Photochemistry of Isopulegone

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(Received May 1, 1967)

Recently important contributions[1] have been appeared and have prompted us to report herein our own independent study on the photochemistry of β,γ-unsaturated carbonyl compound (*l*-isopulegone).

During the course of the investigation of the photochemistry of various types of ketones, irradiation of *l*-isopulegone (I) in methanol (6.5 hr) with high-pressure mercury lamp was found to lead to the three photochemical rearrangement products (A, B and C) in 68, 25 and 7% yields, respectively.

These rearrangement products were separated to each component by the usual distillation under reduced pressure and preparative gas-liquid chromatography technique.

The following results suggest the structure II for compound A. a) Presence of hydroxyl group (3521 cm^{-1}) and olefinic methylene group (1689, 881 cm^{-1}) in its IR spectrum.

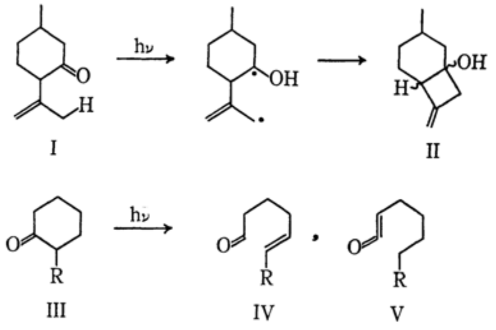
b) Absorption of 1 mol of hydrogen on catalytic reduction to give the corresponding dihydroderivative, of which hydroxyl group was resistant to oxidation with Jone's reagent, as well as acetylation with acetic anhydride.

c) Disappearance of olefinic methyl group of *l*-isopulegone and appearance of allylic methylene group at 2.61 (m) in its NMR spectrum (Table 1).

Similarities of physical and chemical evidences of compound B with compound A suggest that the former is the stereoisomer of the later.

IR spectrum of compound B: 3650 cm^{-1} (hydroxyl group), 1692 and 870 cm^{-1} (olefinic methylene group).

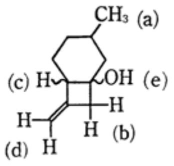
Although it is well known[2] that 2-alkylcyclohexanone (III) is transformed predominantly into formyl derivative (IV) or ketene derivative (V) on photoirradiation, it was thus found that *l*-isopulegone gave the intriguing methylenecyclobutanol derivatives, which might be formed through the following pathway.



R = alkyl

The stereochemistry of the compounds A and B, as well as the structure of the minor product, compound C, will be discussed in the near future.

Table 1. NMR spectra* of compounds A and B

	Proton	Ratio	A	B
	a	3	0.96 (d, 6 cps)	0.90 (d, 6 cps)
	b	2	2.61 (m)	2.0—3.0 (m)
	c	1	2.79 (m)	2.0—3.0 (m)
	d	2	4.75 (m)	4.75 (m)
	e	1	3.14 (s)	1.41 (s)

* Measured in carbon tetrachloride on a Varian A-60 spectrometer; they are expressed in terms of ppm, using tetramethylsilane as an internal standard.

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[1] a) N. C. Yang and Do-Minh Thap, *Tetrahedron Letters*, **1966**, 3671; b) E. F. Kiefer and D. A. Carlson, *ibid.*, **1967**, 1617.

[2] G. Quinkert, *Angew. Chem. Internat. Edit.*, **4**, 211 (1965).