

A Photochemically Initiated Rearrangement of 1,2,3,4,4a,5,6,7-Octahydro-1,1,4a-trimethylnaphthalene

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RECENT work has shown that 1-alkylcyclohexenes and 1-alkylcycloheptenes undergo photosensitized double-bond isomerizations and addition reactions.¹ The characteristic features of these reactions support the suggestion that excitation of the olefin leads to a polar species whose behaviour resembles that of a carbonium ion. In the course of further studies along these lines with 1,1,10-trimethyl-1,2,3,4,4a,5,6,7-octahydro-1,1,4a-trimethylnaphthalene (III) we have observed yet another reaction typical of carbonium ions, namely 1,2-methyl migration.² This finding provides additional insight into the behaviour of photochemically excited olefins and illustrates the potential synthetic usefulness of such species.

Methylation of octalone (I) in *t*-butyl alcohol containing potassium *t*-butoxide³ afforded the trimethyloctalone (II)⁴ [$\lambda_{\max}^{(alm)}$ 5.85 μ (CO)] and this compound yielded the corresponding octalin (III) [$\lambda_{\max}^{(alm)}$ 9.92, 10.02, 10.16, 10.25, 11.39, 12.54, and 15.09 μ ; δ (CCl₄)[†] 5.49 (vinyl H triplet, $J = 3.5$ c./sec.), 1.18, 1.10, and 1.05 p.p.m. (three CH₃ singlets)] upon Wolff-Kishner reduction⁵ of the semicarbazone derivative, m.p. 221–223°. Irradiation[†] of the octalin (III) (0.30 g.) in 60% aqueous *t*-butyl alcohol (140 ml.) containing *m*-xylene (1.3 ml.) gave, after 30 hr., the isomeric olefin (VIII) [$\lambda_{\max}^{(alm)}$ 3.25, 6.11 (C=CH₂), 9.38, 9.96, 10.60, 10.79, 11.18, 11.51, 11.70, 11.82, 12.19, and 12.61 μ ; δ (CCl₄)[‡] 4.68 (C=CH₂), 1.05, and 0.83 p.p.m. (two CH₃ singlets)] in 16% yield. The remaining products consisted mainly of tertiary alcohols as evidenced by the infrared [$\lambda_{\max}^{(alm)}$ 3.0 μ] and n.m.r. (no absorption beyond 3.5 p.p.m.) spectra. These materials presumably arise from hydration of olefin (III) and the endocyclic isomer of olefin (VIII).¹ Both the yield of isomerized olefin (VIII) as well as the rate of isomerization increased sharply when the reaction was conducted in 10–15% acetic acid in *t*-butyl alcohol. Formic acid gave comparable results when substituted for the acetic acid. Under these conditions, olefin (VIII) could be obtained in 40–50% yield after only 8 hr. of irradiation.

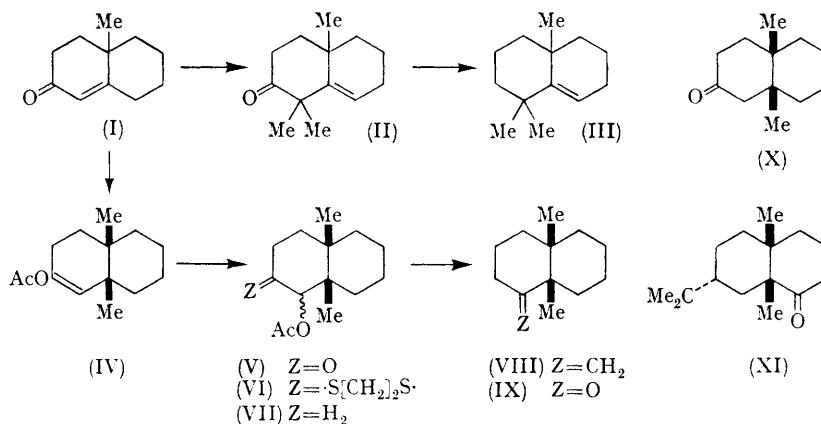
An authentic specimen of olefin (VIII) was

