Tetrahedron Letters No. 14, pp 1311 - 1314, 1972. Pergamon Press. Printed in Great Britain.

SEQUENTIAL WAGNER-MEERWEIN REARRANGEMENTS IN THE PROTOLYSIS OF MONODECHLOROALDRIN and MONODECHLOROISODRIN into A UNIQUE SATURATED KETONE.

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(Received in UK 8 February 1972; accepted for publication 24 February 1972)

Detailed studies have described the fate of complex secondary cations formed in solvolysis of derivatives of the stereoisomeric tetracyclododecanes (or their olefinic analogues) which characterise the skeletal features of the polychlorocyclodienes isodrin (I) and aldrin (III). Notable examples disclose skeletal interconversions by Wagner-Meerwein (1,2-sigmatropic) shifts in cationic intermediates derived from both parent tetracyclododecenyl ions.[1] In contrast, the hexahalogenated ions show reduced activity;[2] instead, whilst very slow conversion of aldrin cations into isodrin derived structures [3] does occur, it is usually only isodrin-like cations which readily undergo rearrangement and/or transannular cyclisation, due to the proximate π- bond participation at the incipient electrophilic site, giving products such as (V) [2] and (VI).[4] Rationalization of this contrasting mobility is made on the grounds of reduced carbonium ion lifetime due to the heavily chlorinated periphery of these structures, which ensures neutralisation of aldrin-like cations before rearrangement can proceed. We have found evidence however which suggests that skeletal flexibility may be an additional important factor.

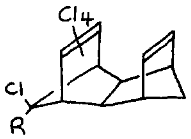
Isodrin is recovered unchanged from neat sulphuric acid, but stirring monodechloroisodrin (VII) or monodechloroaldrin (VIII) [5] with sulphuric acid ca. 20 hr. at 25° gives in each case the same saturated ketone (IX) (35-45% after preparative TLC on silicagel) m.p. 166-168° ν_{max} 1785 vs (ν_{max} characteristic of ClC=CCl missing),and several minor products (each ≯ 0.3%) which are common to both protolyses, and for two of which mass spectral and infrared data suggest structures M1 (=X) and M2 (m/e 310 and 328 respectively, $M^{+\cdot}$).* Comparative nmr data shows that ketone (IX) -for which the ir CO ν_{max} implies an α-halogenated strained ring environment- is not simply related to the known [5] ketone (X) (ν_{max} 1786 vs cm.$^{-1}$) but mass spectral fragmentations accord with its being isomeric, having certain groups of ions in common (e.g. m/e 275, 247 and

113, M-$Cl^{+\cdot}$ M-Cl-$CO^{+\cdot}$ and M-$C_6H_4Cl_3O^{+\cdot}$ respectively). The nmr spectrum of ketone (IX) is complex with multiplets at:[†] τ 6.8(1H H3); 6.92, 7.06(d of t 1H H8) overlapping with 7.07(m 1H H10); 7.30(m 1H H9) overlapping 7.34(m 1H H6); 7.60(d of t 1H H2); 8.52(ABq, J 11Hz 2H H5,H4); 8.76(q J_{H7-H9} 6.7, J_{H7-H8} 12.7Hz 1H H7) and 5.44(s 1H H1). The signal due to the methylene proton H7 at unusually high field in proportion to the *strong* deshielding of the geminal proton H8 follows [6] from the severe compression of H8 against the bridgehead chlorine, molecular models indicating $H_r + Cl_r \leqslant$ internuclear separation. These assignments are confirmed by double-resonance and deuterium labelling experiments; e.g. treatment of (VIII) with 98% D_2SO_4-D_2O and silicagel chromatography gives (IX)-d_1-B m.p. 166-168° (CH_2 ABq at 8.52 $\longrightarrow$ unresolved m, 8.4) and similar deuterolysis of (VII) and work up gives (IX)-d_1-A m.p. 166-168° (τ 8.76 removed), the mass spectra of the two deuterated isomers closely corresponding (m/e 311 $M^{+\cdot}$ 276 M-$Cl^{+\cdot}$ and 248 M-Cl-$CO^{+\cdot}$). These observations conform with structure (IX), and with olefin protonation initiating product formation. Similarly, protolysis of alcohol (XI)-d_2 and silicagel purification gives (IX)-d_2 m.p. 166° (m/e 312, 277 and 249 - $M^{+\cdot}$ M-$Cl^{+\cdot}$ and M-Cl-$CO^{+\cdot}$ respectively) (CH_2 ABq at τ 8.52 removed); for the similarly made trideuterio- analogue (IX)-d_3 m.p. 165° (m/e 313, 278 and 250)[†*] the complex m τ 6.8(H3) is additionally absent, simplifying first order analysis of the remaining nmr lines, which tally for those in (IX). The presence of the α-chloromethylene moiety in (IX) is shown by the appearance of two doublets (τ 5.34, 5.65 J 10Hz, *cis*- CHCl-CHOH) for the major alcohol resulting from 'lithal' reduction; a minor alcohol component has a pair of doublets at higher field (J 3Hz, *trans* CHCl-CHOH) and only the lower field chloromethylene singlets appear if 'lithal-d_4' is used in the reduction.

