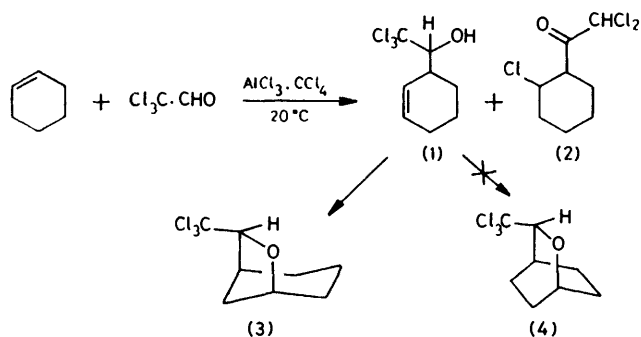


Ene Reactions: Evidence that Oxabicyclo[3.2.1]octanes, not Oxabicyclo[2.2.2]octanes, are formed from the AlCl_3 -catalysed Reactions of Chloral with Cyclohexene and the Thermal Addition of Chloral to Cyclohexa-1,3-diene

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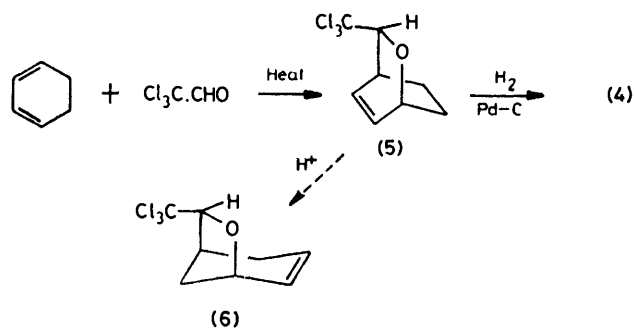
The oxabicyclo[3.2.1]octane (3) is formed in the AlCl_3 -promoted rearrangement of the ene adduct (1), itself obtained from the AlCl_3 -catalysed ene addition of chloral to cyclohexene. This structural assignment, initially made on the basis of mechanistic reasoning, is consistent with the chemical and spectroscopic evidence and is confirmed by an X-ray crystallographic study. Since this compound was previously assigned the oxabicyclo[2.2.2]octane structure (4) on the basis of an 'unambiguous' synthesis which utilised the 'Diels-Alder' addition of chloral to cyclohexa-1,3-diene, the diene reaction between carbonyl compounds and cyclohexa-1,3-dienes may not be reliable generally for the construction of oxabicyclo[2.2.2]octenes; indeed, the Diels-Alder adduct of chloral and cyclohexa-1,3-diene is obtained only when more than the usual precautions are taken in conducting the (sealed tube) reaction. Mechanisms for the various processes are discussed. Direct methods were employed in the determination of structure (3) from diffractometer data. Crystals are monoclinic, space group $P2_1/c$ with $Z = 4$ in a unit cell of dimensions: $a = 8.527(4)$, $b = 10.244(4)$, $c = 12.176(5)$ Å, $\beta = 111.12(3)^\circ$; the structure was refined by full-matrix least-squares to R 0.0925 for 1 092 independent reflections. The low m.p. of (3) necessitated the mounting of the crystal in a sealed capillary and this, together with its high solubility in most solvents, contributed to the difficulty in obtaining good quality single crystals for the X-ray study.

CYCLOHEXENE reacts with chloral in the presence of an aluminium chloride catalyst (5 mol %) to give the ene adduct (1)^{1,2} and a ketonic product (2).² Prolonged contact between the ene adduct and the catalyst results in the formation of a bicyclic ether and the same ether [hereafter called (X)] is formed, without isolation of the ene adduct, if the reaction is carried out using a higher catalyst concentration (>20 mol %).^{3,4} The formation of (1) and its rearrangement to (X) has previously been studied by Klimova *et al.*,¹ and Smushkevich *et al.*⁵ have reported (X) to be 3-trichloromethyl-2-oxabicyclo[2.2.2]octane (4) on the basis of an apparently unambiguous independent synthesis. Although this appeared to dispose of the problem, (4) was not the structure we anticipated either on mechanistic grounds or on the basis of expected thermodynamic stabilities. Conclusive evidence is now provided which shows that (X) is, in fact, 7-trichloromethyl-6-oxabicyclo[3.2.1]octane (3), and predominantly the *exo*-isomer.



Smushkevich *et al.*⁵ carried out a thermal reaction between cyclohexa-1,3-diene and chloral. The isolated product was assumed to be the Diels-Alder adduct 3-trichloromethyl-2-oxabicyclo[2.2.2]oct-5-ene (5) which

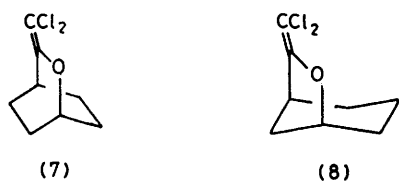
on hydrogenation gave a compound identical to (X). When we first repeated this work † the product from the Smushkevich reaction sequence proved to be not identical with (X), but several subsequent preparations gave only



material that was identical with (X). Because of this lack of consistency and of an available stock of authentic (4), an X-ray study of (X) was started. Meanwhile, by paying attention to the various possible variables in the thermal reaction of chloral with cyclohexa-1,3-diene, it was found that the Diels-Alder adduct (5) could be obtained by utilising *freshly* purified and distilled chloral, by degassing the contents of the reaction ampoule by the freeze-thaw procedure, and by carrying out the reactions *in vacuo*. Presumably, extra care is needed to exclude the presence of chloral hydrate and, therefore, prevent the subsequent appearance of HCl in the reaction medium. Hydrogenation of the adduct (5) thus obtained gave the compound (4) which was not identical in physical and spectroscopic properties with (X). Both (4) and (X) were separately subjected to reaction with sodamide in liquid ammonia (elimination

† The assistance of Mr. P. G. Roberts and Mr. A. T. Steel, who performed some of our preliminary experiments as part of their undergraduate project work, is warmly acknowledged.

