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PHOTOLYSIS OF (-)- CIS-CARAN-4-ONE

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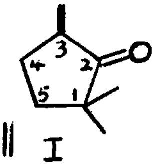
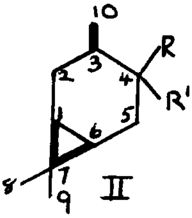
A recent communication (1) on the above subject prompts us to record our related work, which has also led us to the structure (I) for the major photo-product, but which includes more comprehensive chemical evidence for this structure.

Irradiation of (-)-<u>cis</u>-caran-4-one (II; R,R'=O) (2) in dry ether for eight hours using a Hanovia, 400 watt, medium pressure mercury lamp, with a quartz filter, gave a mixture of photo-products in 50% yield. Repeated chromatography on Kieselgel with light petroleum(95)-ether(5) as solvent, gave 1,1,3-trimethyl-5-vinylcyclopentan-2-one (I) in about 12% yield without the need for chemical separation.

The ketone (I), $[\alpha]_D^{20}$+ 20.9° ($\underline{c}$ 1.0 in $CHCl_3$) (cf.1) absorbed maximally at 2950 Å (log ε 1.5), with end absorption, in the ultraviolet, and at 1738, 1640, 998, and 917 cm^{-1} in the infrared (cf.1). Both spectra are in agreement with structure (I). Its n.m.r. spectrum (CCl_4) showed signals at τ 4 - 5.1 (multiplet, 3H, ABX system of the vinyl group), 7.3 - 8.4 (4H, hydrogens at C3, C4, C5), 9.0 and 9.18 (singlets, each 3H, C1-methyls), and at 8.92 (doublet; J=7.5c./sec., C3-methyl). Its mass spectrum established its molecular weight as 152, but was otherwise uninformative.



I



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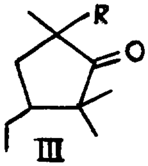
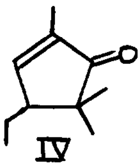
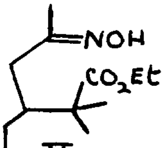


III



IV



V

The ketone (I) was reluctant to form derivatives because of its hindered carbonyl group. It absorbed one mole of hydrogen (cf.1) over palladised charcoal giving (III; R=H), $[\alpha]_D^{20}$+ 12.04° [$\underline{c}$ 0.44 in $CHCl_3$], ν_{max} 1738 cm^{-1}. It had no olefinic signals in its n.m.r. spectrum.

The n.m.r. spectrum of (I) in CD_3OD after deuterium exchange with NaOD in D_2O

gave signals at τ 4 - 5.1 (vinyl group), 8.86 (broad singlet, 3H, C3-methyl), 8.97 and 9.2 (singlets, each 3H, C1-methyls) and showed the disappearance of one proton in the region τ 7 - 8.4. This confirmed the presence of only one hydrogen adjacent to the carbonyl group.

Quantitative bromination of (III; R=H) in acetic acid again confirmed the environment of the carbonyl group. One atom of halogen was absorbed giving a product (III; R=Br) whose n.m.r. spectrum showed signals at τ 8.75 and 9.2 (singlets, each 3H, C1-methyls), and a strongly deshielded singlet at τ 8.25 (3H, C3-methyl). Treatment of the bromo-compound with refluxing base gave a mixture of products from which the α,β- unsaturated ketone (IV) was isolated by chromatography on silica. This showed maxima at 2270 Å in the ultraviolet, and at 1706 and 1639 cm^{-1} in the infrared, both spectra being characteristic of the cyclopent-2-enone system. The n.m.r. spectrum of (IV) at 100 Mc./sec. displayed signals at τ 2.92 (broad singlet, 1H, H4), 8.25 (broad singlet, 3H, C3-vinylic methyl), and at 8.96 and 9.09 (singlets, each 3H, C1-methyls).

Treatment of the dihydro-ketone (III; R=H) with isoamyl nitrite and ethoxide afforded a product which showed OH absorption at 3400 cm^{-1}, C=O absorption at 1708 cm^{-1} and C=N absorption at 1616 cm^{-1}, in general agreement with the expected structure (V).

Finally the photo-product (I) was unchanged by refluxing with 10% methanolic potash. We therefore assign the trans- arrangement of the C3- and C5- substituents. However, the $[\alpha]_D$ given by our ketone (I) is very similar to that of the equilibrated mixture of cis- and trans- isomers obtained (1) by the oxidation of (-)-cis-caran-trans-4-ol (II; R=β-H, R'=α-OH) (2). It is therefore likely that our photo-product (I) was equilibrated by chromatography on the silica column.

With regard to the oxidation of the caran-4-ol (II; R=β-H, R'=α-OH) we feel it necessary to state that we (2) did not use Jones's procedure as ascribed to us in the recent paper (1). Our use of Brown's procedure (3) avoided the formation of the ketone (I), a fact confirmed by H.C. Brown and A. Suzuki (4).

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