Crystal and Molecular Structure of a Novel 1 : 1 Cycloadduct of [2,2](2,5)-Furanophane (13,14-Dioxatricyclo[8,2,1,1^{4,7}]tetradec-4,6,10,12-tetraene) with Tetrachlorocyclopropene

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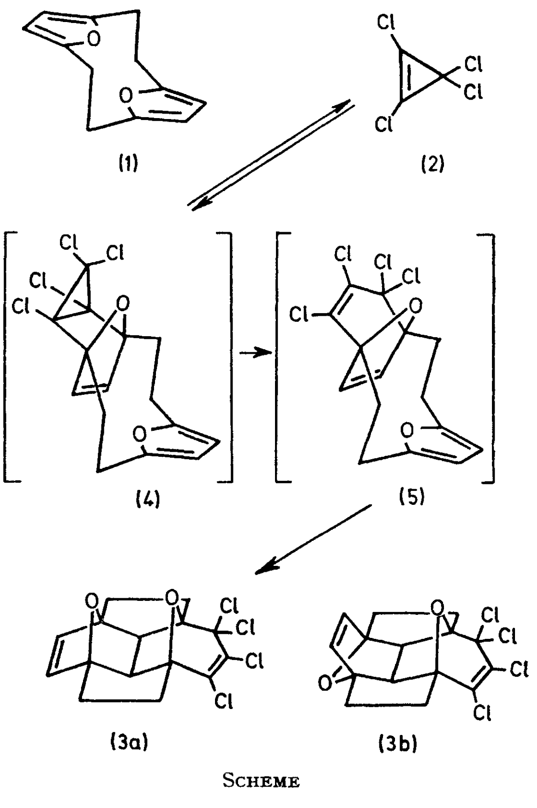
Summary An unusual cycloaddition reaction of [2,2](2,5)-furanophane with tetrachlorocyclopropene yields a crystalline 1 : 1 adduct, the structure of which has been determined by *X*-ray diffraction to be 5,6,7,7-tetrachloro-16,17-*syn*-dioxahexacyclo[9,2,2,1,1,^{4,8}, 0^{4,14}, 0^{8,15}]-heptadeca-5,12-diene.

CYCLOADDITION reactions of [2,2](2,5)-furanophane (**1**)[1] are rare because of the ready cycloreversions common to furan systems.[2,3] The reaction of (**1**) with dimethyl acetylenedicarboxylate is the only reported example of the standard Diels–Alder type, with the product undergoing subsequent intramolecular cycloaddition.[3] We have examined reactions of (**1**) with tetrachlorocyclopropene (**2**)[4] as a possible route to a new class of aromatic cyclophanes containing a troponoid ring system. This reaction gives a crystalline 1 : 1 cycloadduct in high yield whose unique structure has been determined by a single crystal *X*-ray diffraction study.

The furanophane (**1**) reacts smoothly and nearly quantitatively with an equimolar quantity of (**2**) in refluxing benzene (in contrast to no reaction with the parent cyclopropene) to yield a crystalline 1 : 1 adduct (**3**), m.p. 148—149°; M^+ (70 eV) 364.

The n.m.r. spectrum ($CDCl_3$) of (**3**) exhibits a narrow olefinic AB quartet centered at τ 3·49 (2H, J 6·0 Hz), a second AB quartet (2H, J 6·2 Hz) at τ 6·95 and 7·34, and a complex multiplet in the range τ 7·14—7·84 (8H). The unsymmetrical appearance of the n.m.r. spectrum and the



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evidence for only two vinyl-type protons rules out structures (**4**) and (**5**) (see Scheme), but appears to be consistent with either condensed structure (**3a**) (*syn*-dioxa-bridges) or (**3b**) (*anti*-dioxa-bridges) formed by intramolecular cycloaddition from the ring-opened monoadduct (**5**). Although molecular models suggest that the *syn*-structure (**3a**) should be considerably less strained than *anti*-(**3b**), spectral data alone could not resolve this structural question.

Colourless crystals from hexane were studied by X-ray diffraction using Mo-K_{α} radiation: $C_{15}H_{12}Cl_4O_2$, $M = 366{\cdot}1$; monoclinic, space group $P2_1/c$ (No. 14), $a = 14{\cdot}436$, $b = 9{\cdot}109$, $c = 11{\cdot}659$ Å, $\beta = 102{\cdot}87°$, $U = 1494{\cdot}6$ Å, $D_m = 1{\cdot}52$ (flotation in aqueous KI) g/cm^3, $Z = 4$, $D_c = 1{\cdot}626$ g/cm^3.

The intensities of 2038 reflections (1285 non-zero) with $2\theta \leqslant 50°$ were measured by a θ–2θ scan technique using a Syntex $P1$ diffractometer. The chlorine atoms were located in a Patterson function and the remaining light atoms in a Fourier synthesis. Refinement was by full-matrix least-squares methods to R 0·088, with all atoms anisotropic. The addition of the hydrogen atoms and two additional cycles reduced R to 0·076.

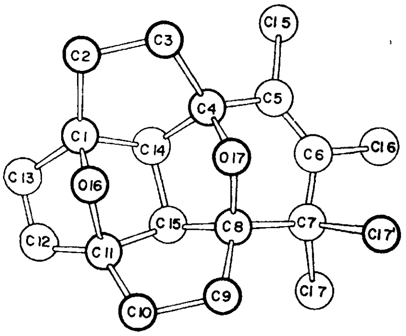

FIGURE. *A view of the molecule showing the atomic numbering and the* syn-*configuration. The double bonds are between* C(5)–C(6) [1·32(1) Å] *and between* C(12)–C(13) [1·36(1) Å].

The atomic numbering and the molecular shape is illustrated in the Figure. The molecule has the *syn*-configuration and the distances of 1·36(1) Å from C(12)–C(13) and 1·32(1) Å from C(5)–C(6) unambiguously locate the double bonds in the molecule. The distances C(6)–Cl(6) of 1·733(9) Å and C(5)–Cl(5) of 1·722(8) Å are also in agreement with a C(sp^2)–Cl bond distance.[5] The two C(sp^3)–Cl distances of 1·802(9) and 1·804(9) Å are significantly longer than the C(sp^2)–Cl distances, in agreement with a difference in hybridization of the carbon atoms. The remaining C–C distances range from 1·50(1) to 1·60(1) Å and do not appear unusual considering the fused ring systems present in the molecule. Similarly the C–O distances ranging from 1·42(1) to 1·45(1) Å are normal.

The initial cycloadduct formed reversibly from (**2**) and (**1**) (*trans*-conformation) is suggested to have the *exo*-configuration (**4**) on the basis of recent evidence supporting stereoselective *exo*-adductions of cyclopropenes with furan and its derivatives.[6] Regardless of stereochemistry, however, adduct (**4**) would be expected to undergo the ready electrocyclic[7] ring-opening and stereospecific 1,2-chlorine migrations common to tetrahalogenocyclopropene–furan adducts under these conditions[8] to afford (**5**), the immediate precursor of (**3a**).

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