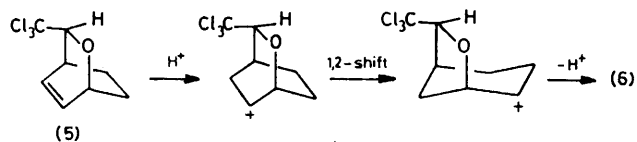
of HCl), to give respectively (7) and (8). These two compounds were clearly distinguishable by comparison of their ^{13}C n.m.r. spectra. The symmetry in (7) resulted in the production of only six discrete resonances, whereas in (8) separate signals for each of the eight



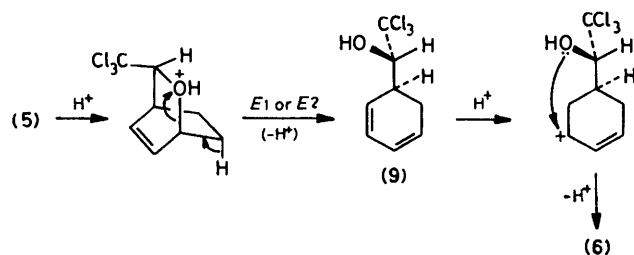
carbon atoms in the molecule were observed. This clearly establishes the oxabicyclo[3.2.1]octane skeleton for (8) and also, therefore, in its precursor (X) = (3). Subsequently, the X-ray structural studies (see below) provided confirmation of this assignment.

The course of the thermal reaction between cyclohexa-1,3-diene and chloral was studied in more detail by heating equimolar quantities of the two compounds at 130°C for periods of 30–45 h in ampoules sealed in air. In most cases a bicyclic ether, identical with that obtained by Smushkevich [*i.e.* (6)], was isolated along with an alcohol product. The relative proportions of the alcohol and (6) varied according to the reaction time and almost exclusive ether formation was observed in the 45-h reactions. When more rigorously purified reagents were employed, however, and the contents of the ampoule thoroughly degassed using the freeze-thaw procedure and the thermolysis conducted *in vacuo*, a different bicyclic ether [*i.e.* (5)] was obtained together with only traces of the alcohol. In a similar experiment the ampoule was opened after 24 h reaction time, the contents analysed by ^1H n.m.r. spectroscopy, and the ampoule resealed and heated for a further 18 h. The initial analysis showed exclusive formation of (5), but after the full 42 h the quantity of (5) had diminished appreciably and the products now comprised (6) and the alcohol.

It seems clear, therefore, that (6) is derived from (5), and is not formed by an independent route from cyclohexa-1,3-diene and chloral. Two simple mechanisms (Schemes 1 and 2) account for this basic transformation;



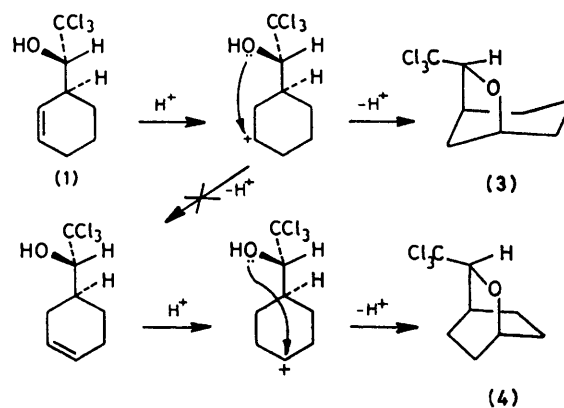
SCHEME 1



SCHEME 2

both require the presence of a protonic acid catalyst which, presumably, is HCl resulting from the partial hydrolysis of chloral at 130°C with the source of water being traces of chloral hydrate. We prefer Scheme 2 since it accounts for an alcohol intermediate (9) and the available evidence is consistent with this structure. Thus, isolation of the alcohol was possible and, although rapid deterioration of this compound prevented a full characterisation, the n.m.r. spectra could be obtained. The appearance in the ^{13}C n.m.r. spectrum of *four* olefinic carbon resonances, *each of doublet multiplicity* in the off-resonance spectrum, indicated a cyclohexa-1,3-diene rather than a -1,4-diene. A 1,4-diene, of course, would be the product expected if the alcohol were formed independently from the thermal ene addition of chloral to cyclohexa-1,3-diene.

The production of (3) = (X) from (1) in the presence of AlCl_3 is accounted for in Scheme 3, which essentially



SCHEME 3

utilises the final two steps of Scheme 2. The source of the necessary protonic acid is probably from the equilibrium interaction of the ene adduct [(1) = (ROH)] with AlCl_3 [equation (1)]. The fact that the oxabicyclo[3.2.1]octane is formed rather than the oxabicyclo[2.2.2]octane is reflected, in mechanistic terms, by the economy



of the transformation (1) \rightarrow (3) in comparison with (1) \rightarrow (4). When coupled with the expected greater thermodynamic stability of the bicyclo[3.2.1]octane over the bicyclo[2.2.2]octane in a process that is likely to be subject to thermodynamic control, the observed outcome of the reaction is not particularly surprising. More noteworthy is the failure, under normal conditions, to produce the Diels–Alder adduct (5) from the thermal addition of chloral to cyclohexa-1,3-diene. In view of the relative ease of the transformation (5) \rightarrow (6) in the presence of trace acid, it seems that the use of the Diels–Alder route to make structural correlations in the area of oxabicyclo[2.2.2]octanes should be applied with some caution.

