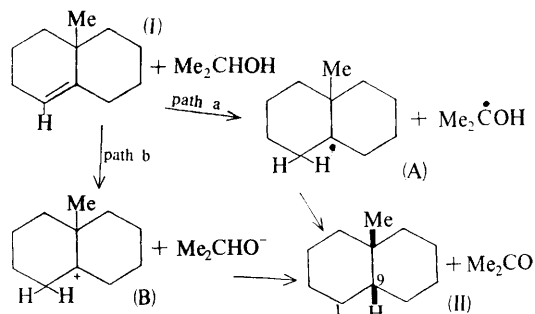


The Photochemically Initiated Hydrogenation of 10-Methyl- $\Delta^{1(9)}$ -octalin

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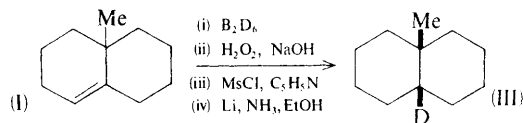
In the course of our studies on photosensitized reactions of cyclic olefins¹ we found that irradiation† of 10-methyl- $\Delta^{1(9)}$ -octalin (I) in isopropyl alcohol-xylene afforded *cis*-9-methyldecalin (II) as the only isolable hydrocarbon product. Previous workers² have observed photochemically initiated reductions of double bonds, albeit under vastly different reaction conditions, and attributed such reductions to radical intermediates [*cf.* path a, (I)→(A)]. In light of our previous findings^{1,3} with substituted cyclohexenes, we felt that an ionic intermediate [*cf.* path b, (I)→(B)] should be considered in the present case. We now report evidence which reinforces this view.



Irradiation† of the octalin (I) in 2-deuterio-propan-2-ol-xylene afforded a [$^3\text{H}_1$]-*cis*-9-methyl-decalin as the only detectable hydrocarbon product.

† A Hanovia 450 w high-pressure mercury-vapour lamp (type L) was used with a water-jacketed Vycor immersion well.

According to the free-radical mechanism (path a) the deuterium should appear at C-1 in this decalin whereas the ionic mechanism (path b) predicts deuterium incorporation at C-9 [*cf.* (II)]. An authentic specimen of the C-9 deuteriated decalin (III) was synthesized from the octalin (I) according to the following sequence. This compound and the photochemically-derived deuteriodecalin exhibited identical i.r., n.m.r., and mass spectra. We therefore favour an ionic mechanism (path b) for the reduction of the octalin (I) by isopropyl alcohol.⁴



Although decalin (II) constituted the major product of our photochemical reactions, approximately half of the starting octalin was converted into a mixture of compounds with relatively long gas-chromatographic retention times. These same compounds were formed upon irradiation of octalin (I) with acetone,⁵ a finding which accounts for our failure to detect more than trace amounts of acetone and pinacol from reactions conducted in isopropyl alcohol. A typical experiment yielded the following products: acetone (trace), pinacol (trace), decalin (II) (50%), 9-decalyl isopropyl

ethers (10%),^{1c} octalin-acetone condensation products (40%).

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¹ (a) J. A. Marshall and M. J. Wurth, *J. Amer. Chem. Soc.*, 1967, **89**, 6788; (b) J. A. Marshall and A. R. Hochstetler, *Chem. Comm.*, 1967, 732; (c) J. A. Marshall and R. D. Carroll, *J. Amer. Chem. Soc.*, 1966, **88**, 4092.

² cf. N. C. Yang, D. P. C. Tang, Do-Mink Thap, and J. S. Sallo, *J. Amer. Chem. Soc.*, 1966, **88**, 2851; N. C. Yang and S. Murov, *ibid.*, p. 2852 and references cited therein; R. R. Sauers, W. Schinski, and M. M. Mason, *Tetrahedron Letters*, 1967, 4763.

³ P. J. Kropp and H. J. Krauss, *J. Amer. Chem. Soc.*, 1967, **89**, 5199; P. J. Kropp, *ibid.*, 1966, **88**, 4091.

⁴ Dr. P. J. Kropp has examined the reduction of a norbornene derivative which undoubtedly proceeds *via* an ionic pathway. P. J. Kropp, unpublished results.

⁵ cf. P. de Mayo, *Adv. Org. Chem.*, 1960, **2**, 372.