

THE REACTION OF CIS- AND TRANS-1,2-
DIACETOXYCYCLOHEXANE WITH ANHYDROUS HYDROGEN FLUORIDE

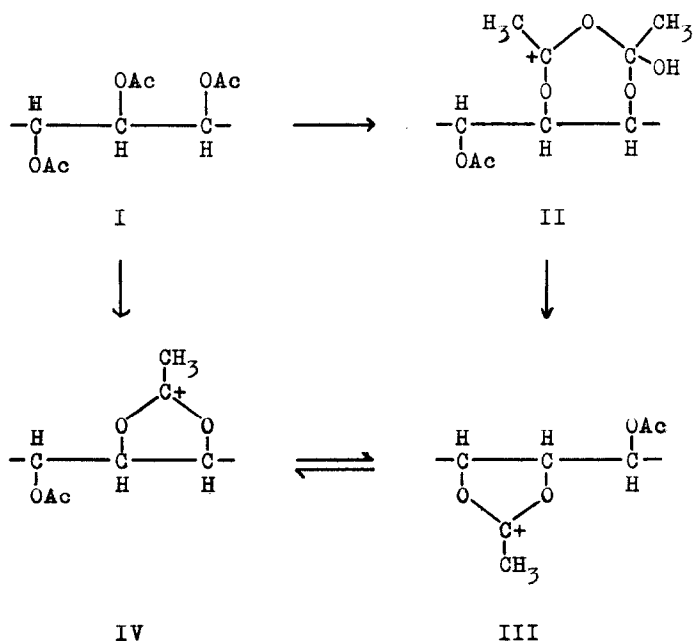
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(Received 2 December 1966)

The reaction of sugar esters,¹ cyclitol esters,² and 1,6-anhydroglycitol esters³ with anhydrous hydrogen fluoride may lead to Walden inversion at one or more carbon atoms. The mechanism of this type of rearrangement has been discussed by Hedgley and Fletcher^{1,2} and by Pedersen^{4,5} and it has been proposed that the reaction involves 1,3-dioxolenium ions as intermediates.

Hedgley and Fletcher^{1,2} found that cyclitol esters or 1,6-anhydroglycitol esters will only undergo Walden inversion with hydrogen fluoride when they contain three acyloxygroups in a contiguous cis-trans sequence (I). They proposed that the first step in the reaction is the formation of a sevenmembered ring (II) which then rearranges to the dioxolenium ion (III) with inversion at the middle carbon atom. Angyal et. al.⁶ considered (II) unlikely and proposed that (I) could form the dioxolenium ion (IV) which is in equilibrium with (III). The rearrangement of some sugar esters

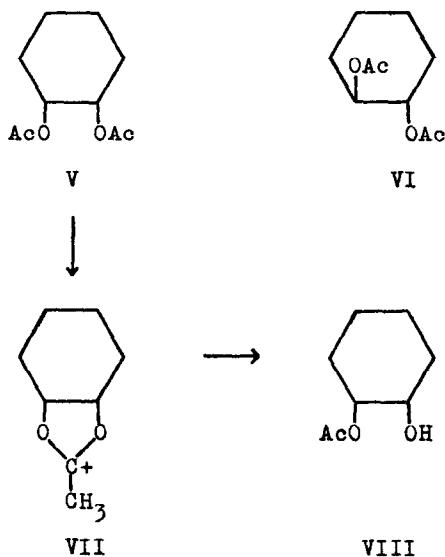


with hydrogen fluoride may be explained by the same mechanism whereas other sugar esters must react by a somewhat different mechanism.^{4,5}

In order to gain further insight into the mechanism of this type of rearrangement the reaction of *cis*- and *trans*-1,2-diacetoxycyclohexane with anhydrous hydrogen fluoride has been studied by NMR spectroscopy.

Cis- and *trans*-1,2-diacetoxycyclohexane (V and VI) were dissolved in anhydrous hydrogen fluoride and the solutions were kept at room temperature while NMR spectra were run at intervals. Spectra taken a few minutes after the solutions were made resembled the spectra of (V) and (VI) in deuteriochloroform (TABLE I) indicating that the compounds are essentially unchanged. The spectrum of the *trans*-compound

(VI) did not change in the course of several days showing that (VI) is stable in hydrogen fluoride solution.



