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A POSSIBLE ELECTRON-IONIZATION INDUCED ELIMINATION OF DIOXETANE FROM THE DEGLYCOLIZATION PRODUCT OF LITHIUM ALUMINUM HYDRIDE REDUCTION OF THE ETHYLENE ACETAL OF METHYL O-FORMYLBENZOATE

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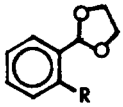
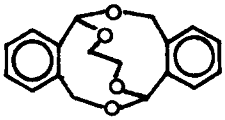
Reduction of the ethylene acetal of methyl o-formylbenzoate with lithium aluminum hydride afforded 1,2 bis(2-oxaindan-1-yloxy)ethane(V a), whose interesting mass spectroscopic behavior is discussed.

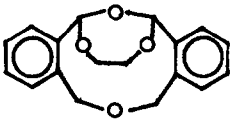
A decade ago, Brown and Sargent reported the unexceptional reduction of carbomethoxyacetal I to hydroxyacetal II[1]. When we repeated this work, all attempts to purify the crude product[2] by bulb-to-bulb distillation resulted in the separation of an organic-immiscible liquid. The unpurified oil, on standing, yielded a solid, mp 123-4°, that was homogeneous on thin layer chromatography. The compound evinced only ether infrared absorption. On the basis of this plus 'H, ^{13}C n.m.r. and mass spectra (298(M^+), 238, 179, 135, 119, 91), as well as elemental analysis and chemical degradation, we favored acetals III, IV or V as the most likely structures for our product, which would result from an intermolecular deglycolization of intermediate hydroxyacetal II. However, the mass spectrum of the compound resulting from treatment of (I) with $LiAlD_4$ showed m/z 302(M^+) plus fragments at m/z 242, 181, 137, 121, and 93. This meant that the M^+ -60 fragment resulted from a loss of the ethylenedioxy group $-OCH_2CH_2O-$ and not from two $-CH_2O-$ or $-CD_2O-$ moieties. This seemed to rule out structure V in favor of III and IV. Extrusion of $-OCH_2CH_2O-$ from the latter two compounds could produce a m/z 238 ion, whereas V could not do so directly.



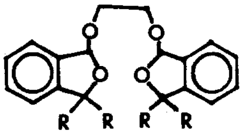
I ($R = CO_2CH_3$)
II ($R = CH_2OH$)



III



IV



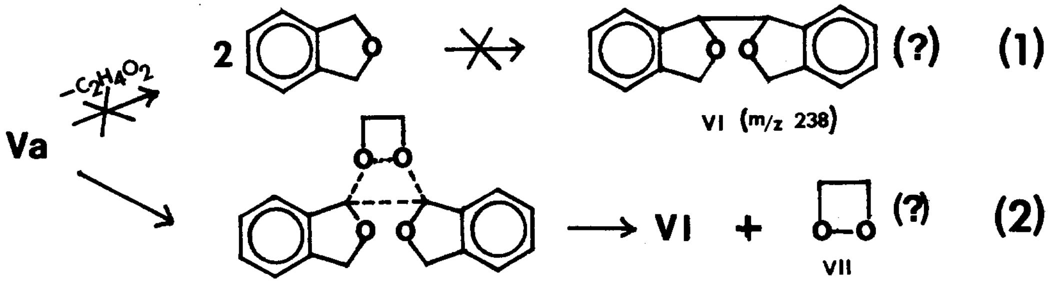
Va(R=H)
Vb(R=D)

In order to arrive at a final structure determination, a clear crystal was mounted on a Syntex $P2_1$ computer-controlled automatic diffractometer. Using graphite monochromated Mo K_α radiation, the crystal was found to be monoclinic with cell dimensions a = 16.561(7), b = 7.841(3), c = 6.282(3)Å; β = 110.74(3)°; V = 762.8(5)Å^3. The space group was uniquely determined to be $P2_1/c$ requiring a center of symmetry in the molecule. A total of 692 observed reflections out of a possible 2388 unique reflections were collected. The structure was solved by direct methods. Several cycles of refinement led to a final convergence with a residual R_f = 0.064. The observed bond distances and angles are in agreement with accepted values.

The structure consists of discrete molecules of 1,2-bis(2-oxaindan-1-yloxy)ethane Va stacked along the b cell dimension and related by the 2_1 screw axis; the center of symmetry is located between the methylenes of the ethane bridge.

The X-ray result was unanticipated in view of the mass spectra. We sought to determine the origin of the anomalous M^+-60 fragment. To this end, we ran the mass spectrum of a mixture of (Va) and (Vb) dissolved in acetone. Plots of intensity vs. scan number of m/z 238, 240, and 242 showed that the compounds were well mixed and distilled from the probe together. Also there was no fractional distillation of compounds with different boiling points, circumstantial evidence against the samples containing a mixture of compounds (i.e., Va containing an impurity of MW 238).

The intensity of m/z 240 was very low -- the intensity expected for the ion m/z 238 with two ^{13}C (naturally occurring). This shows that an intramolecular process such as (2), not a cleavage-recombination path such as (1), is probably involved in the observed loss of 60 from the molecular ion.



Experiments in progress are directed toward inducing the "(V)-238" reaction outside of the mass spectrometer, with the hope of characterizing the "238" and "60" fragments, possible structures for which are (VI) and (VII)(dioxetane) respectively.

Acknowledgements:

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REFERENCES AND NOTES

1. C. Brown and M.V. Sargent, J. Chem. Soc. C, 1818 (1969).
2. We have found that crude (II) is stable in dilute solution over a little solid anhydrous potassium carbonate, and can be used for subsequent reactions by filtering the solution and distilling off the solvent *in vacuo* just prior to use.

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