prepared as follows. Addition of methylmagnesium iodide to octalone (I) in the initial presence of cupric acetate⁶ and subsequent treatment of the reaction mixture with acetyl chloride, to trap the resulting enolate,⁷ afforded the enol acetate (IV) [$\lambda_{\max}^{(alm)}$ 5.70 (CO), 5.92 (C=C), 8.18, 8.61, 9.04, and 9.17 μ ; δ (CCl₄)[†] 4.94 (vinyl H), 2.00 (CH₃·CO), and 0.92 p.p.m. (two CH₃ singlet)]. Oxidation of this compound with *m*-chloroperoxybenzoic acid in benzene gave the expected epoxyacetate (a mixture of stereoisomers). This material rearranged upon pyrolysis (165°)⁸ to the acetoxy-ketone (V) [$\lambda_{\max}^{(alm)}$ 5.7–5.8 (CO), 8.08, 9.39, and 9.53 μ], a mixture of stereoisomers (3:1 based on integration of the n.m.r. spectrum). Desulphurization of the thio-ketal derivative (VI) with W-2 Raney nickel⁹ in ethanol under 3 atmospheres of hydrogen afforded the acetate (VII) [$\lambda_{\max}^{(alm)}$ 5.78 (CO), 8.02, 9.72, and 10.20 μ], a 3:1 mixture of epimers based on the n.m.r. spectrum. Conversion of this acetate into the corresponding alcohol *via* treatment with ethereal lithium aluminium hydride followed by oxidation with chromic acid yielded ketone (IX) [$\lambda_{\max}^{(alm)}$ 5.88 (CO), 9.50, 9.88, 10.48, 10.72, and 12.15 μ ; δ (CCl₄)[‡] 1.00 and 0.92 p.p.m. (two CH₃ singlets)]. Finally, condensation with methylene-triphenylphosphorane in dimethyl sulphoxide¹⁰ converted ketone (IX) into the desired olefin (VIII). Identity with the previously prepared sample was established by comparison of i.r. and n.m.r. spectra as well as gas-chromatographic behaviour on several different columns. Both samples appeared homogeneous by these criteria.

We have already noted that the conjugate addition reaction between the octalone (I) and methylmagnesium iodide proceeds with a high degree of stereoselectivity, to give the *cis*-fused decalone (X),⁷ a compound related to the naturally occurring sesquiterpene valeranone (XI). The photochemically initiated methyl migration which we observe with olefin (III) is likewise remarkably stereoselective and thus offers another potential route to such structures. We cannot yet evaluate the mechanistic significance of the stereochemical discrimination exhibited in this rearrangement,

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

[‡] Me₄Si as internal standard.



but the marked rate-enhancement by acids fits within the framework of the previously advanced

postulate whereby the excited olefin gives rise to a species with polar character.¹

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¹ P. J. Kropp, *J. Amer. Chem. Soc.*, 1966, **88**, 4091; J. A. Marshall and R. D. Carroll, *ibid.*, p. 4092.

² Cf., Y. Pöcker, in P. de Mayo "Molecular Rearrangements", Interscience, New York, 1963, pp. 6-8.

³ Cf., J. A. Marshall and N. H. Andersen, *J. Org. Chem.*, 1966, **31**, 667.

⁴ M. Yanagita, M. Hirakura, and F. Seki, *J. Org. Chem.*, 1958, **23**, 841.

⁵ Huang-Minlon, *J. Amer. Chem. Soc.*, 1946, **68**, 2487.

⁶ J. A. Marshall, W. I. Fanta, and H. Roebke, *J. Org. Chem.*, 1966, **31**, 1016.

⁷ Cf., H. O. House and V. Kramer, *J. Org. Chem.*, 1963, **28**, 3362.

⁸ Cf., J. A. Marshall and G. L. Bundy, *Tetrahedron Letters*, 1966, 3359.

⁹ R. Mozingo, *Org. Synth.*, 1955, Coll. Vol. **3**, p. 181.

¹⁰ R. Grunwald, M. Chaykovsky, and E. J. Corey, *J. Org. Chem.*, 1963, **28**, 1128.