The spectrum of the cis-compound (V), on the other hand, underwent a complete change in the course of 6-8 hours as seen by the replacement of the 6 proton signal at 2.50 with two 3 proton signals at 2.88 and 2.61 (TABLE 1). The signal at 2.88 is typical of 2-methyl-1,3-dioxolenium ions^{7,8,9} and the signal 2.61 corresponds to acetic acid in hydrogen fluoride. This indicates that cis-1,2-diacetoxycyclohexane (V) is converted to the 2-methyl-1,3-dioxolenium ion (VII) and acetic acid when treated with hydrogen fluoride at room temperature. (VII) is stable in hydrogen fluoride solution as seen by the NMR spectra which showed no change in the course of several days.

TABLE 1
Chemical Shifts in δ -Values

Compound	$-\text{CH}_3$	H_1 and H_2	$-\text{CH}_2-$
V in HF after 10 min.	2.48	5.3-5.6	1.6-2.4
VI in HF after 10 min.	2.38	5.0-5.3	1.2-2.3
V in HF after 20 hours	2.88, 2.61	5.8-6.0	1.6-2.5
VII as BF_4^- salt in CD_3CN	2.76	5.7-5.9	1.6-2.3
VIII in CD_3CN	2.09	3.95, 4.95	1.3-1.9

NMR spectra were measured at -10° on a Varian A-60 instrument. The HF solutions were contained in a Teflon tube which fitted closely into an ordinary glass sample tube. Chemical shifts are in δ -values relative to $(\text{CH}_3)_3\text{SiCH}_2\text{CH}_2\text{CH}_2\text{SO}_3\text{Na}$ for HF solutions. For solutions in CD_3CN TMS was used as standard.

The formation of the ion (VII) was confirmed by its isolation as a crystalline tetrafluoroborate obtained by addition of boron trifluoride in carbon tetrachloride to a solution of V which had been kept in anhydrous hydrogen fluoride for 20 hours. The tetrafluoroborate of VII was obtained in 66 % yield after recrystallization from nitromethane-ether. Its melting point ($98-101^\circ$) and NMR spectrum in trideuterioacetonitrile (TABLE 1) proves its identity with the 2-methyl-cis-4,5-tetramethylene-1,3-dioxolenium tetrafluoroborate described by Winstein et. al.⁷ Addition of a drop of water to the solution of the salt (VII) in trideuterioacetonitrile resulted in

immediate formation of cis-2-acetoxycyclohexanol (VIII)⁷ as seen through the NMR spectrum (TABLE 1).

The conversion of (V) to (VII) with hydrogen fluoride is similar to the formation of 2-methyl-1,3-dioxolenium cations from 1,2-diacetoxy-compounds and FSO_3H .⁸

These results indicate that the first step in the rearrangement of compounds of type (I) with hydrogen fluoride is the formation of a 2-methyl-1,3-dioxolenium ion (IV), as suggested by Angyal,⁶ and that (II) is probably not an intermediate in this reaction.

Recently Paulsen et. al.⁹ have succeeded in isolating 2-methyl-1,3-dioxolenium salts derived from carbohydrates by treating β -acetochlorosugars with antimony pentachloride. When treated with aqueous sodium acetate these dioxolenium salts undergo rearrangements which are similar to the rearrangements that take place when sugar esters are treated with hydrogen fluoride.¹⁰

The results of Paulsen et. al. strongly support the theory that 1,3-dioxolenium salts are intermediates in the hydrogen fluoride induced rearrangements of sugar esters. By a study of the NMR spectra of a number of sugar acetates and benzoates dissolved in anhydrous hydrogen fluoride the present author has found that stable 2-methyl- or 2-phenyl-1,3-dioxolenium cations are indeed formed, in most cases in quantitative yield. The results of these investigations will be published elsewhere.

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