

Syntheses of 2-Methyl-*cis*-4,5-tetramethylene-1,3-dioxenium Tetrafluoroborate

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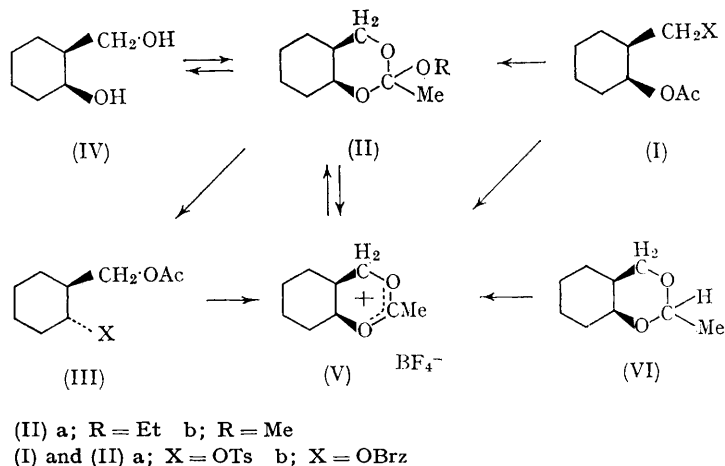
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RECENTLY we reported¹ that the ethanolysis of *cis*-2-toluene-*p*-sulphonyloxymethylcyclohexyl acetate (Ia) and of *trans*-2-acetoxymethylcyclohexyl toluene-*p*-sulphonate (IIIa) in the presence of potassium acetate afforded 2-ethoxy-2-methyl-*cis*-1,3-dioxadecalin (IIa) in 71% and 22.5% yield, respectively, as the isolable product. Lately we have also achieved the methanolysis of (Ia); quantitative formation of 2-methoxy-2-methyl-*cis*-1,3-dioxadecalin (IIb) was proved by the quantity of 2*N*-sodium methoxide consumed in the reaction and by gas-chromatographic analysis. (No compound containing an olefinic bond and formed by a reaction producing acetic acid could be detected among the reaction products.) Compound (IIb) was isolated in 94% yield in very pure state [b.p.₁₀ = 112–115°, n_D^{20} = 1.4575; synthesized from (IV) with methyl orthoacetate]. Since the use of methanol permitted practically complete elimination of side-reactions, an attempt has been made to isolate the cyclic acetoxonium ion, the suggested¹ intermediate of the solvolytic reaction of (Ia) and (IIIa), in the form of its tetrafluoroborate salt (V); during these experiments use was made of

the results obtained by Anderson, Friedrich, and Winstein² in the preparation of the corresponding 1,3-dioxolenium salt.

When an ethereal solution of (IIb) is treated with boron trifluoride etherate,³ 2-methyl-*cis*-4,5-tetramethylene-1,3-dioxenium tetrafluoroborate (V) is obtained in almost quantitative yield; the product (m.p. 50–52°) may be recrystallized from dichloromethane-diethyl ether. The analogous reaction of (IIa) affords (V) in fair yields, as an oil, not easily crystallized. Crystalline (V) can be reconverted into (IIb) in moderate yields by treatment with the stoichiometric quantity of 2*N*-sodium methoxide.

In dilute dichloromethane (Ib) or (IIIb) reacts with silver tetrafluoroborate,⁴ dissolved in the same solvent, in an initially rapid reaction, and as concluded from the amount of precipitated silver *p*-brosylate, the conversion is complete in 70 minutes. (V) may be isolated from the solution in high yield. The corresponding isomers of (Ib) and (IIIb), *trans*-2-toluene-*p*-sulphonyloxymethylcyclohexyl acetate and *cis*-2-acetoxymethylcyclohexyl toluene-*p*-sulphonate, fail to react with silver tetrafluoroborate under identical conditions.



¹ Ö. K. J. Kovács, G. Schneider, and L. K. Láng, *Proc. Chem. Soc.*, 1963, 374.

² C. B. Anderson, E. C. Friedrich, and S. Winstein, *Tetrahedron Letters*, 1963, 2037.

³ H. Meerwein, K. Bodenbrenner, P. Borner, K. Kunert, and K. Wunderlich, *Annalen*, 1960, **632**, 38.

⁴ H. Meerwein, V. Hederick, and K. Wunderlich, *Arch. Pharm.*, 1958, **291**, 541.

We have also synthesized (V) in a third way:⁵ when 2-methyl-*cis*-1,3-dioxadecalin (VI) reacts with trityl fluoroborate in acetonitrile (V) may be isolated in good yield.

These syntheses and the isolation of 2-methyl-*cis*-4,5-tetramethylene-1,3-dioxenium tetrafluoroborate (V) constitute chemical proof of the exis-

tence of the cyclic acetoxonium ion suggested by us earlier¹ as the intermediate of the solvolytic reactions of (Ia) and (IIIa).

A similar investigation of the four isomers,⁶ corresponding to (I) and (VII), containing a 4-*t*-butyl group is in progress.

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⁵ H. Meerwein, V. Hederick, H. Morschel, and K. Wunderlich, *Annalen*, **1960**, **635**, **1**.

⁶ Ö. K. J. Kovács and I. Kővári, to be published.