

The (sp^2)C—Br lengths are significantly shorter than the (sp^3)C—Br lengths in the tribromo diketone. There are two different types of C—O bonds, (sp^2)C—O and (sp^3)C—O, the bond lengths of the former being about 0.1 Å shorter than those of the latter.

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CSIR, for collecting the intensity data, and Dr L. P. L. Piacenza for supplying the sample.

References

- International Tables for X-ray Crystallography* (1962). Vol. III, pp. 202, 203, 206, 216. Birmingham: Kynoch Press.
SOMMERVILLE, P. & LAING, M. (1978). *Acta Cryst.* **B34**, 670–671.

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1,9-Epoxy-2,8,10-tribromo-9-ethoxy-7,11-diphenylspiro[5.5]undec-1(2)-ene*

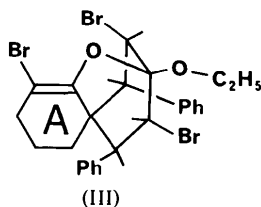
BY POLLY SOMMERVILLE AND MICHAEL LAING

Chemistry Department, University of Natal, Durban 4001, South Africa

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Abstract. $C_{25}O_2H_{25}Br_3$, $M_r = 597$, monoclinic, $P2_1/c$, $a = 8.27$ (1), $b = 15.94$ (2), $c = 17.49$ (2) Å, $\beta = 96.2$ (1)°, $V = 2291$ Å³, $D_c = 1.74$, $D_m = 1.72$ (2) g cm⁻³, $Z = 4$, $\mu(\text{Mo } K\alpha) = 56.5$ cm⁻¹. $R = 0.066$ for 1681 observed data; three Br and 12 phenyl C atoms anisotropic, 22 H atoms included. This compound is the third product of the bromination of 7,11-diphenylspiro[5.5]undecane-1,9-dione. O(1) has bridged to C(9) where O(2) has reacted with ethanol to form a ketal adjacent to a vinylic bromide ether grouping. Ring *B* is a boat with the phenyl at C(7)-*endo* (pseudo-axial) *trans* to Br at C(8)-*exo* (pseudo-equatorial), and the phenyl at C(11)-*exo* (pseudo-equatorial) *trans* to Br at C(10)-*endo* (pseudo-axial).

Introduction. Bromination of the spirodiketone 7,11-diphenylspiro[5.5]undecane-1,9-dione in chloroform and ethanol yields a tribromide (III) as well as the dibromide (II) (Sommerville & Laing, 1978*b*). It was obvious that its structure differed from that of the tribromodiketone (I) obtained from bromination in glacial acetic acid (Sommerville & Laing, 1978*a*) but



* Bromides of a Diphenyl Spiro Diketone. III.

Table 1. *Final fractional atomic coordinates* ($\times 10^4$) *and isotropic thermal parameters, with standard deviations in parentheses*

| | <i>x</i> | <i>y</i> | <i>z</i> | <i>B</i> (Å ²) |
|-------|------------|-----------|-----------|----------------------------|
| Br(1) | 8584 (2) | 5915 (1) | 3830 (1) | * |
| Br(2) | 11650 (2) | 3139 (1) | 1267 (1) | * |
| Br(3) | 6112 (2) | 4493 (1) | 1088 (1) | * |
| O(1) | 9112 (11) | 4807 (6) | 2495 (5) | 3.70 (21) |
| O(2) | 9720 (11) | 4839 (6) | 1255 (5) | 3.80 (22) |
| C(1) | 8752 (16) | 4357 (8) | 3109 (7) | 2.88 (30) |
| C(2) | 8509 (16) | 4691 (9) | 3751 (8) | 3.65 (33) |
| C(3) | 8117 (18) | 4282 (9) | 4475 (8) | 4.26 (36) |
| C(4) | 8616 (19) | 3354 (10) | 4426 (9) | 5.35 (41) |
| C(5) | 8041 (17) | 2983 (9) | 3671 (8) | 4.26 (34) |
| C(6) | 8602 (16) | 3441 (9) | 2973 (7) | 3.23 (32) |
| C(7) | 7296 (16) | 3329 (8) | 2274 (7) | 2.98 (31) |
| C(8) | 7871 (16) | 3805 (9) | 1584 (8) | 3.50 (33) |
| C(9) | 9381 (16) | 4321 (8) | 1840 (7) | 3.09 (31) |
| C(10) | 10767 (17) | 3722 (9) | 2137 (8) | 3.65 (33) |
| C(11) | 10277 (16) | 3097 (9) | 2727 (7) | 3.18 (31) |
| C(12) | 11585 (16) | 2962 (9) | 3371 (8) | * |
| C(13) | 11976 (17) | 2135 (9) | 3625 (8) | * |
| C(14) | 13108 (19) | 2007 (10) | 4248 (10) | * |
| C(15) | 13865 (18) | 2646 (12) | 4640 (10) | * |
| C(16) | 13528 (18) | 3469 (11) | 4404 (10) | * |
| C(17) | 12398 (17) | 3603 (10) | 3758 (8) | * |
| C(18) | 6746 (16) | 2442 (9) | 2093 (8) | * |
| C(19) | 5438 (16) | 2115 (9) | 2446 (8) | * |
| C(20) | 4984 (18) | 1261 (10) | 2356 (9) | * |
| C(21) | 5780 (18) | 768 (9) | 1871 (9) | * |
| C(22) | 7046 (18) | 1054 (10) | 1521 (9) | * |
| C(23) | 7541 (17) | 1895 (9) | 1604 (8) | * |
| C(24) | 11191 (17) | 5361 (9) | 1382 (8) | 4.05 (36) |
| C(25) | 11432 (20) | 5756 (10) | 596 (9) | 5.54 (42) |

