# 1,10-Epoxy-2,8-dibromo-9-ethoxy-7,11-diphenylspiro[5.5]undeca-1(2),8(9)-diene*

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**Abstract.** $C_{25}O_2H_{24}Br_2$, $M_r = 516$, triclinic, $P\bar{1}$, $a = 11\cdot45$ (1), $b = 12\cdot23$ (1), $c = 10\cdot05$ (1) Å, $\alpha = 117\cdot6$ (1), $\beta = 79\cdot1$ (1), $\gamma = 116\cdot6$ (1)°, $V = 1115$ Å$^3$, $D_c = 1\cdot54$, $D_m = 1\cdot53$ (2) g cm$^{-3}$, $Z = 2$, $\mu$(Mo $K\alpha$) = $38\cdot8$ cm$^{-1}$. $R = 0\cdot057$ for 2200 observed data; two Br and 12 phenyl C atoms anisotropic, 24 H atoms included. Bond rearrangements have taken place. O(1) has bridged to C(10) while O(2) has reacted with ethanol to form an ethoxy group, simultaneously generating two vinylic bromide ethers.

**Introduction.** When the spiro diketone 7,11-diphenylspiro[5.5]undecane-1,9-dione is brominated in chloroform and ethanol, a dibromide (II) is obtained. A crystallographic study of (II) was undertaken at the request of Dr L. P. L. Piacenza (University of Durban–Westville) to determine its structure and compare it with the related tribromo diketone derivative (Sommerville & Laing, 1978).



(II)
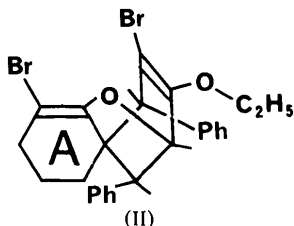
Suitable crystals were obtained from methanol and $CH_2Cl_2$. Data were collected from a crystal $0\cdot3 \times 0\cdot3 \times 0\cdot3$ mm on a Philips four-circle diffractometer with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0\cdot7107$ Å) for $\theta$ between 3 and 22°. The $\omega$–$2\theta$ scan mode and a scan width of $1\cdot2°$ were used; each peak was counted for 30 s, and the background counting time was 30 s for each peak. Of the 2725 reflexions measured, 2200 were classed as observed [$I > 1\cdot65\sigma(I)$]. 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. A temperature-sharpened Patterson map showed that there were only two Br atoms, and subsequent Fourier maps gave the coordinates of the lighter atoms. The structure was refined by block-diagonal least squares with the two Br and 12 phenyl C

atoms anisotropic; all H atoms (excluding those of the $CH_3$ of the O-ethyl group) were included in the structure factor calculations. Weighting was proportional to $1/\sigma(F)$. Scattering factors were for neutral atoms (*International Tables for X-ray Crystallography*, 1962); that of Br was corrected for anomalous dispersion. The final $R$ was $0\cdot057$ for 2200 observed data.† Final positional parameters are in Table 1 with

Table 1. *Final fractional atomic coordinates* ($\times 10^4$) *and isotropic thermal parameters for the non-hydrogen atoms*

Standard deviations are in parentheses.

| | $x$ | $y$ | $z$ | $B(\text{Å}^2)$ |
|---|---|---|---|---|
| Br(1) | −834 (1) | 9200 (1) | 7236 (1) | * |
| Br(2) | 1126 (1) | 4428 (1) | 5818 (1) | * |
| O(1) | 972 (4) | 8705 (5) | 8560 (5) | 3·50 (10) |
| O(2) | 937 (5) | 6256 (5) | 9144 (6) | 4·71 (12) |
| C(1) | 1340 (6) | 8729 (7) | 7179 (8) | 2·90 (14) |
| C(2) | 753 (7) | 9003 (7) | 6463 (8) | 3·29 (15) |
| C(3) | 1246 (7) | 9274 (8) | 5123 (9) | 4·16 (17) |
| C(4) | 2492 (7) | 9027 (8) | 4554 (9) | 4·09 (17) |
| C(5) | 3366 (7) | 9429 (7) | 5832 (8) | 3·33 (16) |
| C(6) | 2642 (6) | 8619 (7) | 6740 (8) | 2·85 (14) |
| C(7) | 2410 (7) | 7067 (7) | 5848 (8) | 3·25 (15) |
| C(8) | 1733 (7) | 6355 (7) | 6844 (8) | 3·41 (16) |
| C(9) | 1529 (7) | 6939 (7) | 8250 (8) | 3·37 (16) |
| C(10) | 1955 (7) | 8468 (7) | 9001 (8) | 3·50 (16) |
| C(11) | 3212 (6) | 9141 (7) | 8301 (8) | 2·93 (14) |
| C(12) | 3907 (7) | 10656 (7) | 9131 (8) | * |
| C(13) | 3273 (8) | 11501 (8) | 9910 (9) | * |
| C(14) | 4014 (9) | 12921 (9) | 10630 (9) | * |
| C(15) | 5348 (8) | 13478 (8) | 10516 (9) | * |
| C(16) | 5970 (7) | 12636 (8) | 9731 (9) | * |
| C(17) | 5270 (7) | 11251 (7) | 9046 (8) | * |
| C(18) | 3693 (6) | 6913 (7) | 5223 (8) | * |
| C(19) | 4077 (7) | 6839 (8) | 3805 (8) | * |
| C(20) | 5269 (8) | 6797 (8) | 3264 (9) | * |
| C(21) | 6066 (8) | 6775 (8) | 4125 (9) | * |
| C(22) | 5665 (8) | 6807 (8) | 5519 (9) | * |
| C(23) | 4476 (7) | 6860 (8) | 6066 (8) | * |
| C(24) | −165 (12) | 6528 (12) | 10129 (14) | 9·83 (34) |
| C(25) | −1241 (13) | 5848 (14) | 9115 (15) | 11·52 (40) |