We have already shown that the AlCl_3 -catalysed ene addition of chloral to cyclohexene is stereoselective, with

the (*RR*) + (*SS*) enantiomers predominating in the diastereoisomeric mixture of adducts (1).⁴ Ring closure according to Scheme 3 should not result in epimerization at either of the chiral centres and, accordingly, it follows that the predominant stereoisomer of structure (3) should have the Cl₃C group in the *exo*-configuration. The molecular structure, as defined by the *X*-ray crystallographic results, show this conclusion to be correct. The fact that the 7-trichloromethyl-6-oxabicyclo[3.2.1]octane prepared from cyclohexa-1,3-diene and chloral *via* the compounds (5) and (6) was identical in all respects with the material (3) obtained by rearrangement of (1), indicates that in (5) the Cl₃C group is *syn* to the double bond. In turn, this requires that the Diels-Alder reaction of chloral with cyclohexa-1,3-diene occurs predominantly or exclusively by *endo*-addition.

Finally, in view of the results discussed above, it seems highly likely that the bicyclic ethers obtained from the AlCl₃-promoted rearrangement of chloral-cycloalkene ene adducts⁴ all have the (*n* + 3)-oxabicyclo[*n*.2.1]-alkane structure.

Crystallography.—Oscillation and Weissenberg photographs were taken about the *c* axis of a colourless crystal of 7-trichloromethyl-6-oxabicyclo[3.2.1]octane (3) measuring *ca.* 0.35 × 0.35 × 0.35 mm and mounted in a capillary tube, and *X*-ray intensity data were obtained for the crystal mounted on an Enraf-Nonius CAD4 automatic four-circle diffractometer by use of Cu-*K*_α radiation. A 1/3 θ-ω scan up to the value θ 66° was employed. A total of 1 853 reflections were measured, of which 1 092 had *I* > 3σ(*I*) and were considered observed.

Crystal Data.—C₈H₁₁Cl₃O, *M* = 229.5. Monoclinic, space group *P*2₁*c*, *a* = 8.527(4), *b* = 10.244(4), *c* = 12.176(5) Å, β = 111.12(3)°, *U* = 992.2 Å³, *D*_c = 1.536 g cm⁻³, *Z* = 4, *F*(000) = 472, Cu-*K*_α radiation, λ = 1.541 78 Å, μ(Cu-*K*_α) = 79.33 cm⁻¹.

Structure Analysis.—The multiresolution program MULTAN⁶ yielded a result with a high figure of merit of 1.2113. This solution was used in the *E* map calculation and the co-ordinates of the three strongest peaks in the map proved to be the chlorine atoms while the fourth peak was oxygen. Four of the next five peaks proved to be carbon atoms and the remaining four carbons were identified from slightly lower intensity peaks. Five cycles of full-matrix least-squares refinement on the twelve atomic positions, with isotropic temperature factors, led to convergence at *R* 0.150. In subsequent refinements, atomic temperature factors were allowed to vary anisotropically, and after two such cycles the agreement factor had converged to *R* 0.108. A Fourier-difference synthesis revealed the presence of a number of peaks from which all eleven hydrogen atom positions could be identified. Using fixed co-ordinates and an isotropic temperature factor *U*_{iso} 0.06 for the hydrogen atoms, while temperature factors of other atoms were allowed to vary anisotropically, further cycles of full-matrix refinement reduced *R* to 0.0979. The hydrogen atom co-ordinates and *U*_{iso} were then allowed to vary

and a weighting scheme, based on a Chebyshev polynomial, was finally introduced which reduced *R* to 0.0925.

Final atomic positions are listed in Table 1. Observed and calculated structure factors and thermal parameters are listed in Supplementary Publication No. SUP 22991 (14 pp.).†

TABLE 1
Atomic co-ordinates, with standard deviations in parentheses

| | <i>x/a</i> | <i>y/b</i> | <i>z/c</i> |
|---|------------|------------|------------|
| (a) Non-hydrogen atoms (× 10 ⁴) | | | |
| C(1) | 3 520(10) | 1 566(8) | 464(7) |
| C(2) | 1 760(10) | 1 660(10) | 470(10) |
| C(3) | 1 050(10) | 3 070(10) | 240(10) |
| C(4) | 1 570(10) | 3 800(10) | -663(9) |
| C(5) | 3 330(10) | 3 483(9) | -571(8) |
| O(6) | 4 486(7) | 3 731(5) | 626(5) |
| C(7) | 4 620(10) | 2 585(8) | 1 312(8) |
| C(8) | 3 540(10) | 2 030(10) | -719(8) |
| C(9) | 6 440(10) | 2 247(8) | 1 970(7) |
| Cl(1) | 6 504(3) | 957(2) | 2 954(2) |
| Cl(2) | 7 547(3) | 1 761(3) | 1 058(2) |
| Cl(3) | 7 501(3) | 3 607(2) | 2 816(2) |
| (b) Hydrogen atoms (× 10 ³) | | | |
| H(1) | 400(10) | 70(10) | 70(8) |
| H(2A) | 100(20) | 120(10) | 0(10) |
| H(2B) | 180(20) | 150(20) | 140(10) |
| H(3A) | 160(10) | 350(10) | 93(9) |
| H(3B) | -20(10) | 306(7) | 10(6) |
| H(4A) | 80(30) | 350(20) | -140(20) |
| H(4B) | 140(20) | 490(10) | -50(10) |
| H(5) | 410(20) | 400(10) | -100(10) |
| H(7) | 410(10) | 286(8) | 191(8) |
| H(8A) | 250(20) | 170(10) | -130(10) |
| H(8B) | 460(10) | 191(9) | -75(8) |

Computation was achieved with the aid of the program CRYSTALS⁷ and the molecular structure diagrams used the plotting program PLUTO.⁸

DISCUSSION

Bond lengths and angles of the main atoms in the atomic skeleton of the ether (3) are listed in Table 2. The atom numbering convention, which follows IUPAC rules, is given in Figure 1, a perspective view of the molecule. Hydrogen atoms (Table 1) are numbered according to the carbon atoms to which they are attached and the label H(A) in every case indicates an axial disposition with respect to the six-membered ring. The arrangement of molecules in the unit cell is shown in Figure 2.

