The Reaction of Hexachloronorbornadiene with Furan

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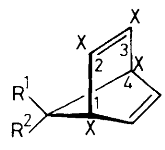
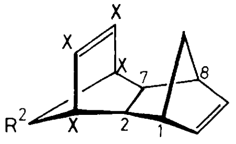
Chemical evidence, supported by an *X*-ray crystal structure determination, shows that a furan adduct of hexachloronorbornadiene unambiguously belongs to the *endo–exo* series of cycloadducts (typified by aldrin), and not the *endo–endo* series of isomers.

Whilst cycloaddition of electron-deficient dienes with norbornadiene (**1**) is ~96% stereoselective for *endo–exo* adducts typified by aldrin (**4**)[1,2] and its analogues, *e.g.* (**5**),[3] the presence of even a single electronegative 7-substituent in the dienophile, as in (**2**), results in a marked preference for *endo*-addition, particularly at the alkene site *syn* to the substituent,[1,2,3] and the major products, *e.g.* (**6**) and (**7**), belong to the *endo–endo* series of adducts typified by isodrin (**8**).[4] Isodrin (**8**) results from the stereospecific exothermic addition of cyclopentadiene with hexachloronorbornadiene (**3**) ('NBD–Cl_6'), where *exo* approach of the diene is sterically inhibited by the dichloromethano bridge, an effect also seen in 1,3-dipolar cycloadditions.[5] The π/π proximal character in isodrin has been amply demonstrated by chemical[6] and photochemical[7] cyclisation and by the observation of dyotropic 2H group-transfer rearrangement in certain derivatives, *e.g.* (**9**) and related heterocyclic compounds.[8]

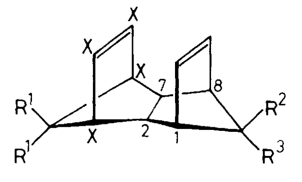
The expectation that NBD–Cl_6 will likewise react *endo*-



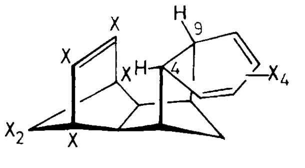
(**1**) $R^1 = R^2 = X = H$
(**2**) $R^1 = X = H, R^2 = Bu^tO$ (or AcO)
(**3**) $R^1 = R^2 = X = Cl$



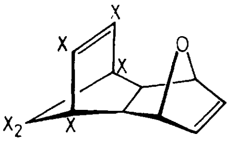
(**4**) R = X = Cl
(**5**) R = OMe, X = Cl



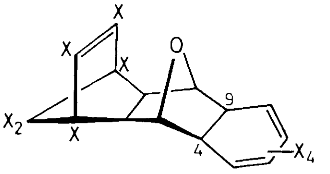
(**6**) $R^1 = Cl$ (or MeO), $X = Cl, R^2 = Bu^tO$ (or AcO), $R^3 = H$
(**7**) $R^1 = Cl$ (or MeO), $X = Cl, R^2 = H, R^3 = Bu^tO$ (or AcO)
(**8**) $R^1 = X = Cl, R^2 = R^3 = H$



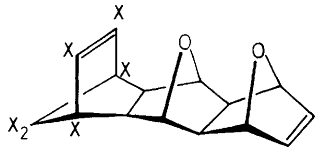
(**9**) X = Cl



(**10**)/(**A**) X = Cl



(**11**) X = Cl



(**12**)/(**B**) X = Cl

stereospecifically with cyclohexa-1,3-diene and cyclohepta-1,3-diene giving bridge-expanded isodrin analogues has been realised[9] and a similar reaction with furan might also be expected.

According to the literature[10] a furan monoadduct, m.p. 139°, is formed by exposure of NBD–Cl_6 to excess furan (165°, ambient pressure or sealed vessel). We have found however that heating NBD–Cl_6 with furan (1 : 2 mol ratio, sealed tube, 165°) gives an adduct (**A**), m.p. 137—139°, and significant amounts of a bis-adduct (**B**), m.p. 242—245° (and polymeric material), the ratio of the two adducts varying according to the conditions. The ^1H n.m.r. spectrum of adduct (**A**) [δ 6.49 (t, 2H, H-9, 10), 4.90 (m, 2H, H-1,8), 2.79 (s, 2H, H-2,7)] reveals no evidence of the H-1,8/H-2,7 spin-coupling characteristic of isodrin and its analogues,[11] the singlet character of H-2,7 more closely resembling that found for the *endo–exo* compounds (**4**) and (**5**), consistent with a H-1/H-2 torsional angle of ~90°, rather than ~40° in the *endo–endo* series of compounds (**6**—**8**). However, strongly electronegative substituents attenuate methine proton vicinal couplings, which may vanish entirely, and recourse to chemical evidence shows that adduct (**A**), exposed to $C_5H_5NH^+Br_3^-$ (1 mol, HOAc, 20°, 18 h) gives (88%) a single *unsaturated* dibromo-adduct, m.p. 204—206° [*m/z* 522($M^{+\cdot}$); $\nu_{max.}$ 1606 cm^{-1} (ClC=CCl); ^1H n.m.r. {[$^2H_6$]Me_2SO} δ 4.78 (d, 1H, *endo* H-9), 4.45 (q, 1H, *exo* H-10), 4.51 (m, 2H, H-1,8), 3.55 (q 2H H-2,7)] consistent with the uncomplicated, 1,2-bromine addition characteristic of *endo–exo* compounds (**4**) and (**5**), rather than π/π-cyclisation observed on treatment of isodrin (**8**) with bromine.[6] Adduct (**A**) is therefore *endo–exo* compound (**10**) and not its anticipated *endo–endo* stereoisomer. Further structural confirmation is manifest in the very rapid reaction of adduct (**A**) with tetrachlorothiophene dioxide at 25 °C (in contrast, isodrin (**8**) reacts only very slowly[12]) giving (90%) a tetrachlorocyclohexadiene-annulated derivative (**11**), m.p. 279—282 °C [*m/z* 522($M^{+\cdot}$); characteristic[13] u.v. absorption, $\lambda_{max.}$ (ε) 263 (3 473), 274 (5 278), 284 (7 577), 296 (8 238), 310 (4 911); ^1H n.m.r. δ 4.85 (s 2H), 3.13 (s 2H), 3.05 (s 2H)]. Compound (**11**) shows no tendency to rearrange by 2H group-transfer[8] in contrast to compound (**9**) and oxygen-bridged 9,10-dihydroisodrin-like compounds,[14] indicative of its stereochemistry, the relevant allylic hydrogens H-4,9 not being appropriately π-bond proximate.