* Anisotropic thermal parameters for these atoms have been deposited.

Table 2. *Interatomic distances* (Å), *angles* (°), *torsion angles* (°) *and least-squares planes*

Selected intramolecular bond lengths (±0·02 Å)

| | | | | |
|---|---|---|---|---|
| C(1)–C(2) | 1·30 | | C(10)–C(11) | 1·53 |
| C(2)–C(3) | 1·48 | | C(11)–C(6) | 1·54 |
| C(3)–C(4) | 1·54 | | Br(1)–C(2) | 1·91 |
| C(4)–C(5) | 1·53 | | Br(2)–C(8) | 1·91 |
| C(5)–C(6) | 1·52 | | C(9)–O(2) | 1·39 |
| C(6)–C(1) | 1·52 | | O(2)–C(24) | 1·51 |
| C(6)–C(7) | 1·59 | | C(24)–C(25) | 1·42 |
| C(7)–C(8) | 1·51 | | C(7)–C(18) | 1·54 |
| C(8)–C(9) | 1·29 | | C(11)–C(12) | 1·50 |
| C(9)–C(10) | 1·52 | | O(1)–C(1) | 1·38 |
| | | | O(1)–C(10) | 1·47 |

Selected bond angles (±2°)

| | | | | |
|---|---|---|---|---|
| C(1)–C(2)–C(3) | 126 | | C(5)–C(6)–C(7) | 113 |
| C(2)–C(3)–C(4) | 111 | | C(5)–C(6)–C(11) | 118 |
| C(3)–C(4)–C(5) | 113 | | C(6)–C(7)–C(8) | 109 |
| C(4)–C(5)–C(6) | 111 | | C(7)–C(8)–C(9) | 125 |
| C(5)–C(6)–C(1) | 108 | | C(8)–C(9)–C(10) | 119 |
| C(6)–C(1)–C(2) | 124 | | C(9)–C(10)–C(11) | 110 |
| Br(1)–C(2)–C(1) | 119 | | C(10)–C(11)–C(6) | 98 |
| Br(1)–C(2)–C(3) | 115 | | C(11)–C(6)–C(7) | 107 |
| C(1)–O(1)–C(10) | 106 | | C(6)–C(7)–C(18) | 112 |
| O(1)–C(1)–C(2) | 124 | | C(8)–C(7)–C(18) | 113 |
| O(1)–C(1)–C(6) | 110 | | C(6)–C(11)–C(12) | 115 |
| C(1)–C(6)–C(7) | 110 | | C(10)–C(11)–C(12) | 116 |
| C(1)–C(6)–C(11) | 100 | | Br(2)–C(8)–C(9) | 121 |
| | | | Br(2)–C(8)–C(7) | 114 |

| | |
|---|---|
| O(2)–C(9)–C(8) | 124 |
| O(2)–C(9)–C(10) | 117 |
| O(1)–C(10)–C(9) | 106 |
| O(1)–C(10)–C(11) | 104 |
| C(9)–O(2)–C(24) | 118 |
| O(2)–C(24)–C(25) | 104 |

Torsion angles in vinyl systems

| | | | |
|---|---|---|---|
| O(1)–C(1)–C(2)–Br(1) | 7 | C(3)–C(2)–C(1)–C(6) | 1 |
| O(2)–C(9)–C(8)–Br(2) | 4 | C(7)–C(8)–C(9)–C(10) | 2 |

