A Simple Construction of the Iceane Skeleton *via* an Intramolecular Diels–Alder Reaction

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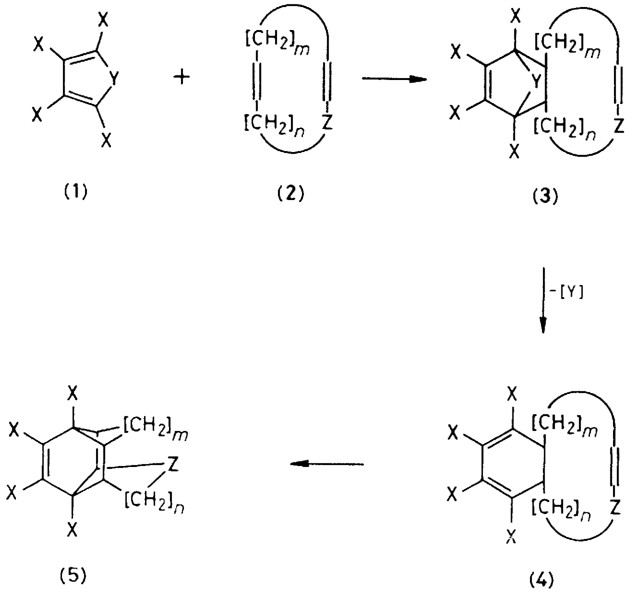
Annelation of 11,11-dichloro- and 11,11-dibromo-tricyclo[4.4.1.0^{1,6}]undeca-3,8-diene (**6**) with tetrachlorothiophen 1,1-dioxide is followed by an intramolecular Diels–Alder reaction to produce the hexacyclo[7.4.1.1.^{6,11}0.^{2,7}0.^{5,13}0.^{9,11}]pentadec-3-ene system (**9**) which has the iceane skeleton contained within it.

In recent years, the intramolecular Diels–Alder reaction[1] has become an effective method by which to synthesize a large variety of interesting bridged polycyclic species. In particular, ready entry into tri- and tetra-cyclic ring systems has been achieved by the reaction of α-pyrone,[2] cyclopentadienone acetals,[3] and thiophen dioxides[4] (**1**) with appropriately substituted bis-dienophiles (**2**) (Scheme 1).

This synthetic method exploits the reverse chelotropic reactions of intermediates of the type (**3**) to generate substituted cyclohexa-1,3-dienes (**4**). In the presence of a suitably disposed double bond, the resultant adduct (**4**) can then undergo a second, internal addition to produce a wide range of polycyclic compounds (**5**).

As part of a continuing interest in the development of design

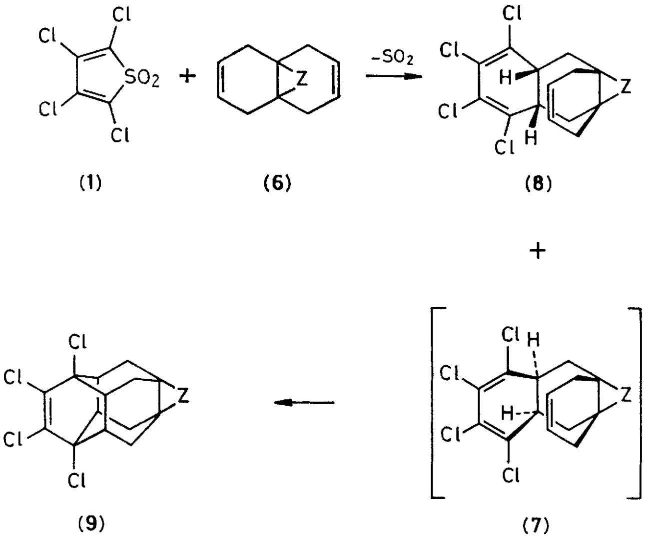


Scheme 1. X = H, Cl, or Ph;
Y = OCO, C(OMe)$_2$, CO, or SO$_2$;
Z = CH$_2$, O, or S. *m* = 0, 2, or 3; *n* = 0 or 2.

and methodology in the synthesis of strained ring compounds,[5] we have been able to adapt the above chemistry to the construction of polyfunctional iceane derivatives. In this communication, we report the preparation of the hexacyclic compounds (**9a, b**), in three steps from naphthalene (Scheme 2).

