# Photolysis of (+)-*cis*-Caran-5-one

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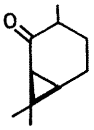
IRRADIATION of caran-2-one (I) affords principally *p*-menth-3-en-2-one (II) and 3,3-dimethylocta-4,6-dienal (III).[1] The nonconjugated (—)-*cis*-caran-4-one (IV) likewise yields mainly (+)-*trans*-1,1,3-trimethyl-5-vinylcyclopentan-2-one (V)[2,3] and a mixture of *cis*- and *trans*-2-methyl-2-(3-methyl-2-oxocyclobutyl)but-3-ene (VI).[2] We have shown that irradiation of (+)-*cis*-caran-5-one (VII)[4] in ether affords principally (—)-*cis*-*m*-menth-8-en-5-one (VIII), (—)-*cis*-*m*-menthan-5-one (IX), (—)-*m*-menth-3-en-5-one (X), and other minor products, two of which are probably the epimeric *cis*-*m*-menthan-5-ols. 3,3,6-Trimethylhepta-4,6-dienal (XI) has not yet been encountered (*cf.* ref. 1).

The photolysis products separated by elution from silicic acid, followed by preparative g.l.c. on Carbowax columns had the following characteristics. Ketone (VIII), $[\alpha]_D^{20}$ — 2·1° (*c* 0·8 in $CHCl_3$), $\nu_{max}$ (liquid) 3067 (=$CH_2$), 1712 (C=O), 1645 (C=C), and 890 (C=$CH_2$) cm.$^{-1}$, displayed signals at $\tau$ 5·2 (*s*, =$CH_2$), 7·76 (m, $CH_2$·CO·$CH_2$), 8·25 (s, $CH_3$·C=), and 8·95 (d, *J* 6 Hz., $CH_3$·C). On hydrogenation it afforded the second photo-product (IX), $[\alpha]_D^{20}$ — 2·01° (*c* 0·55 in $CHCl_3$), $\nu_{max}$ (liquid) 1712 cm.$^{-1}$, $\tau$ 7·6—8·8 (9H), 8·98 (d, *J* 6 Hz, $CH_3$·C), and 9·09 [*d*, *J* 6 Hz., $(CH_3)_2C$].

The third photo-product (X), $[\alpha]_D^{20}$ — 70° (*c* 0·7 in $CHCl_3$), $\lambda_{max}$ (EtOH) 234 (log $\epsilon$ 4·05) and 310 nm. (log $\epsilon$ 1·6), $\nu_{max}$ (liquid) 1664 (C=C·C=O) and 1621 (C=C) cm.$^{-1}$, displayed signals at $\tau$ 4·28 (s, =CH), 7·3—8·4(6H), and 8·87 (d, $J$ 6 Hz, 9H). Hydrogenation of (X) over palladised charcoal afforded (g.l.c.) the saturated ketone (IX).

Support for our structural assignments ensued as follows. (1) Reduction of a mixture of (VIII) and (IX) with lithium aluminium hydride, conversion of the derived alcohols to their tosylates and hydrogenolysis of these with lithium aluminium hydride afforded a product which on hydrogenation over palladised charcoal gave *m*-menthane. (2) Treatment of (+)-*cis*-caran-5-one (VII) with boron trifluoride in ether gave the photo-product (VIII) in small yield, and the unsaturated ketone (X) in over 90% yield. Similar treatment of the photo-product (VIII) gave (X). (3) With hydrochloric acid, according to concentration, (+)-*cis*-caran-5-one (VII) gave either the unsaturated ketone (X) or (+)-*cis*-8-chloro-*m*-menthan-5-one (XII), m.p. 50—51° $[\alpha]^{20}_{D}$ + 17° (*c*, 0·48 in$CHCl_3$) $\lambda_{max}$ (EtOH) 285 nm. (log $\epsilon$ 1·25), $\nu_{max}$ (Nujol) 1715 (C=O), and 817 (Cl) cm.$^{-1}$, displayed signals ($CCl_4$) at $\tau$ 7·5—8·7(8H), 8·40 and 8·46 [s, $(CH_3)_2C$], and 8·9 (d, $J$ 5 Hz., $CH_3$·C). Treatment of the chloro-ketone (XII) with 6% methanolic KOH gave a quantitative yield of (+)-*cis*-caran-5-one (VII).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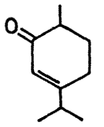
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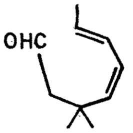
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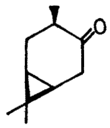
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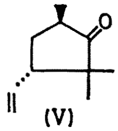
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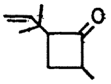
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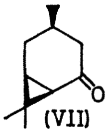
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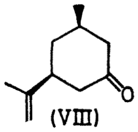
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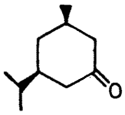
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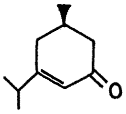
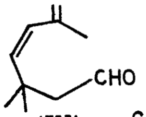

(X)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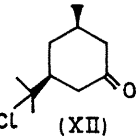
(XII)

The ionic reaction of acid with caran-5-one is formally similar to the photochemical, but probably free-radical, reaction (*cf.* ref. 5).

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