Atoms defining the least-squares planes and, in square brackets, deviations (Å) of atoms from them

Plane 1: C(6), C(7), C(8), C(9), C(10), C(11)

[C(6) –0·36, C(7) 0·07, C(8) 0·10, C(9) –0·02, C(10) –0·27, C(11) 0·48, Br(2) 0·31, O(1) –1·68, O(2) 0·06, C(12) 0·58, C(18) 1·40]

Plane 2: C(1), C(2), C(5), C(6)

[C(1) 0·11, C(2) –0·06, C(5) 0·05, C(6) –0·10, C(3) –0·48, C(4) –0·83]

Plane 3: C(1), C(2), C(3), C(6), Br(1), O(1)

[C(1) 0·06, C(2) 0·04, C(3) –0·06, C(6) 0·01, Br(1) 0·01, O(1) –0·07, C(4) 0·03, C(5) –0·64]

Plane 4: C(7), C(8), C(9), C(10), Br(2), O(2)

[C(7) –0·03, C(8) –0·01, C(9) 0·00, C(10) 0·04, Br(2) 0·04, O(2) –0·03, C(6) 0·19, C(11) –0·75]

estimated standard deviations in parentheses. Some bond lengths and angles are given in Table 2. The numbering and stereochemistry are given in Fig. 1.
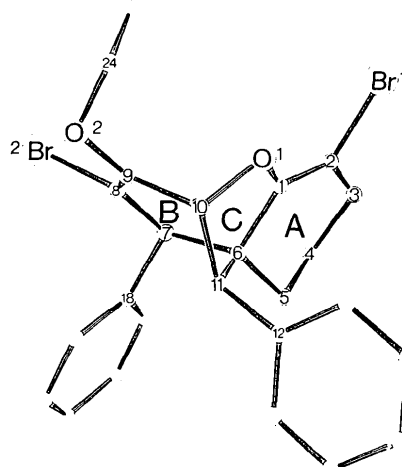


Fig. 1. A projection of the molecule showing the numbering system. C(1)–C(2) and C(8)–C(9) are double bonds. Rings *A* and *B* are 'sofas', with atoms C(5) and C(11) respectively being out of the mean plane of the other five atoms.

**Discussion.** Although the spiro undecane skeleton is retained, two unexpected bond rearrangements have taken place (see Fig. 1). O(1) has formed a bridge to C(10), simultaneously creating a double bond between C(1) and C(2). O(2) of the keto group on ring *B* has reacted with ethanol in the solvent to yield an ethyl ether and a double bond between C(8) and C(9). The molecule thus contains two chemically inert vinylic bromide ether groups. The formation of an epoxy bridge between C(1) and C(10) is not unreasonable because the O(1)···C(10) separation was very short in (I), the related tribromo diketone (Sommerville & Laing, 1978).

Ring *B* and the five-membered O-containing ring, *C*, are rigid and slightly strained (as shown by the deviations from coplanarity of the atoms of the vinyl system: see Table 2). The configurations of the phenyl groups on ring *B* are: phenyl at C(7), pseudo-axial [torsion angle C(1)–C(6)–C(7)–C(18) 173°]; phenyl at C(11), pseudo-equatorial [C(1)–C(6)–C(11)–C(12) 84°]. Ring *B* is slightly more puckered than ring *A* (see Table 2); in both cases, it is the C atom *β* to the C–O group which is about 0·7 Å out of the mean plane of the six atoms of the vinylic system.

The bridging of O(1) to C(10) causes a twisting of the rigid and planar O(1)–C(1)–C(2)–C(3) vinyl system about the bond C(1)–C(6) with the result that C(5) cannot be coplanar with the six atoms of the vinyl system. Nevertheless, it is still part of the rigid framework, and only C(4) is potentially mobile, *i.e.* able to cause a change in the conformation of ring *A* by pseudorotation about bonds C(5)–C(4) and C(3)–C(4).

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.

### 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.

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

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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)°, $V = 2291$ Å$^3$, $D_c = 1·74$, $D_m = 1·72$ (2) g cm$^{-3}$, $Z = 4$, $\mu$(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-diphenyl-spiro[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



(III)
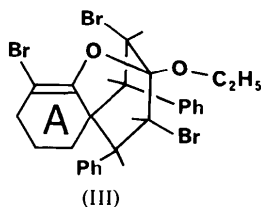
* Bromides of a Diphenyl Spiro Diketone. III.

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

|        | $x$        | $y$       | $z$       | $B$ (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.