

The Solvolysis of 6-Methylenecyclodecyl Toluene-*p*-sulphonate

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SEVERAL recent reports^{2,3} have been concerned with transannular bridging reactions of exo-methylene ketones and toluene-*p*-sulphonates (Ia and Ib) to form adamantan-1-ol (II) and its derivatives. The reactions of (I) closely parallel an analogous ring closure of β -caryophyllene derivatives⁴ in that both systems can be regarded as involving a substituted cyclononylmethylene as the basic skeleton. We report results which further suggest that the reaction of medium-size⁵ cyclanes which incorporate an appropriately positioned exo-methylene unit and a (potential) positive centre results in formation of bicyclic systems with substitution at the bridgehead.

6-Methylenecyclodecanol (III), m.p. 40–41°, was prepared in 75% yield by reaction of methylenetriphenylphosphorane with 6-hydroxycyclodecanone⁶ in dimethyl sulphoxide⁷ at 65°. Reaction of (III) with toluene-*p*-sulphonyl chloride in pyridine at –10° gave the toluene-*p*-sulphonate ester (IV). The ester (IV) decomposed within

one hour at room temperature (in a vacuum desiccator) to a mixture⁸ of components. Successful recrystallization was achieved using hexane-ether at isopropyl alcohol-dry ice temperatures. The ester (IV) appears to have a double melting point, m.p. *ca.* 45° and 85°. Whether this phenomenon is due to a rearrangement⁹ or other causes cannot yet be explained.

Immediately after preparation and purification, (IV), in 75% acetone-water, containing an excess of calcium carbonate, at room temperature rapidly evolved carbon dioxide. The product, isolated in 90% yield, was shown (by alumina-column and thin-layer chromatography) to be a mixture of an alcohol (93%) and an olefin (7%). The alcohol, m.p. 55–56°, was *cis*-bicyclo[4,4,1]-undecan-1-ol¹⁰ (V). The olefin fraction consisted of two, possibly three, components; the major one had an identical retention time with bicyclo[4,4,1]undec-1-ene¹⁰ (VI).

Under similar conditions, (IV) was solvolyzed

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² M. Eakin, J. Martin, and W. Parker, *Chem. Comm.*, 1965, 206.

³ H. Stetter, J. Gartner, and P. Tacke, *Angew. Chem.*, 1965, 4, 153.

⁴ *Cf.*, e.g., P. de Mayo, "The Mono and Sesquiterpenoids," Interscience Publishers, New York, 1956, pp. 292–296.

⁵ The medium-size cyclanes are generally defined as those containing eight to eleven members.

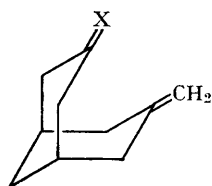
⁶ H. E. Holmquist, H. S. Rothrock, C. W. Theobald, and B. E. Englund, *J. Amer. Chem. Soc.*, 1956, 78, 5339.

⁷ R. Greenwald, M. Chaykovsky, and E. J. Corey, *J. Org. Chem.*, 1963, 28, 1128.

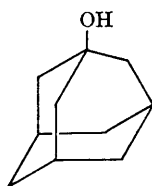
⁸ Gas-liquid chromatography indicated the presence of at least six partially resolved components.

⁹ *Cf.* The rearrangement of *trans*-cyclodec-5-en-1-yl *p*-nitrobenzoate observed by H. L. Goering and W. D. Closson, *J. Amer. Chem. Soc.*, 1961, 83, 3511.

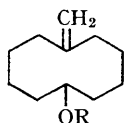
¹⁰ W. G. Dauben, T. L. Westman, and F. T. Bond, Abstracts, 141st Meeting, American Chemical Society, Washington, D.C., March 28, 1962, pp. 29–30; *cf.*, also E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Co., 1962, New York, p. 300.



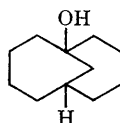
(Ia); X=O
(Ib); X=H, Ts



(II)



(III) R=H
(IV) R=OTs



(V)



(VI)

in glacial acetic acid or acetic acid-sodium acetate to a mixture of 74% (V), 19% (VI), and 7% of a mixture of two olefins. These latter two unidentified olefins had g.l.c. retention times different from those for *cis*- and *trans*-5-methylenecyclodecene. Again this reaction suggests a marked degree of transannular reaction. In contrast to *cis*- and *trans*-5-cyclodecen-1-yl *p*-nitrobenzoates,⁹ 5-methylenecyclodec-1-yl *p*-nitrobenzoate was recovered unchanged after warming (85°) for 3 hours in a 75% dioxan-water solution.

The rapidity with which (IV) is solvolized and the high yield of bicyclic product further amplifies the fact that transannular participation of an exo-methylene, when appropriately positioned (or constrained), in solvolysis of medium-size cyclanes is apparently general.

Solvolytic rate measurements are being examined in order to answer questions about effects of ring-strain, solvent nucleophilicity and conformation.

(Received, August 25th, 1965; Com. 542.)