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SELECTIVE 'LITHAL' DEHALOGENATION OF POLYCHLOROTETRACYCLODODECADIENYL ALKYLETHERS OF THE ISODRIN GROUP AND PROTOLYSIS OF THE PRODUCTS.

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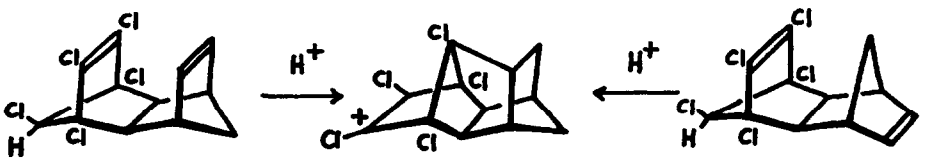
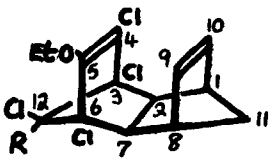
We reported[1] the hitherto unobserved complete sequential 1,2-sigmatropic rearrangement of cations derived by protolysis of monodechloroaldrin (1) and -isodrin (2), with ^{1}H nmr, and deuterium labelling evidence in independent partial confirmation of earlier mechanistic proposals for the similar rearrangement of cations derived solvolytically from analogous non-chlorinated tetracycloalkenyl arenesulphonates.[2] Removal of only one of the chlorine atoms in the hexachloro- compounds appears to be essential for rapid protolytic rearrangement into cation A. In the meantime it has been reported that the presence of the oxygen atom in dieldrin (17) can also promote skeletal rearrangements.[3] We have also explored alkoxy substituent effects on cation rearrangements in the tetracyclododecadienyl series. In addition we have probed the utility of $LiAlH_4$-tetrahydrofuran as a selective reagent for dehalogenation[4] of hexachlorocyclodiene pesticide types, and outline preliminary findings.



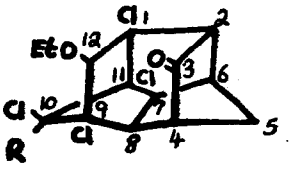
(1) A (2)

Confirming expectation[5] vinyl ether (3)[6] [τ (100 MHz, $CDCl_3$) 3.77m, 4.09m (H-9,10) 6.74s (w/2 5Hz H-2,7 deshielded by 12-anti-Cl) 6.99m (w/2 9-10Hz H-1,8) 8.35m (H-11,11 ABq) 6.02q, 8.64t (OEt)] is stereoselectively dechlorinated by $LiAlH_4$/THF (65°, 48hr.) giving principally tetrachloro vinyl ether (6) m.p. 64-66° [τ 3.77m, 4.10m (H-9,10) 5.66s (H-12) 6.98bs (H-2,7; H-1,8) 8.39m (H-11,

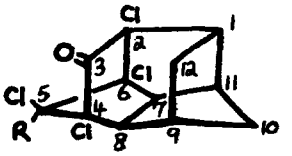
11 ABq) 5.61q, 8.64t (OEt)*]and small amounts of other dechlorinated compounds.† In analogy to vinyl ether (3)[6] monodechloro compound (6) is epoxidised and rearranged in AcO_2H/AcOH to half-cage ketone (7) m.p. 167-168° ν_{max} 1754vs cm.$^{-1}$ [τ 5.57d, 5.97d (H-10,12 ^4J ~1.5Hz[7]) 6.27cm (CH_2O) 6.66cm (H-2) 6.99m (H-4,6) 7.08dm (J 10Hz, H-7,8) 8.22 (H-5,5 ABq) 8.78t (CH_3)]. Similarly both compounds (3) and (6) are hydrolysed in conc. H_2SO_4 to half-cage ketones (5)[6] and (8)[8] (95% yield). [(5): ν_{max} 1790vs cm.$^{-1}$ τ 6.74d, 6.76d, (H-7 and H-8 overlapping) 7.01dd, 7.35mm (H-1, 9,11**) 7.95dm, 8.46dm (endo- and exo-12-H, ^2J 15Hz) 8.35 (H-10,10 ABq)]. As expected, treatment of e.g. vinyl ether (3) with D_2SO_4 introduces exo-12-d stereospecifically (^{1}H nmr: endo-12-H collapses to 's', exo-12-H absent). Clearly these protolytic reactions involve oxonium ions, the resulting stabilisation being more than adequate to compensate for eclipsing interactions at least in part responsible for C4-C9 cyclisation[1] in the cations derived from dienes (1) and (2); vinyl ether polarisation can account for kinetically effective protonation only at sp^2 C9, and for C4-C10 cyclisation in rearrangement of the epoxides into ketones (4) and (7).