* Anisotropic thermal parameters for these atoms have been deposited.

Table 2. *Interatomic distances (Å) and angles (°) and least-squares planes*(a) Selected intramolecular bond lengths (± 0.02 Å)

| | | | |
|-------------|------|-------------|------|
| C(1)—C(2) | 1.28 | Br(1)—C(2) | 1.96 |
| C(2)—C(3) | 1.49 | Br(3)—C(8) | 1.95 |
| C(3)—C(4) | 1.54 | Br(2)—C(10) | 1.99 |
| C(4)—C(5) | 1.48 | C(9)—O(2) | 1.37 |
| C(5)—C(6) | 1.54 | O(2)—C(24) | 1.47 |
| C(6)—C(1) | 1.48 | C(24)—C(25) | 1.54 |
| C(6)—C(7) | 1.55 | C(7)—C(18) | 1.51 |
| C(7)—C(8) | 1.54 | C(11)—C(12) | 1.49 |
| C(8)—C(9) | 1.52 | O(1)—C(1) | 1.35 |
| C(9)—C(10) | 1.54 | O(1)—C(9) | 1.42 |
| C(10)—C(11) | 1.52 | | |
| C(11)—C(6) | 1.59 | | |

(b) Selected bond angles ($\pm 2^\circ$)

| | | | |
|-----------------|-----|-------------------|-----|
| C(1)—C(2)—C(3) | 129 | C(8)—C(9)—C(10) | 109 |
| C(2)—C(3)—C(4) | 107 | C(9)—C(10)—C(11) | 113 |
| C(3)—C(4)—C(5) | 112 | C(10)—C(11)—C(6) | 105 |
| C(4)—C(5)—C(6) | 115 | C(11)—C(6)—C(7) | 107 |
| C(5)—C(6)—C(1) | 112 | C(6)—C(7)—C(18) | 116 |
| C(6)—C(1)—C(2) | 122 | C(8)—C(7)—C(18) | 114 |
| Br(1)—C(2)—C(1) | 118 | C(6)—C(11)—C(12) | 115 |
| Br(1)—C(2)—C(3) | 113 | C(10)—C(11)—C(12) | 113 |
| C(1)—O(1)—C(9) | 115 | Br(3)—C(8)—C(7) | 110 |
| O(1)—C(1)—C(2) | 123 | Br(3)—C(8)—C(9) | 112 |
| O(1)—C(1)—C(6) | 115 | O(2)—C(9)—C(8) | 110 |
| C(1)—C(6)—C(7) | 106 | O(2)—C(9)—C(10) | 115 |
| C(1)—C(6)—C(11) | 109 | O(1)—C(9)—O(2) | 110 |
| C(5)—C(6)—C(7) | 109 | O(1)—C(9)—C(8) | 110 |
| C(5)—C(6)—C(11) | 113 | O(1)—C(9)—C(10) | 104 |
| C(6)—C(7)—C(8) | 108 | C(9)—O(2)—C(24) | 118 |
| C(7)—C(8)—C(9) | 110 | O(2)—C(24)—C(25) | 106 |
| | | Br(2)—C(10)—C(9) | 111 |
| | | Br(2)—C(10)—C(11) | 111 |