The most critical requirement for the formation of (**9**) was the control of the stereochemistry of the initial Diels–Alder reaction so that the second intramolecular cyclization could take place. The product (**9**) could result only by cycloaddition to (**6**) of the diene component on the side *anti* to the bridge Z. It was considered that the alternative mode of addition (*i.e. syn* to Z) would be less favoured the larger the size of Z.

In practice, the propellane (**6a**)[7] failed to react with either α-pyrone or the cyclopentadienone acetal (**1**) [X = Cl, Y = C(OMe)$_2$]. However, when an undiluted mixture of compound (**6a**) and the more reactive thiophen dioxide (**1**)[4b] (X = Cl, Y = SO$_2$) was heated at 130 °C for 4 h, sulphur dioxide was evolved and the polycycle (**9a**) and the triene (**8a**) were isolated in nearly quantitative yield, in a ratio of 2 : 3. Evidently, under these conditions, the triene (**7a**), which must be the precursor to the hexacyclic compound (**9a**), reacts further. When the reaction product was taken up in dichloromethane–light petroleum (b.p. 60—70 °C), compound (**9a**) crystallized out readily as colourless rhombic crystals, m.p. 242—243 °C. Its structure was shown to be 2,3,4,5,10,10-hexachloro-hexacyclo-[7.4.1.1.^{6,11}0.^{2,7}0.^{5,13}0.^{9,11}]pentadec-3-ene on the basis of the following data. Elemental analysis and peaks at 402, 404, 406, 408, and 410 in the mass spectrum were consistent with the molecular formula $C_{15}H_{12}Cl_6$. An absorption at 1603 cm^{-1} characteristic of the ClC=CCl moiety[4b] was present in the i.r. spectrum. The 60 MHz ^{1}H n.m.r. spectrum exhibited a broadened singlet (4H) at δ 2.35 superimposed on one resonance of an AB quartet (8H) at δ 2.22 and 1.48, J = 15 Hz. This spectrum is very similar to that of iceane itself.[8] Signals at 131.8 (s), 82.8 (s), 74.7 (s), 46.1 (d), 28.7 (s), and 24.6 (t) p.p.m. were observed in the combined 20.1 MHz broad band and off-resonance ^{13}C n.m.r. spectra which are in accordance with the symmetry of structure (**9a**).



Scheme 2. a; Z = CCl$_2$.
b; Z = CBr$_2$.

The isomeric compound (**8a**) (m.p. 148—149 °C) was isolated from the mother liquors of the crystallization of carbocycle (**9a**) after concentration and three recrystallizations, from light petroleum (b.p. 60—70 °C), of the residue. A resonance at 5.51 (br.s, 2H) in the ^{1}H n.m.r. and at 123.7 p.p.m. in the ^{13}C n.m.r. spectra clearly demonstrated the presence of an isolated double bond. In addition, the ^{13}C n.m.r. broad band and off-resonance data were consistent with the existence of eight types of carbon nuclei: 132.0 (s), 123.7 (s), 123.7 (d), 74.0 (s), 39.1 (d), 31.3 (t), 26.2 (t), and 25.5 (s) p.p.m. The triene (**8**) remained unchanged when heated up to 170 °C which indicates that it has the wrong stereochemistry for internal cyclization.

The reaction between the propellane (**6b**)[9] and tetrachlorothiophen dioxide afforded an equal amount of the triene (**8b**) and the cyclized compound (**9b**) (by ^{1}H n.m.r.). The increase in the amount of the desired product (**9b**) can be attributed to the greater directing effect of the larger *gem*-dibromomethylene group in the molecule (**6b**) compared to that of the smaller *gem*-dichloromethylene group in compound (**6a**). We are also investigating what effect the size of other groups (Z) has on the ratio of products of the type (**8**) and (**9**).

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