was prepared by the same method as described for the β isomer except that it was extracted from the aqueous pyridine with pet ether. On evaporation of the dried solution a product slowly crystallized, m.p. 20°. (Found: C, 61·0; H, 6·3; O, 26·25. $C_{17}H_{20}N_2O_6$ requires; C, 58·6; H, 5·8; O, 27·5%). ν_{max} 1750, weak band 1510 cm^{-1}.

2-*Hydroxymethyl*-3-*isopropenyl*-*methylcyclopentane*. A specially purified sample of photocitral-A (2 g) was dissolved in methanol (25 ml) containing sodium borohydride (1 g) and allowed to stand at room temp for 30 min. The mixture was poured into water and the product isolated by extraction with pet ether as a colourless oil after evaporating of the solvent, b.p. 98°/14 mm. (Found: C, 77·25; H, 11·5. $C_{10}H_{18}O$ requires; C, 77·85; H, 11·7%). The 3,5-*dinitrobenzoate* was obtained as a non-crystallizable gum (Found: C, 59·6; H, 6·3; O, 28·1. $C_{17}H_{20}N_2O_6$ requires; C, 58·6; H, 5·8; O, 27·5%), ν_{max} 1750, 900 cm^{-1}.

The mixed 3,5-*dinitrobenzoate esters of photocitrals* A *and* B. The mixed alcohols were obtained by reducing the mixture of photo-aldehydes (2 g) known to contain approximately 40% of the B isomer with lithium aluminium hydride (1 g) in ether (75 ml) by refluxing for 20 hr. The reaction mixture was worked up as described previously for the isomeric bicyclic alcohols and the mixed 3,5-dinitrobenzoate esters were obtained in the same way: ν_{max} 1750 and a weak band at 1510 cm^{-1}.

D-1,6,6-*Trimethylbicyclo*[2,1,1]*hexan*-5α-*aldehyde* (XII, R = H). The alcohol (3 g) in pyridine was added to chromic oxide (8 g) in pyridine (50 ml) at 40° and allowed to stand for 2 hr. The mixture was diluted with pet ether (100 ml) and the solids filtered off. The filtrate was washed free of pyridine, dried and evaporated yielding the aldehyde as an oil, yield 1·2 g. The product was distilled but only 250 mg was obtained, b.p. 78–80°/13 mm. The aldehyde rapidly absorbed oxygen from the air. (Found: C, 75·9; H, 10·4; O, 13·7. $C_{10}H_{16}O_{1\cdot5}$ requires: C, 75·0; H, 10·1; O, 15·0%). The 2,4-*dinitrophenylhydrazone* separated as long orange needles from 60–80° pet ether, m.p. 141°. Although two samples were prepared each analysed as though half a molecule of cyclohexane was trapped in the crystal lattice. (Found: C, 60·4, 60·9; H, 7·0, 7·0; N, 15·4, 15·45. $C_{16}H_{20}N_4O_4 \cdot \frac{1}{2}C_6H_{12}$ requires; C, 60·95; H, 7·0; N, 15·0%).

The D,L-form isolated from the photocitral analysed correctly.

2,4-*Dinitrophenylhydrazone of* D,L-1,6,6-*trimethylbicyclo*[2,1,1]*hexan*-5α-*aldehyde*. The mixed 2,4-dinitrophenylhydrazones prepared from an unseparated photocitral mixture (1·0 g) were fractionally crystallized from 80–100° pet ether (20 ml). The derivatives of the two isomers were quite different in colour thus enabling the fractional crystallization to be followed visually. The pure photocitral-B derivative was isolated as orange plates, m.p. 115–117°. (Found; C, 57·85; H, 6·2; N, 17·3. $C_{16}H_{20}N_4O_4$ requires; C, 57·85; H, 6·0; N, 16·9%). The mixed m.p. of the D,L- and the D-derivatives was 125–128° and the products had identical IR spectra.

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