(c) Least-squares planes of the form $Ax + By + Cz = D$, where A , B and C are the direction cosines of the normal to the plane referred to the orthogonal axes a , b , c^* . The deviations in Å of the most relevant atoms from the planes are given in square brackets.

| | A | B | C | D |
|--|--------|--------|-------|------|
| Plane 1: C(6), C(7), C(8), C(9), C(10), C(11) | | | | |
| | -0.119 | 0.820 | 0.559 | 6.09 |
| [C(6) 0.52, C(7) -0.19, C(8) -0.31, C(9) 0.47, C(10) -0.15, C(11) -0.34, Br(3) 0.27, Br(2) -1.87, O(1) 1.78, O(2) 0.53, C(12) 0.00, C(18) -1.48] | | | | |
| Plane 2: C(1), C(2), C(5), C(6) | | | | |
| | 0.925 | -0.139 | 0.354 | 7.12 |
| [C(1) -0.02, C(2) 0.01, C(5) -0.01, C(6) 0.01, C(3) 0.12, C(4) 0.68] | | | | |
| Plane 3: C(1), C(2), C(3), C(6), Br(1), O(1) | | | | |
| | 0.948 | -0.073 | 0.309 | 7.46 |
| [C(1) 0.02, C(2) 0.02, C(3) 0.02, C(6) -0.04, Br(1) -0.04, O(1) 0.03, C(4) 0.50, C(5) -0.18] | | | | |

chemical methods did not lead to an unequivocal structure. For this reason, a crystallographic analysis was performed.

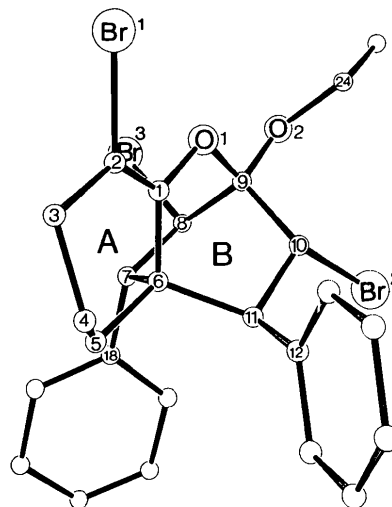


Fig. 1. A projection of the molecule showing the numbering system. Ring A is a sofa, but it is $C(4)$ which is out of the plane of the other five atoms and not $C(5)$ as was found in (II) (Sommerville & Laing, 1978*b*).

Suitable crystals were obtained from a mixture of methanol and CH_2Cl_2 . Data were collected from a crystal $0.6 \times 0.3 \times 0.15$ mm on a Philips four-circle diffractometer with graphite-monochromated $\text{Mo } K\alpha$ radiation ($\lambda = 0.7107$ Å) for θ between 3 and 20° . The ω - 2θ scan mode was used with a scan width of 1.0° ; each peak was counted for 25 s, and the background counting time was 25 s for each peak. Of the 2229 reflexions measured, 1681 were classed as observed with $I > 1.65\sigma(I)$. Three reflexions were used as standards and their intensities measured every hour; no decomposition was detected. The intensities were corrected for Lorentz and polarization effects only. The appearance of the temperature-sharpened Patterson map was unusual. Three large peaks near the origin showed that there were three Br atoms in the molecule; yet only one large peak (height of 500 units *vs* 1800 for the origin peak) was present on the Harker section at $u\frac{1}{2}w$. This peak results from the chance overlapping of the three Harker peaks which is caused by the following approximate relationship between the x and z coordinates of the Br atoms:

$$x_1 - x_3 = 0.25, \quad x_2 - x_3 = 0.5, \quad x_2 - x_1 = 0.25$$

$$z_1 - z_3 = 0.25, \quad z_2 - z_3 = 0.0, \quad z_1 - z_2 = 0.25.$$

The coordinates of the lighter atoms were obtained from the subsequent Fourier maps. The structure was refined by block-diagonal least squares with the three Br and 12 phenyl C atoms anisotropic; all H atoms (except those of the methyl of the *O*-ethyl group) were included in the structure factor calculations. Weighting was proportional to $1/\sigma(F)$; scattering factors for neutral atoms were used (*International Tables for X-ray Crystallography*, 1962), that of Br was corrected

for anomalous dispersion. The final R was 0.066 for 1681 observed data.* Final positional parameters are given in Table 1, with estimated standard deviations in parentheses. Bond lengths and angles are in Table 2. The numbering system and stereochemistry are shown in Fig. 1.

