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THE ACID-CATALYZED WAGNER-MEERWEIN REARRANGEMENT OF DIELDRIN

John W. ApSimon, John A. Buccini[1] and Alfred S.Y. Chau*
Department of Chemistry, Carleton University, Ottawa, Canada K1S 5B6
*Environment Canada, Canada Center for Inland Waters, Burlington, Canada L7R 4A6

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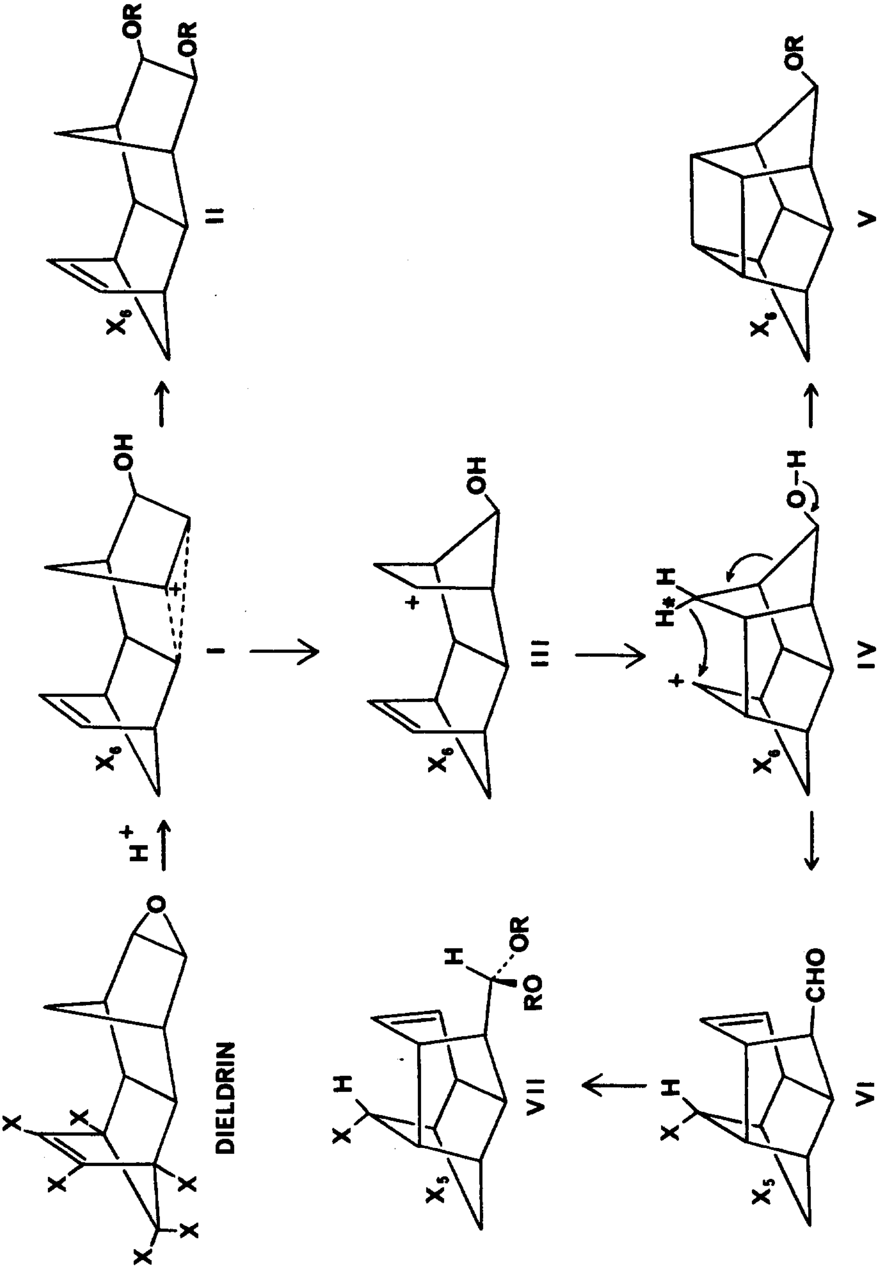
In acidic media, aldrin[2] and its dechloro-derivatives[3] undergo Wagner-Meerwein type rearrangements to form derivatives of isodrin: an analogous rearrangement of dieldrin has not yet been reported. Reaction of dieldrin with various acids is reported to give either 4-oxo-4,5-dihydroaldrin[4,5] or the normal trans products resulting from opening of the epoxide ring[6]. This letter reports a Wagner-Meerwein type skeletal rearrangement of dieldrin in either acetic anhydride/sulfuric acid or boron trifluoride/methanol mixtures to give compounds of general formula VII as the major products.