(3) R=Cl
(6) R=H



(4) R=Cl
(7) R=H

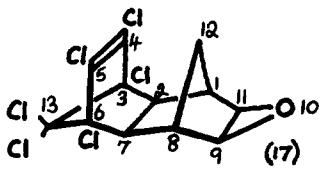


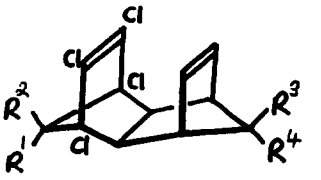
(5) R=Cl
(8) R=H

The syn- and anti-11-t-butoxy derivatives (9) and (10) of isodrin have recently[9] become available; $LiAlH_4$/THF reduction of e.g. t-butyl ether (10) gives the pentachloro-analogue (11) m.p. 152-154° [τ 4.05't' (H-9,10) 5.42s (H-12) 6.46t (syn-11-H) 6.68t (H-2,7) 7.23sext (H-1,8) 8.83s (t-BuO)], together with other products, e.g. bis-dechloro compound (12) m.p. 112° [τ 4.05m (H-9,10) 6.40bm (syn-11-H) 6.54m (H-2,7) 7.34bm (H-1,8) 7.10d, 7.49d (^2J 7Hz, H-12,12)]. Similar results are observed with syn-t-butoxy compound (9), and in addition small amounts of compounds are formed which are resolved only by glc techniques and appear from ^{1}H nmr to derive from further replacement of bridgehead and vinylic chlorine atoms. These reductions therefore appear to follow the electrochemical reduction sequence.[10]

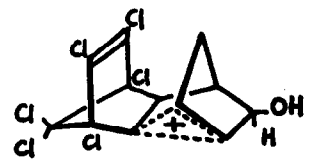
Stirring pentachloro compound (11) in CCl_4/H_2SO_4, (25°) gives hexachloro compound (13) (ca. 66%) m.p. 125-126° as the only well defined product separable. The stereo-chemistry at C11 is assigned on the basis of ^4J nmr spin coupling to H-9,10 and the relative chemical shift of

ring-junction protons, H-2,7 due to their deshielding by proximate Cℓ or OH groups.[9] [τ 3.91t (H-9,10) 5.43s (H-12) 6.07t (H-11) 6.50t (H-2,7) 6.96m (H-1,8)]. A relatively deep-potential 4π delocalised cation[11] stereospecifically discharged by chlorine anion at the bridge accounts for this result. Mechanistically different processes obtain however for the acetolysis of t-butyl ethers (9) and (10) in 1% H_2SO_4/Ac_2O (85°/1¼ hr.).[3] The former must cleave to alcohol (16) as a source of acetate (14) m.p. 216-217° [τ 4.01t (H-9,10) 5.34bs (anti-11-H) 6.62t (H-2,7) 6.72 sext (H-1,8) 8.00s (CH_3)]. t-Butyl ether (10) gives the stereoisomeric acetate (15) m.p. 172.5

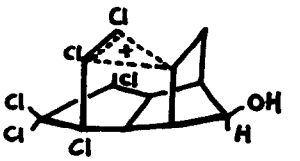




(9) $R^{1,2}$=Cl R^3=O^{t}Bu R^4=H
(10) $R^{1,2}$=Cl R^3=H R^4=O^{t}Bu
(11) R^1=H R^2=Cl R^3=H R^4=O^{t}Bu
(12) $R^{1,2}$=H R^3=H R^4=O^{t}Bu
(13) R^1=H R^2=Cl R^3=H R^4=Cl
(14) $R^{1,2}$=Cl R^3=OAc R^4=H
(15) $R^{1,2}$=Cl R^3=H R^4=OAc
(16) $R^{1,2}$=Cl R^3=OH R^4=H



B



C

- 173.5° [τ 4.07t (H-9,10) 5.53t (syn-11-H) 6.62t (H-2,7) 7.01sext (H-1,8) 7.99s (CH_3)] most likely via a 4π delocalised cation as before. Reflecting the properties of the parent hydrocarbon cation,[11] no evidence for rearranged products is found here nor in the protolytic hydrolysis of the syn butyl ether (9) (5% acid, 25% aqs. dioxan, 85°/5½hr.) into > 90% alcohol (16), m.p. 182 - 183.5° [τ 3.93bs (H-9,10) 6.11bs (anti-11-H, coupled to H-9,10) 6.72t (H-2,7) 6.94m (H-1,8) 7.79m (OH, shifted downfield ca. 1 ppm in the presence of Eu(fod)$_3$].