The ether (3) possesses a low melting point and is rather soluble in organic solvents. Thus, difficulty was experienced in growing suitable crystals for the *X*-ray diffraction study and the selected crystal was therefore not of as high a quality as we would have liked. The inevitable effect on the precision of the diffraction data has resulted in relatively large standard deviations for the hydrogen atom co-ordinates. Accordingly, we prefer to invoke few bond length and angle comparisons when these involve hydrogen atoms.

† For details of Supplementary Publications see Notice to Authors No. 7, in *J. Chem. Soc., Perkin Trans. 1*, 1980, Index issue.

TABLE 2

Molecular geometry, with standard deviations in parentheses

(a) Interatomic distances (Å)

| | | | |
|------------|---------|------------|----------|
| C(1)–C(2) | 1.51(1) | C(9)–Cl(3) | 1.78(1) |
| C(1)–C(7) | 1.53(1) | C(1)–H(1) | 0.95(10) |
| C(1)–C(8) | 1.52(1) | C(2)–H(2A) | 0.79(13) |
| C(2)–C(3) | 1.54(1) | C(2)–H(2B) | 1.12(17) |
| C(3)–C(4) | 1.52(1) | C(3)–H(3A) | 0.91(10) |
| C(4)–C(5) | 1.50(1) | C(3)–H(3B) | 0.98(8) |
| C(5)–O(6) | 1.46(1) | C(4)–H(4A) | 0.99(21) |
| C(5)–C(8) | 1.52(1) | C(4)–H(4B) | 1.14(15) |
| O(6)–C(7) | 1.42(1) | C(5)–H(5) | 1.08(13) |
| C(7)–C(9) | 1.51(1) | C(7)–H(7) | 1.00(9) |
| C(9)–Cl(1) | 1.77(1) | C(8)–H(8A) | 0.97(14) |
| C(9)–Cl(2) | 1.77(1) | C(8)–H(8B) | 0.93(10) |

(b) Interatomic angles (°)

| | | | |
|------------------|----------|------------------|---------|
| C(2)–C(1)–C(7) | 108.7(8) | H(2B)–C(2)–C(1) | 109(8) |
| C(2)–C(1)–C(8) | 109.2(8) | H(2B)–C(2)–C(3) | 101(9) |
| C(7)–C(1)–C(8) | 102.4(7) | H(2A)–C(2)–H(2B) | 107(11) |
| C(1)–C(2)–C(3) | 112.9(8) | H(3A)–C(3)–C(2) | 105(6) |
| C(2)–C(3)–C(4) | 112.9(9) | H(3A)–C(3)–C(4) | 104(6) |
| C(3)–C(4)–C(5) | 112.6(8) | H(3B)–C(3)–C(2) | 110(4) |
| C(4)–C(5)–O(6) | 109.7(8) | H(3B)–C(3)–C(4) | 116(4) |
| C(4)–C(5)–C(8) | 111.1(8) | H(3A)–C(3)–H(3B) | 108(8) |
| O(6)–C(5)–C(8) | 102.9(7) | H(4A)–C(4)–C(3) | 103(12) |
| C(5)–O(6)–C(7) | 108.9(6) | H(4A)–C(4)–C(5) | 110(12) |
| O(6)–C(7)–C(1) | 105.5(7) | H(4B)–C(4)–C(3) | 104(7) |
| O(6)–C(7)–C(9) | 110.5(6) | H(4B)–C(4)–C(5) | 111(7) |
| C(1)–C(7)–C(9) | 117.6(7) | H(4A)–C(4)–H(4B) | 116(14) |
| C(1)–C(8)–C(5) | 98.8(7) | H(5)–C(5)–C(4) | 127(7) |
| C(7)–C(9)–Cl(1) | 107.8(6) | H(5)–C(5)–O(6) | 95(7) |
| C(7)–C(9)–Cl(2) | 114.3(6) | H(5)–C(5)–C(8) | 108(7) |
| C(7)–C(9)–Cl(3) | 109.9(6) | H(7)–C(7)–C(1) | 112(5) |
| Cl(1)–C(9)–Cl(2) | 108.8(5) | H(7)–C(7)–O(6) | 104(5) |
| Cl(1)–C(9)–Cl(3) | 108.0(5) | H(7)–C(7)–C(9) | 107(5) |
| Cl(2)–C(9)–Cl(3) | 108.0(4) | H(8A)–C(8)–C(1) | 102(8) |
| H(1)–C(1)–C(2) | 110(6) | H(8A)–C(8)–C(5) | 106(8) |
| H(1)–C(1)–C(7) | 110(6) | H(8B)–C(8)–C(1) | 109(6) |
| H(1)–C(1)–C(8) | 116(6) | H(8B)–C(8)–C(5) | 107(6) |
| H(2A)–C(2)–C(1) | 120(9) | H(8A)–C(8)–H(8B) | 130(10) |
| H(2A)–C(2)–C(3) | 105(9) | | |

Relatively few diffraction studies have been reported for the bicyclo[3.2.1]octane system, but reasonable comparisons can be made with 2,2,7,7-tetraphenyl-6-oxabicyclo[3.2.1]octan-5-ol⁹ (TPOBOO) and the carbocycle (–)-2-*exo*-aminobicyclo[3.2.1]octane-2-carboxylic acid monohydrate¹⁰ (ABOC). The chair-like conform-

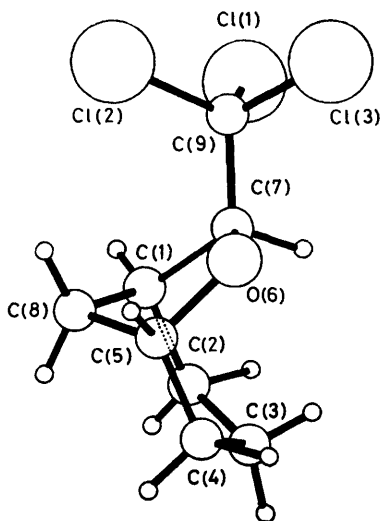


FIGURE 1 Molecular structure of the ether (3)