A mixture of purified dieldrin and acetic anhydride/sulfuric acid (100/1) was refluxed for one hour to yield, after isolation[7], three pure crystalline compounds[8]. One minor product, the diacetate II, R = Ac (11-14% yield), has previously[9] been characterized and correlated with the known exo-cis-diol II, R = H. Another minor product (8-12%) has now been identified as an acetoxy derivative of photoisodrin and assigned formula V, R = Ac [m.p. 219-220°, ν_{max} (Nujol) 1737, 1250, 1070, 1055, 1045, 1013, 800, 755 and 745 cm^{-1}, n.m.r. ($CDCl_3$) δ 2.02 (s, 3H, OAc), 5.12-5.18 (m,1H,HC-OAc), 3.31-3.42 (m,2H) and 3.06-3.29 (m,4H)]. The stereochemistry of the acetoxy group of V is assigned on the basis of the mechanism proposed in the Scheme and has yet to be proved. The major product of this reaction is the gem-diacetate VII, R = Ac [45-60% yield, m.p. 204-205°, ν_{max} (Nujol) 3030, 1760, 1240, 1200, 808, 748 and 715 cm^{-1}]. Assignment of this structure followed from analysis of the n.m.r. spectrum (Figure). Coupling constants and proton chemical shift assignments were deduced from double resonance experiments at 100 MHz (details of which will be reported elsewhere).

SCHEME
X=Cl



The formation of these three unusual products can be explained with one basic reaction pathway, as indicated in the Scheme. The protonated epoxide rearranges to the cation I which can either react with acetic anhydride to form the unusual *cis*-product[9] II or undergo a Wagner-Meerwein type rearrangement to the substituted isodrin carbonium ion III. Formation of the half-