These observations are significant in relation to the protolytic rearrangement of dieldrin (17) via cation C.[3] It appears that since under similar conditions alcohol (16) does not give ion C, and that additionally solvolysis of 9-aldrin alcohol arenesulphonate is also an inefficient source of rearranged products[12] the extra driving force for the relatively efficient formation of ion C from oxirane (17) may be associated with release of ring strain and rehybridisation as antiperiplanar bond participation occurs in protolysis leading to ion B. Alternatively, the stereoelectronics of the oxygen moiety formed may simply allow more effective endo transannular π-bond participation in the initial delocalised ion B by reducing the kinetic propensity for exo nucleophilic discharge to unrearranged

product. Experiments with the endo-oxirane isomer of dieldrin (17) invited themselves. The endo-oxirane, m.p. 139-140°[5] [τ 6.29m (H-9,11) 7.10s (H-2,7) 7.43m (H-1,8) 8.27m (H-12,12) ν_{max} 1600; 830, 1240 cm.$^{-1}$ (CℓC = CCℓ; oxirane)] is readily made by boiling the trans-9,10-bromo-endo-acetoxy derivative of aldrin m.p. 186-188° with aqueous KOH/dioxane. The endo isomer unlike dieldrin[3] is not easily rearranged via an ion like C in BF_3/MeOH; the product appears to be that derived by more rapid oxirane ring opening and methoxylation.[13] This result supports the view that antiperiplanar C—C participation and/or the stereoelectronic properties of the exo-oxygenated moiety specifically control the rearrangement of dieldrin.

Footnotes and References

* All new compounds had the correct nmr signal intensities and were satisfactorily characterised by mass spectrometry and/or elemental analysis.

** Tentative assignment of nmr signals.

† Main product separations performed by preparative TLC on silica-gel using petroleum-dichloro methane.

1. C.H.M.Adams, D.J.Cawley and K.Mackenzie, J.Chem.Soc.(Perk II) 1973, 909. 2. L. de Vries and S.Winstein, J.Amer.Chem.Soc., 1960, 82 5363. 3. J.W.ApSimon, J.A.Buccini and A.S.Y.Chan, Tetrahedron Letters, 1974, 539. 4. Chemical methods for the selective dehalogenation of polychloro cyclodiene compounds are limited: (i) Zn/HAc will remove both geminal halogens, but will not remove the single chlorine atom at C-12 in e.g. compound (1)[8] (cf. K.L.Williamson, Y.Fang Li Hsu and E.I.Young, Tetrahedron, 1968, 24 6007); (ii) MeO^- or t-BuO^-/Me_2SO[8] and Co/$NaBH_4$ (D.Bienick, P.N.Moza, W.Klein and F. Korte, Tetrahedron Letters, 1970, 4055) will stereoselectively remove anti-12-chlorine in aldrin and isodrin and similar compounds. However C.W.Jefford, D.Kirkpatrick and F. Delay have recently advocated the use of $LiAlH_4$ in Et_2O, dimethoxyethane or tetrahydrofuran for selective removal of halogen from polyhalogenatedbicyclic compounds (J.Amer.Chem.Soc., 1972, 94 8905). 5. S.B.Soloway, A.M.Damiana, J.W.Sims, H.Bluestone and R.E.Lidov, J.Amer.Chem.Soc., 1960, 82 5377; S.B.Soloway (Dissertation, 1955) does however record that mono-dechlorination of dieldrin is achieved by heating with $LiAlH_4$/Et_2O for 1 week. 6. K.Mackenzie, J.Chem.Soc., 1962, 457. 7. J.Meinwald and Y.Meinwald, J.Amer.Chem.Soc., 1963, 85 2514 (cf. refs. 1, 8). 8. C.H.M.Adams and K.Mackenzie, J.Chem.Soc.(C), 1969, 480. 9. K.Mackenzie, Tetrahedron Letters, 1974, 1203; K.B.Astin and K.Mackenzie, J.Chem.Soc.(Perk II), in press. 10. A.Cisak, Roczniki Chemii, 1968, 42 907; J.A.Bukowski and A. Cisak, ibid., p.1339. 11. E.L.Allred and J.C. Hinshaw, Tetrahedron Letters, 1968, 1293. Cf. S.Winstein, M.Shatavsky, C.Norton and R.B.Woodward, J.Amer.Chem.Soc., 1955, 77 4183. 12. C.W.Bird, R.C.Cookson and E.Crundwell, J.Chem.Soc., 1961, 4809. 13 endo-exo-1,8,9,10,11,11-hexachloro-exo-5-methoxytetracyclo[6,2,1,$1^{1,8}0^{2,7}$]dodec-9-en-endo-4-ol m.p. 147-148° τ 6.1dm (H-9) 6.64s (OMe) 6.64d, 7.40d (J = 8Hz H-2,7) 7.10m(H-10) 7.52m (H-1,8) 7.86bs (OH) 8.60 (H-11,11 ABq) ν_{max} 3630, 1601 cm^{-1} (OH, CℓC = CCℓ).