Further structural confirmation derives from an *X*-ray crystal structure determination for the dibromo-derivative of adduct (**A**) and the main molecular features are shown in Figure 1.† The absolute stereochemistry of the dibromo-compound shows unequivocally that the dichloroethene element and oxygen-bridge are *syn* to each other, as expected for an *endo–exo* ring-fused system. The chlorine substituents on C(4) and C(5) lean towards the oxygen atom (O-11); the planes defined by C(4)-C(5)-C(3)-C(6) and C(4)-C(5)-C(14)-C(15) show a dihedral angle of 10°, a further example of 'π-tilting' due to pyramidalisation of sp^2 carbons C(4) and C(5) in a norbornene ring.[15] The bromine atoms lie axial and equatorial with respect to the C(1)-C(8)-C(9)-C(10) plane, and the closest intermolecular non-bonded contacts occur between C(1—13) and H-9 (2.918 Å) whilst the shortest intramolecular distance is 1.98 Å for O-11/H-10.

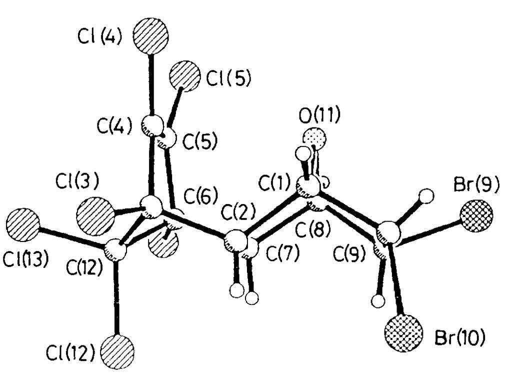


Figure 1

The bis-adduct (**B**) [*m/z* 432 ($M^{+\cdot}$); ^1H n.m.r. δ 6.35 (s, 2H, CH=CH), 4.93 and 4.51 (each s, 2H, bridgehead H's), 2.82 and 1.85 (each s, 2H ring-junction H's)] may be assigned structure (**12**) on the basis of n.m.r. proton signal comparison with the *exo–exo* fused isobenzofuran adduct of 7-oxabenzonorbornadiene[16] where bridgehead (δ 5.41) and ring-junction (δ 1.98) proton spins are also uncoupled.

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† *Crystal data*: $C_{11}H_6OCl_6Br_2$, $M = 526.70$, $a = 8.089$ (3), $b = 14.484$ (7), $c = 13.619$ (8) Å, $\beta = 98.4$ (4)°, $U = 1578$ (1) Å^3. Space group $P2_1/n$ (non standard setting No. 14), μ(Mo-K_α) = 61.0 cm^{-1}, $F(000) = 1008$, Mo-K_α *X*-radiation (graphite monochromator) $\lambda = 0.71073$ Å, D_c 2.22 g cm^{-3}. $R(R_w) = 0.047$ (0.046) for 2072 reflexions with $F > 2\sigma(F)$. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

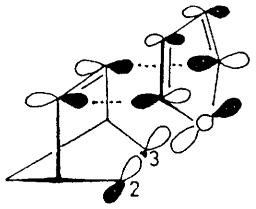

Figure 2

Compared to alicyclic 1,3-dienes, furan obviously exhibits exceptional behaviour towards NBD–Cl_6 [and towards the 7-oxanorbornene element generally,[16] *cf.* bis-adduct (**12**)]; a steric effect associated with the CH_2 group[17] could rationalize specificity for *endo–endo* approach of cyclopentadiene (together with maximum π/π overlap), but if the transition state for furan/NBD–Cl_6 addition is examined using localised MO models[18] an electronic factor may also be discerned. If it is assumed that diene-LUMO/dienophile-HOMO interaction contributes to a lowering of transition state energy, the presence on oxygen of a significant π-component of the correct phase for non-bonding favourable secondary interaction at C(2) and C(3) in the dienophile HOMO may, in the absence of a steric effect, strongly favour *exo* aproach of furan to the *endo* face of NBD–Cl_6, (Figure 2).

The orbital coefficients at the non-bonding sp^2 carbons in the relevant MO's for furan and cyclopentadiene are attenuated (compared to those at the bonding sp^2 carbon sites and for the π-component on furan oxygen), reducing secondary stabilising interactions between sp^2 carbon centres, whilst the CH_2 π-component in cyclopentadiene is much smaller than that on furan-oxygen.

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