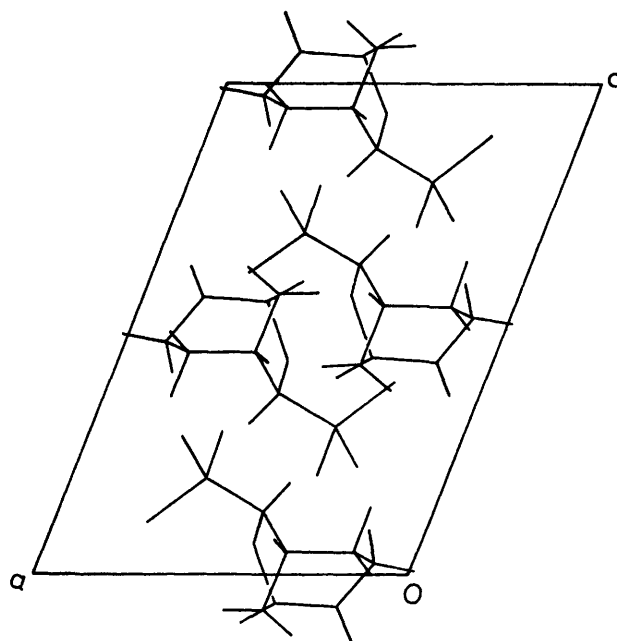


FIGURE 2 Arrangement of molecules in the unit cell of (3)

ation of the six-membered ring of (3) (see Figure 1) is distorted. The torsion angles (Table 3) for this ring about the C(1)–C(2) axis are -58.6 , C(2)–C(3) 37.8 , C(3)–C(4) -36.7 , C(4)–C(5) 57.9 , C(5)–C(8) -73.3 , and C(8)–C(1) 72.8° , in contrast with the expected torsion angle of $\pm 54.7^\circ$ for cyclohexane.¹¹ However, they compare fairly closely with the corresponding values for ABOC. The C(1), C(2), C(4), and C(5) atoms of this ring form the plane of equation $0.043x + 0.505y + 0.863z = 1.378$ (orthogonal co-ordinates in Å) from which the distances of the relevant atoms are C(1) 0.005, C(2) -0.005 , C(3) 0.475, C(4) 0.005, C(5) -0.006 , and C(8) -0.890 Å. There is fair agreement with the analogous values for both TPOBOO and ABOC. The one-atom bridge angle C(1)–C(8)–C(5) of 98.8° is expectedly small, and is within experimental error of the TPOBOO angle (99.4°) and significantly smaller than the analogous angle in ABOC (102.2°) indicating, possibly, one consequence of oxygen rather than carbon at position 6 in the molecular systems.

The ether (3) also comprises five- and seven-membered rings. The five-membered ring has an almost untwisted conformation (*cf.* TPOBOO and C(1), C(7), O(6), and C(5) form the plane of equation $0.925x - 0.290y -$

TABLE 3

Torsion angles (°) for the main atoms of ether (3)

| | | | |
|---------------------|---------|----------------------|---------|
| C(7)–C(1)–C(2)–C(3) | 52.3 | C(4)–C(5)–O(6)–C(7) | 88.5 |
| C(8)–C(1)–C(2)–C(3) | -58.6 | C(8)–C(5)–O(6)–C(7) | -29.8 |
| C(2)–C(1)–C(7)–O(6) | -89.6 | C(4)–C(5)–C(8)–C(1) | -73.3 |
| C(2)–C(1)–C(7)–C(9) | 146.7 | O(6)–C(5)–C(8)–C(1) | 44.1 |
| C(8)–C(1)–C(7)–O(6) | 25.9 | C(5)–O(6)–C(7)–C(1) | 2.3 |
| C(8)–C(1)–C(7)–C(9) | -97.8 | C(5)–O(6)–C(7)–C(9) | 130.4 |
| C(2)–C(1)–C(8)–C(5) | 72.8 | C(1)–C(7)–C(9)–Cl(1) | -66.8 |
| C(7)–C(1)–C(8)–C(5) | -42.3 | C(1)–C(7)–C(9)–Cl(2) | 54.2 |
| C(1)–C(2)–C(3)–C(4) | 37.8 | C(1)–C(7)–C(9)–Cl(3) | 175.8 |
| C(2)–C(3)–C(4)–C(5) | -36.7 | O(6)–C(7)–C(9)–Cl(1) | 172.0 |
| C(3)–C(4)–C(5)–O(6) | -55.3 | O(6)–C(7)–C(9)–Cl(2) | -67.0 |
| C(3)–C(4)–C(5)–C(8) | 57.9 | O(6)–C(7)–C(9)–Cl(3) | 54.6 |

$0.246z = 1.985$ with atomic distances from this plane of C(1) 0.008, C(7) -0.013, O(6) 0.013, C(5) -0.008, and C(8) 0.691 Å. These values correlate rather well with those for ABOC and indicate that the twist conformation noted for TPOBOO is not due to the presence of the O(6) atom, but rather it arises from steric compression for which the 7,7-diphenyl substituents are responsible. Hence, the torsion angles about C(1)-C(7) 25.9, C(7)-O(6) 2.3, O(6)-C(5) -29.8, C(5)-C(8) 44.1, and C(8)-C(1) -42.3° of the five-membered ring are mainly within $\pm 2^\circ$ of the ABOC values, but differ, by more than 16° in some cases, from the TPOBOO figures. Likewise, the torsion angles for the seven-membered ring are also in good agreement with the ABOC values, the largest discrepancy being for C(7)-C(1)-C(2)-C(3) 52.3° which is 4.6° smaller than for the carbocycle.