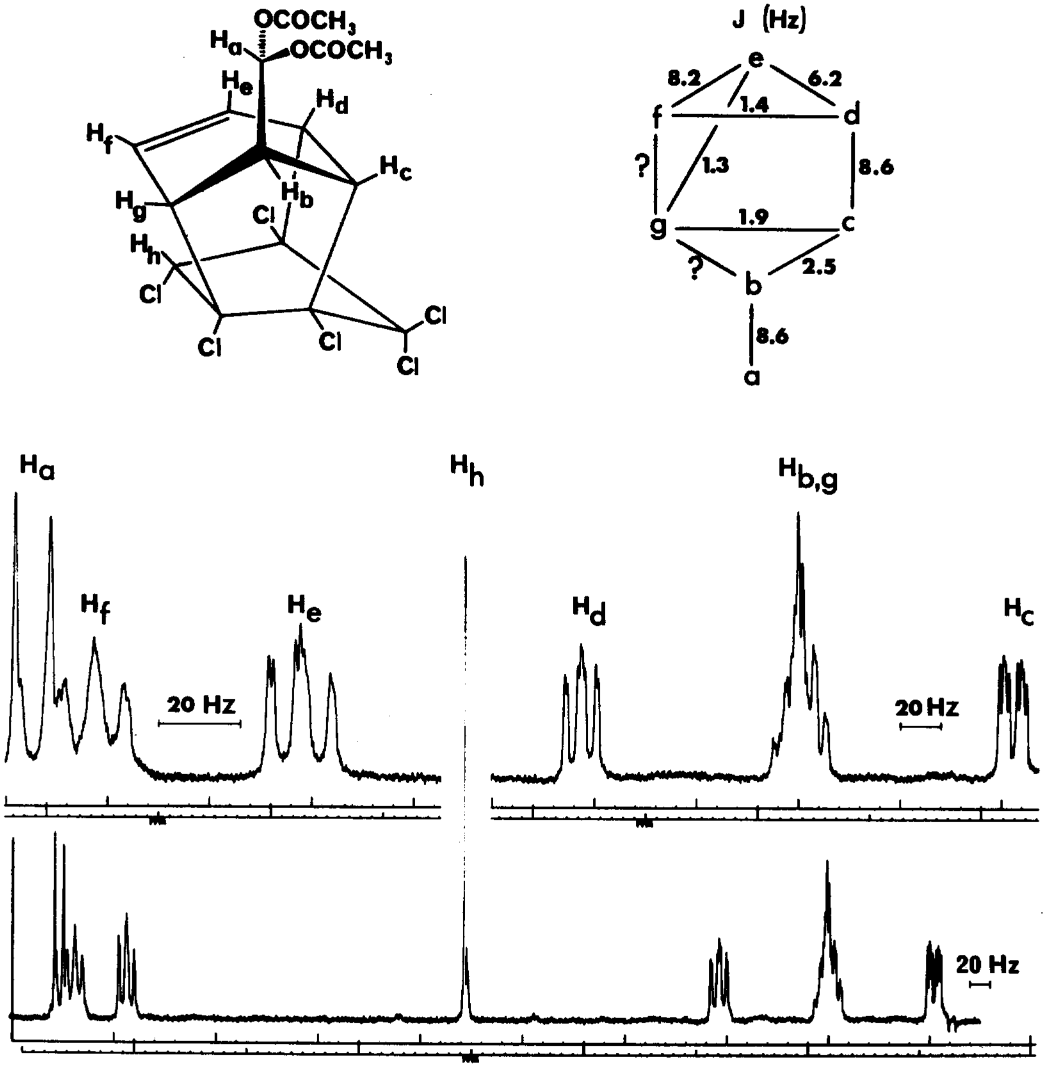


Figure: The 220 MHz (CDCl$_3$) n.m.r. spectrum of the *gem*-diacetate VII: δ 2.06, 2.09 (not shown, 2s, OAc), 2.75 (H$_c$), 3.10-3.35 (H$_b$,H$_g$), 3.70 (H$_d$), 4.80 (s,H$_h$), 6.25 (H$_e$), 6.50 (H$_f$) and 6.55 (H$_a$).

cage cation IV followed by loss of H^{+}_{*} produces the novel "bird-cage" compound V, R = H which is then rapidly acetylated. Alternatively, the aldehyde VI may form by hydride transfer of H_{*} and loss of the hydroxy proton. The aldehyde is then rapidly converted to the *gem*-diacetate VII.

This reaction of dieldrin with acetic anhydride/sulfuric acid was first reported by Baker and Skerrett[5] as the first step in an analytical method for dieldrin residues. It was stated that a *gem*-diacetate derivative was formed and these authors postulated that it was the *gem*-diacetate of 4-oxo-4,5-dihydroaldrin - a conclusion unchallenged to date. We believe that VII, R = Ac is the compound actually involved in this analytical method for dieldrin.

When dieldrin was reacted with boron trifluoride/methanol (1/1) for 24 hours, one major crystalline product was isolated (50% yield). Comparison of the n.m.r. spectrum of this compound with that of the *gem*-diacetate VII suggested that we had obtained the dimethyl acetal VII, R = CH_3 [m.p. 171-173°, ν_{max} (Nujol) 1160, 1120, 1075, 1035, 808, 748 and 715 cm^{-1}]. This acetal was also obtained in 80% yield on warming the *gem*-diacetate in 6 N HCl/methanol (1/20). The two samples of acetal were identical (i.r., n.m.r., mass spectra, g.l.c. and mixed m.p.). Thus the acid-catalyzed skeletal rearrangement of dieldrin may proceed via the same general mechanism in both systems studied.

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