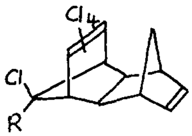
Clearly the formation of ketone (IX) from olefine (VII) implies- in a simplified scheme- diametrical transannular ring closure and Wagner-Meerwein 1,2-sigmatropic shift in the resulting cation, whereas for dechloroaldrin (VIII) and the dechloroaldrin alcohols (XI) etc., 1,2-shift, diametrical ring closure and further 1,2-shift are required to rationalize the data, (Scheme). Mechanism here implies that a probable alternative structure for the ketone is (XII) derived from the ion $C3^{+}$. However this possibility seems to be excluded for the major reaction pathway by the following.

If instead of silicagel chromatography of the crude hydrolysates from the dechloroisodrin/aldrin systems, recrystallisation is effected, only isomers of (IX) e.g.

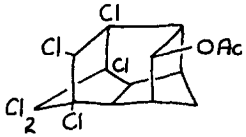
(XIII) and (XIII)-d_3 are isolable as major products, m.p. 150-152° ν_{max} 1785 vs cm.$^{-1}$ m/e 310 and 313 respectively ($M^{+\cdot}$). For (XIII) nmr signals at: τ 6.82(m 1H H3); 6.91 and 7.06(d of t 1H H8); 7.27(m 1H H6); ca. 7.4(m 1H H9), 7.5(m 1H H10), 7.6(m 1H H2) -all overlapping; 8.46(ABq J 12Hz 2H H5,H4); 8.76(q J_{H7-H9} 6.5, J_{H7-H8} 12.5Hz 1H H7) and 5.80(s 1H H1) whilst for (XIII)-d_3 multipluts for H3, H4 and H5 are absent making fairly certain the identifications listed for (XIII). The latter ketone is quantitatively converted to its isomer (IX) on passage in petrol-dichloromethane through a short silica-gel dry column; similarly on solution in ~0.5% t-BuO$^-$ in methanol-d_1 concomitant α H-D exchange occurs through the enolate anion giving (IX)-d_1-C (no nmr singlet at 5.44) m.p. 164°. Prominant in the nmr spectrum of (XIII) is the shift of the H10 signal to rather