The strain in the oxabicyclo[3.2.1]octane system of (3) is shown up by the bond lengths and angles (Table 2). The one-atom bridge angle (98.8° , referred to above) is appreciably smaller than the two-atom bridge angles (108.9 and 105.5°) which, in turn, are smaller than the three-atom bridge angles (112.9 , 112.9 , and 112.6°). The strain in the angles C(1)-C(8)-C(5), C(7)-C(1)-C(8), and O(6)-C(5)-C(8), which have values much less than the tetrahedral value, appears to be relieved by the more or less uniform widening of the angles of the three-atom bridge (mean 112.8°). In the case of both ABOC and TPOBOO, the effect of the strain is relieved mainly by the widening of the C(2)-C(3)-C(4) bond angles to, respectively, 115.4 and 116.1° , and this appears in some measure to be due to the different substitution pattern of those molecules. Indeed, the present molecule (3) is probably the best model available for deducing the molecular dimensions of 6-oxabicyclo[3.2.1]octane itself, for which crystallographic data are not available.

The n.m.r. spectra of the oxabicyclo-[3.2.1]- and -[2.2.2]-octanes of this study showed various characteristic features which deserve specific mention. In the ^1H n.m.r. spectra of both (3) and (6), high field (δ 1.5—1.8) doublets (J 11 Hz) were observed which were absent in the spectra of (4) and (5). This signal is assigned to H(8A) which experiences geminal coupling. Vicinal coupling with the bridgehead protons H(1) and H(5) is very small because the dihedral angles H(8A)-C(8)-C(1)-H(1) and H(8A)-C(8)-C(5)-H(5), respectively (standard deviation) $90(9)$ and $-111(10)^\circ$, are *ca.* 90° . The large chemical-shift difference of the two hydrogen atoms H(8A) and H(8B) is further emphasised by the ^{13}C n.m.r. spectrum, since off-resonance decoupling resulted in a doublet of doublets, rather than a triplet, signal for C(8). Additionally, all three of the bicyclo[3.2.1]octanes (3), (6), and (8) gave multiplets (overlapping doublet of doublets or triplets) for the bridgehead OCH protons [*i.e.* H(5) for (3)], whereas the corresponding H atoms in the bicyclo[2.2.2]octanes (4), (5), and (7) showed complex signals with little or no resolution. Again, in the bicyclo[3.2.1]octanes, one or more of the vicinal hydrogen atoms is largely prevented from coupling with the bridgehead hydrogen-atoms by the

near 90° torsion angles, so there is a reduction in signal complexity in these cases. No useful correlations emerged from comparisons with published n.m.r. data on 6-oxabicyclo[3.2.1]octanes because of the appreciable effects of the various substituents present in these other systems.

EXPERIMENTAL

I.r. spectra were recorded using a Perkin-Elmer 710B spectrophotometer, ^1H n.m.r. spectra using a JEOL JNM-MH-100 spectrometer, and ^{13}C n.m.r. spectra were obtained using either a JEOL JNM-PS-100 or a Bruker WM 250 PFT spectrometer. Shifts are relative to tetramethylsilane as internal standard in CDCl_3 solution; all values are in p.p.m. Melting points were determined on a Kofler block and are uncorrected.

7-Trichloromethyl-6-oxabicyclo[3.2.1]octane (3) by Rearrangement of (1).—To a stirred solution of chloral (7.38 g, 50 mmol) in carbon tetrachloride (30 ml) under an atmosphere of nitrogen, was added finely powdered, anhydrous aluminium chloride (Fluka, 0.33 g, 5 mol%). When the catalyst had dissolved (*ca.* 5 min), cyclohexene (4.1 g, 50 mmol) was added dropwise, the temperature being maintained at 20 — 25°C by external cooling with ice. The solution was stirred for a further 40 h, diluted with ether (100 ml), and extracted with saturated, aqueous sodium hydrogen carbonate (2×50 ml) and water (50 ml). The ethereal solution was dried (Na_2SO_4), filtered, and the solvents removed under reduced pressure to give a mixture of (1) and (2) containing traces of (3). The crude product was redissolved in dry carbon tetrachloride (30 ml) and aluminium chloride (0.5 g) was added to the stirred solution. After 20 h, an identical work-up to that mentioned above afforded a mixture of (2) and (3).

Complete removal of (2) was effected under the conditions of a Grignard reaction. Magnesium turnings (2 g) in dry ether (20 ml) were activated by the addition of a few drops of ethyl iodide and a solution of the above crude product in dry ether (10 ml) was then added dropwise, with stirring. After 6 h the precipitate of magnesium salts and the solution were decanted from excess of magnesium, which was washed with ether, and the mixture was treated with 2M hydrochloric acid (70 ml) until a clear, orange solution was obtained. The combined organic layer was washed with water (3×30 ml), dried (Na_2SO_4), filtered, and the ether removed under reduced pressure. Distillation of the residue gave a colourless liquid, b.p. 78 — 81°C at 1 mmHg, which rapidly darkened and solidified on standing overnight. Recrystallisation from methanol afforded the *product* (3) as a colourless solid (3.7 g, 32%), m.p. 46 — 47°C (Found: C, 41.6; H, 4.9; Cl, 46.1. $\text{C}_8\text{H}_{11}\text{Cl}_3\text{O}$ requires C, 41.86; H, 4.83; Cl, 46.34%); i.r. ν_{max} (KBr) 2950, 2875, 1100, 1070 (C—O), 820, 800, and 770 (C—Cl) cm^{-1} ; δ 4.64 (1 H, m, 5-H), 4.40 (1 H, br s, 7-H), 2.70 (1 H, complex m, 1-H), 2.6—2.4 (1 H, complex m, 8B-H), 2.0—1.6 (6 H, complex m, 2-, 3-, 4-H), and 1.48 (1 H, d, J 11 Hz, 8A-H); δ_{C} 101.28 (s, 9-C), 92.45 (d, 7-C), 79.53 (d, 5-C), 39.18 (d, 1-C), 36.49 (d of d, 8-C), 31.29 (t), 30.47 (t), and 18.65 (t) ($3 \times \text{CH}_2$ ring).

