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CYCLIZATION OF CITRAL BY LIGHT

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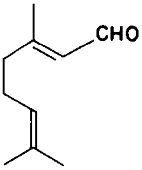
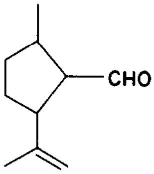
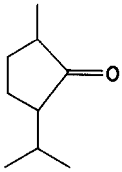
IRRADIATION of citral (I) (mixed cis and trans isomers) with a medium-pressure mercury vapour arc yields a mixture of two isomers in the proportion of about 2:1. The more abundant isomer is an unconjugated, unsaturated aldehyde, ν_{max} 2700, 1720 (CHO) and 890 cm^{-1} ($C = CH_2$), showing no intense ultra-violet absorption. The dihydro-derivative (VII) was treated with methylmagnesium iodide to give an alcohol, which was oxidized to the ketone. Baeyer-Villiger oxidation, hydrolysis, and then further oxidation with chromic oxide in acetic acid produced a ketone (ν_{max} 1745 cm^{-1}), identified as trans-2-isopropyl-5-methylcyclopentanone (III) by comparison of its semicarbazone and 2,4-dinitrophenylhydrazone with authentic samples kindly provided by Professor J. Meinwald.



I



II



III

The resulting structure (II) for photocitral-A is supported by the proton magnetic resonance spectrum (40 Mc/s with tetramethylsilane as internal reference), which showed a doublet centred at 8.98τ ($J = 6.4$ c/s) (CH_3-CH),

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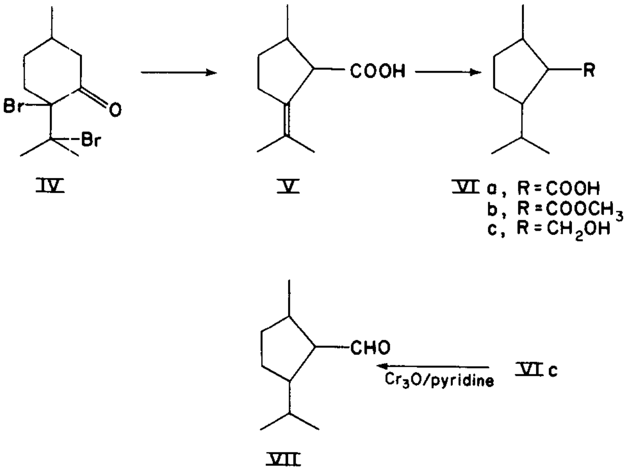
singlets at 8.32τ (CH_3-C=) and 5.31τ (CH_2 = C), and another doublet centred at 0.33τ (J = 2.2 c/s) (CHO-CH).

The acid (VIa) corresponding to the dihydro-aldehyde was made by reducing the product formed by Favorskii rearrangement[1] of pulegone dibromide (IV). Reduction of the ester (VIb) with lithium aluminium hydride, and re-oxidation of the alcohol (VIc) with chromic oxide in pyridine yielded an aldehyde (VII), the 2,4-dinitrophenylhydrazone of which had an infra-red spectrum indistinguishable from that of the derivative of dihydrophotocitral-A.



This photochemical change constitutes a conversion in one step of an acyclic monoterpene into a structure with the carbon skeleton of the terpenes of ants[2] and of catmint,[3] carrying functional groups on the two carbon atoms that are oxygenated in the natural products. The structure

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[1] H. Rupe and K. Schäfer, Helv. Chim. Acta **11**, 463 (1928); O. Isler et al., Ibid. **41**, 160 (1958).

[2] G.W.K. Cavill, Rev. Pure Appl. Chem. **10**, 169 (1960).

[3] J. Meinwald, J. Amer. Chem. Soc. **76**, 4571 (1954; R.B. Bates, E.J. Eisenbraun and S.M. McElvain, Ibid. **80**, 3420 (1958), and earlier papers.

of the second isomer, photocitral-B, and the mechanism of the *trans*formation will be discussed in a full paper.

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