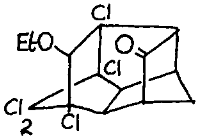
I R=Cl VII R=H
II= epoxide



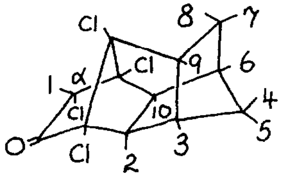
III R=Cl VIII R=H
IV= epoxide

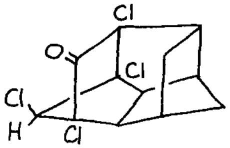


V

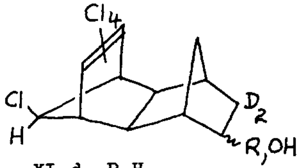


VI

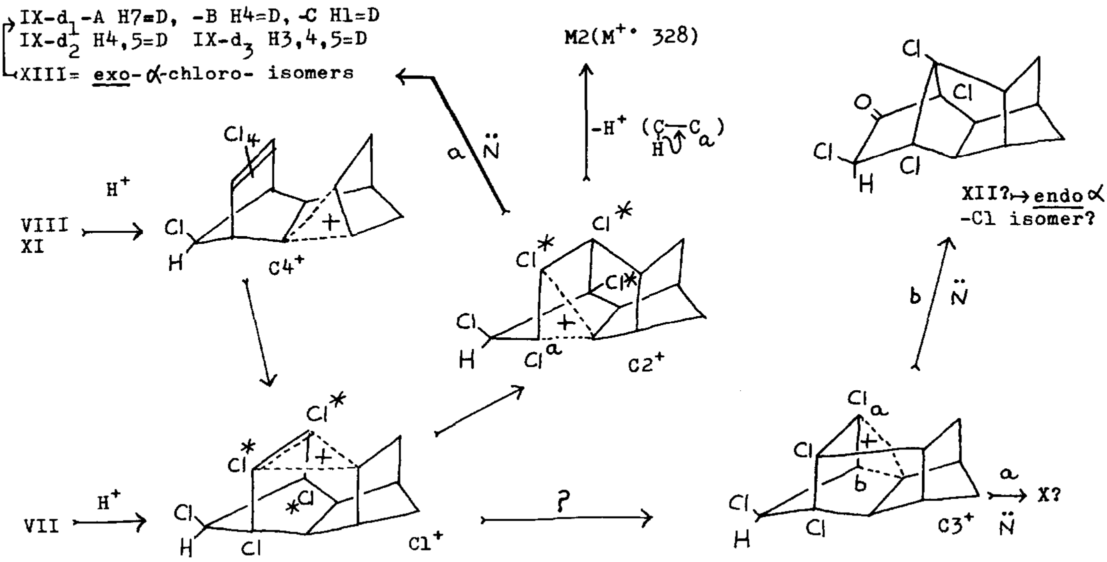




X



XI-d_2 R=H
XI-d_3 R=D



higher field (and similar H10 τ value is found for the α- dechloroketone); models of (IX) show that torsional relief of the Cl/H8 compression results in deflection of the α-*endo* chlorine atom towards the ring junction proton H10 -hence the observed 0.4 τ proximity deshielding.[6] Structure (XII) is therefore unlikely, for such a torsional deflection would actually separate the α-*endo* chlorine and ring junction proton in this case; in fact the H2 chemical shift is identical in (IX) and (XIII). The protonated ketone (XIII) must be too unstable to allow enolisation in strong acid, but for the same reason - an electron withdrawing environment- the stability of the enolate anion is much enhanced and its *exo* protonation to give (IX) relieves *exo* Cl/Cl eclipsing in (XIII).

The formation of ketone (XIII) must involve 1,2-shift in the cation species $C1^+$ which passes into $C2^+$ and is either liganded to nucleophile $\ddot{N}$ (H_2O or HSO_4^-), or else loses a proton (⟼ M2) in a minor pathway. These processes could be favoured by (i) enhanced stability of the cation $C2^+$ in the absence of the second β-chlorine which would characterise the isodrin/aldrin derived species, and (ii) the increase in dihedral angle between the starred chlorines in the cation $C1^+$ as it passes into $C2^+$ and the more sterically accessible penultimate discharged species $C2^+$:N. Another factor seems to us to be the increased flexibility of the dechlorinated bridge systems, e.g. about an axis through the bridge CH_2 and CHCl groups in (VII), the rigidifying effect of steric interaction between the *anti* bridge chlorine and the ring junction hydrogens (seen in nmr data [5]) now being absent; this interaction increases substantially for one of the ring fusion hydrogens as the system moves towards the hexachloro- analogue of intermediate $C2^+$.

We thank the Science Research Council for Research Studentships to C.H.M.A. and D.J.C.

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* All new compounds detailed had satisfactory analytical and/or mass spectral data.

† This unsystematic H numbering adopted purely for convenience and brevity.

†* Full details of these syntheses, nmr and mass spectral data will be reported.