Discussion. A rearrangement, different from that which formed the dibromide (II) (Sommerville & Laing, 1978*b*), has occurred yielding a 1,9-ether bridge and a double bond between C(1) and C(2). O(2) has reacted with the ethanol thus forming a ketal with O(1) of the vinyl bromide system of ring *A*. Ring *B* is forced into a boat conformation and two bromines have substituted α to C(9). The conformation of the substituents on ring *B* is: phenyl at C(7)-*endo* [torsion angle C(1)–C(6)–C(7)–C(18) 171°], *trans* to Br(3) at C(8)-*exo* [C(18)–C(7)–C(8)–Br(3) 97°]; phenyl at C(11)-*exo* [C(1)–C(6)–C(11)–C(12) 79°], *trans* to Br(2) at C(10)-*endo* [C(12)–C(11)–C(10)–Br(2) 95°]. If ring *B* were an ideal boat, the *endo*–*exo* torsion angle would be 120°; the value of about 95° found in (III) reflects a twisting about bonds C(7)–C(8) and C(10)–C(11) to relieve *endo*...*endo* strains between the Br at C(10) and the phenyl ring at C(7) [torsion angles C(6)–C(7)–C(8)–C(9) 8° and C(9)–C(10)–C(11)–C(6) 13°]. Thus the *endo* groups have moved out and away, while the *exo* groups have moved down and in.

The six-membered O-rings impose little strain on the molecule (as shown by the coplanarity of the atoms of

the vinyl system). A model shows that the framework is rigid, and only C(4) is movable to any extent. This mobility is evident in its *B* value which is considerably larger than the *B* of any other atom in the spiro skeleton. Ring *A* is best described as a 'sofa', C(1), C(2), C(6) and C(5) being coplanar within 0.01 Å with C(3) only 0.12 Å out of the plane. C(4) is 0.68 Å away from the plane. C(4) is bent towards the phenyl ring at C(11), presumably so that the H atom on C(5), *syn* to C(11), is bent down and away from C(12) of the phenyl ring. If ring *A* takes the alternative sofa conformation with C(4) folded away from the *exo* phenyl ring, the H atom on C(5) is forced close to C(12) thus generating intramolecular strain. It is possible that the particular 'sofa' conformation adopted by ring *A* is a result of the distortion of ring *B*. Examination of a Dreiding model of (III) shows that if Br(2) and C(18) are forced *inwards*, then the conformational strains resulting from torsion about the bonds C(10)–C(11) and C(7)–C(8) in ring *B* cause ring *A* to 'flip' so that C(4) now points away from the phenyl ring on C(11).

We thank the South African Council for Scientific and Industrial Research for generous financial support, Dr G. Gafner, National Physical Research Laboratory, CSIR, for collecting the intensities, and Dr L. P. L. Piacenza (University of Durban–Westville) for his interest and for supplying the sample.

References

- International Tables for X-ray Crystallography* (1962). Vol. III, pp. 202, 203, 206, 216. Birmingham: Kynoch Press.
SOMMERVILLE, P. & LAING, M. (1978*a*). *Acta Cryst.* **B34**, 670–671.
SOMMERVILLE, P. & LAING, M. (1978*b*). *Acta Cryst.* **B34**, 672–674.

Acta Cryst. (1978). **B34**, 676–679

1,9-Epoxy-2,8,10-tribromo-9-methoxy-7,11-diphenylspiro[5.5]undec-1(2)-ene*

BY POLLY SOMMERVILLE AND MICHAEL LAING

Chemistry Department, University of Natal, Durban 4001, South Africa

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Abstract. C₂₄O₂H₂₃Br₃, $M_r = 583$, monoclinic, $P2_1/c$, $a = 8.58$ (1), $b = 15.84$ (2), $c = 16.62$ (2) Å, $\beta = 96.6$ (1)°, $V = 2244$ Å³, $D_c = 1.73$, $D_m = 1.71$ (2) g cm⁻³, $Z = 4$, $\mu(\text{Mo } K\alpha) = 57.5$ cm⁻¹. $R = 0.054$ for

2007 observed data; three Br and 12 phenyl C atoms anisotropic, 20 H atoms included. This compound is the fourth product of the bromination of 7,11-diphenylspiro[5.5]undecane-1,9-dione and is the *O*-methyl analogue of the *O*-ethyl tribromo ketal compound described previously [Sommerville & Laing, *Acta*

* Bromides of a Diphenyl Spiro Diketone. IV.