A reaction was also carried out using 20 mol % AlCl_3 in the first stage. The crude product, isolated after 18 h, was a mixture of (2) and (3). Pure (3) was obtained as above.

7-Trichloromethyl-6-oxabicyclo[3.2.1]oct-3-ene (6).—A mixture of cyclohexa-1,3-diene (1.6 g, 0.02 mol) and chloral (2.93 g, 0.02 mol), containing quinol (40 mg) to inhibit poly-

merization, was heated in a small Carius tube (sealed under air) for 30 h at 130 °C. The brown liquid was distilled under reduced pressure and the main fraction, a colourless oil, b.p. 78–84 °C at 2 mmHg, which contained two major products (6) and (9), was chromatographed on a Kieselgel G pressure column using chloroform as the developing solvent. The faster-moving component (R_F 0.55), was a solid identified as the *bicyclic ether* (6) (0.58 g, 13%), m.p. 49–50.5 °C (Found: C, 42.5; H, 4.0. $C_8H_9Cl_3O$ requires C, 42.23; H, 3.99%); i.r. ν_{max} (KBr) 3 040 (=CH), 2 980, 2 900, 2 840, 1 630 (C=C), 1 080 (C–O), 800, 775 (CCl), and 700 (*cis*-RCH=CHR', CH o.o.p. def.) cm^{-1} ; δ 5.95 (1 H, complex m, =CH), 5.66 (1 H, complex m, =CH), 4.52 (1 H, m, CHO bridgehead), 4.24 [1 H, br s, CH(CCl₃)O], 2.80 (1 H, complex m, CH bridgehead), 2.7–2.1 (3 H, complex m, ring CH₂ + bridge CH₂, equatorial H), and 1.80 (1 H, d, J 11 Hz, bridge CH₂, axial H); δ_C 130.00 (d, =CH), 128.36 (d, =CH), 100.41 (s, CCl₃), 93.10 [d, CH(CCl₃)O], 74.27 (d, CHO bridgehead), 38.65 (d, CH bridgehead), 35.03 (t, CH₂), and 32.98 (t, CH₂).

2,2,2-Trichloro-1-cyclohexa-2,4-dienylethanol (9).—The slower-moving component from the above chromatography (R_F 0.4), a colourless liquid which decomposed on standing, was identified as the *alcohol* (9) (0.36 g, 8%); i.r. ν_{max} (film) 3 450 (OH), 3 040 (=CH), 2 920, 2 870, 2 820, 1 100 (C–O), 810 (CCl), and 690 (*cis*-RCH=CHR', CH o.o.p. def.) cm^{-1} ; δ 6.1–5.6 (4 H, complex m, =CH), 3.9 [1 H, d of d, J 7 Hz, J_2 3 Hz, collapses to d on D₂O shake, CH(OH)(CCl₃)], 3.3 (1 H, d, J 7 Hz, disappears on D₂O shake, OH), 3.16 [1 H, complex m, CHCH(OH)(CCl₃)], and 2.5–2.3 (2 H, m, ring CH₂); δ_C 127.48 (d, =CH), 126.43 (d, =CH), 124.03 (d, =CH), 123.51 (d, =CH), 103.27 (s, CCl₃), 85.96 [d, CH(OH)(CCl₃)], 34.97 [d, CHCH(OH)(CCl₃)], and 29.06 (t, CH₂).

An identical experiment, but with a longer reaction time (45 h) gave 1.2 g (27%) of the ether (6) after purification by column chromatography; (9) was present in only trace quantities.

3-Trichloromethyl-2-oxabicyclo[2.2.2]oct-5-ene (5).—Freshly distilled cyclohexa-1,3-diene (1.6 g, 0.02 mol) and freshly purified chloral (2.93 g, 0.02 mol) were placed, together with quinol (40 mg), in a small Carius tube equipped with a side arm and a high vacuum Teflon screw-valve. The mixture was frozen in liquid nitrogen, the tube evacuated, sealed, and then allowed to warm up to room temperature. Reliquification was accompanied by the degassing of the reagents. The whole procedure was repeated several times and the tube was finally sealed *in vacuo* and heated in a metal block at 125 °C for 26 h. The pale yellow liquid was distilled *in vacuo* and the colourless liquid, b.p. 84–90 °C at 1.5 mmHg, solidified on standing overnight. Recrystallisation from methanol gave the *product* (5) as a white solid, m.p. 54–55 °C (1.35 g, 30%), which was stable at room temperature (Found: C, 42.0; H, 4.0. $C_8H_9Cl_3O$ requires C, 42.23; H, 3.99%); i.r. ν_{max} (KBr) 3 060 (=CH), 2 940, 2 870, 1 620w (C=C), 1 045 (C–O), 790, 775 (CCl), and 690 (*cis*-RCH=CHR', CH o.o.p. def.) cm^{-1} ; δ 6.6–6.3 (2 H, complex m, =CH), 4.66 (1 H, complex m, CHO bridgehead), 4.31 [1 H, br s, CH(CCl₃)O], 3.27 (1 H, complex m, CH bridgehead), and 2.3–1.3 (4 H, complex m, 2 × CH₂ ring); δ_C 133.05 (d, =CH), 132.08 (d, =CH), 100.83 (s, CCl₃), 86.42 [d, CH(CCl₃)O], 68.42 (d, CHO bridgehead), 32.43 (d, CH bridgehead), 24.58 (t, CH₂), and 23.11 (t, CH₂).

An additional experiment was carried out in which the degassed reagents were heated for 24 h, the tube opened to remove a sample for analysis and then resealed, and heating continued for a further 18 h. Exclusive formation of (5)

was observed after 24 h, but further heating (after possible incursion of moisture) resulted in conversion of (5) into (9) and (6).

7-Trichloromethyl-6-oxabicyclo[3.2.1]octane (3) *from Hydrogenation of* (6).—Compound (6) (0.35 g) in ethanol (10 ml) was hydrogenated at atmospheric pressure and room temperature using 10% Pd–C (0.04 g); the theoretical quantity of hydrogen was absorbed in 10 min. Conventional work-up gave the *product* (0.32 g; 91%) which was identical in every respect to the material prepared by rearrangement of (1).

3-Trichloromethyl-2-oxabicyclo[2.2.2]octane (4).—Hydrogenation of (5) (0.9 g), as for (6), followed by conventional work-up and Kugelrohr distillation at 126 °C and 10 mmHg gave the *product* (0.5 g); i.r. ν_{max} (film) 2 960, 2 875, 1 060 (C–O), 790, and 765 (CCl) cm^{-1} ; δ 4.30 [1 H, br s, CH(CCl₃)O], 4.08 (1 H, complex m, CHO bridgehead), and 2.15–1.3 (9 H, complex m, CH bridgehead + 4 × CH₂ ring); δ_C 101.52 (s, CCl₃), 87.95 [d, CH(CCl₃)O], 68.24 (d, CHO bridgehead), 27.89 (t, CH₂), 27.08 (d, CH bridgehead), 25.96 (t, CH₂), 25.79 (t, CH₂), and 19.53 (t, CH₂).

7-Dichloromethylene-6-oxabicyclo[3.2.1]octane (8).—In a lagged flask, protected by a soda-lime tube, was prepared a solution of sodium amide in liquid ammonia from sodium (0.55 g, 0.024 mol), liquid ammonia (100 ml), and ferric nitrate (25 mg); (3) (0.5 g, 2.2 × 10⁻³ mol) was then added and the mixture stirred magnetically for 7 h, adding liquid ammonia as necessary. The reaction was quenched by the addition of ammonium chloride (1.3 g, 0.024 mol) and the ammonia then allowed to evaporate overnight. The residue was treated with water (75 ml) and then extracted with ether (2 × 50 ml, and 20 ml). The ether extracts were dried (Na₂SO₄), filtered, and the solvent removed under reduced pressure. The *bicyclic ether* (8) (0.35 g, 83%) was isolated by distillation of the oily residue under reduced pressure, b.p. 48–50 °C at 1 mmHg (Found: C, 49.85; H, 5.6. $C_8H_{10}Cl_2O$ requires C, 49.77; H, 5.22%); i.r. ν_{max} (film) 2 940, 2 860, 1 660 (C=C), 1 185, 1 085, (C–O), 905, and 825 (CCl) cm^{-1} ; δ 4.80 (1 H, m, CHO bridgehead), 3.20 (1 H, m, CH bridgehead), and 2.3–1.3 (8 H, complex m, 4 × CH₂); δ_C 156.60 (s, OC=), 92.57 (s, =CCl₂), 81.34 (d, CHO bridgehead), 39.88 (d, CH bridgehead), 38.65 (t, CH₂), 30.00 (t, CH₂), 27.60 (t, CH₂), and 18.65 (t, CH₂).

3-Dichloromethylene-2-oxabicyclo[2.2.2]octane (7).—Dehydrochlorination of (4) (0.33 g, 1.4 × 10⁻³ mol) by reaction with sodium amide in liquid ammonia was achieved as described for (8). The *product* was a white solid; recrystallisation from methanol afforded the *pure ether* (0.22 g, 79%), m.p. 64.5–66 °C (Found: C, 50.1; H, 5.4. $C_8H_{10}Cl_2O$ requires C, 49.77; H, 5.22%); i.r. ν_{max} (KBr) 2 950, 2 875, 1 640 (C=C), 1 235, 1 015 (C–O), and 915 cm^{-1} ; δ 4.48 (1 H, complex m, CHO bridgehead), 3.05 (1 H, complex m, CH bridgehead), and 2.2–1.5 (8 H, complex m, 4 × CH₂); δ_C 154.58 (s, OC=), 93.68 (s, =CCl₂), 72.01 (d, CHO bridgehead), 28.88 (d, CH bridgehead), 26.05 (t, 2 × CH₂), and 23.49 (t, 2 × CH₂).

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REFERENCES

- 1 E. I. Klimova, N. D. Antonova, and Yu. A. Arbuзов, *Zh. Org. Khim.*, 1969, **5**, 1348.

² G. B. Gill, S. J. Parrott, and B. Wallace, *J. Chem. Soc., Chem. Commun.*, 1978, 655.

³ G. B. Gill and B. Wallace, *J. Chem. Soc., Chem. Commun.* 1977, 380.

⁴ G. B. Gill, K. Marrison, S. J. Parrott, and B. Wallace, *Tetrahedron Lett.*, 1979, 4867.

⁵ Yu. I. Smushkevich, V. M. Belov, B. V. Kleev, and A. Ya. Akimova, *Zh. Org. Khim.*, 1967, **3**, 1036.

⁶ G. Germain, P. Main, and M. M. Wolfson, *Acta Crystallogr., Sect. A*, 1971, **27**, 368.

⁷ W. R. Carruthers, personal communication to T. J. King, Nottingham University.

⁸ Cambridge Data Centre, W. D. S. Motherwell, personal communication to T. J. King, Nottingham University.

⁹ C. H. Wei and S. W. Hawkinson, *Acta Crystallogr., Sect. B*, 1978, **34**, 170.

¹⁰ K. K. Chacko, S. K. Bhattacharjee, R. Zand, and R. Water, *Acta Crystallogr., Sect. B*, 1978, **34**, 147.

¹¹ M. Bixon and S. Lifson, *Tetrahedron*, 1967, **23**, 769.