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endo,endo,exo-2,6,10-Tribromo-*exo*-5-methoxy-13-oxa-*trans*-bicyclo[7.3.1]tridecane

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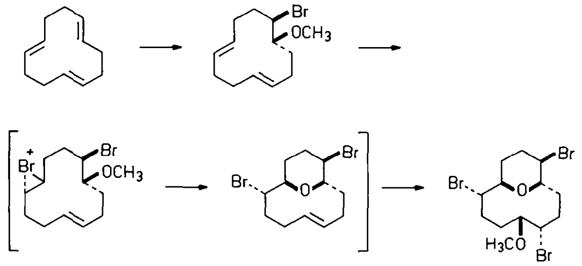
Abstract. $C_{13}H_{21}Br_3O_2$, $M_r = 449\cdot04$, orthorhombic, $P2_12_12_1$, $a = 6\cdot739\,(1)$, $b = 12\cdot270\,(3)$, $c = 19\cdot231\,(2)$ Å, $V = 1590\cdot3$ Å^3, $Z = 4$, $D_x = 1\cdot88$ Mg m^{-3}, λ(Mo $K\alpha$) = $0\cdot71073$ Å, $\mu = 7\cdot53$ mm^{-1}, $F(000) = 880$, $T = 296$ K, final $R = 0\cdot028$ for 1085 unique observed reflections. The title compound was obtained, *via* transannular *O*-heterocyclization, in the methoxybromination of (*E,E,E*)-cyclododeca-1,5,9-triene. The pyran ring has a chair and the oxacyclodecane ring a distorted boat–chair–boat conformation.

Introduction. Two types of transannular cyclizations have been observed in the methoxybromination of cycloalkadienes and cycloalkatrienes with medium- and large-sized rings. Transannular π-cyclizations with formation of bicyclo[*n*.4.0]alkanes have been found for nine-, ten- and eleven-membered cycloalka-1,5-dienes (Haufe & Mühlstädt, 1979), whereas under similar conditions, transannular *O*-heterocyclizations with formation of oxabicyclic compounds have been found for eight-, twelve- and thirteen-membered 1,5-dienes and 1,5,9-trienes (Graefe, Haufe & Mühlstädt, 1976; Haufe, 1984; Haufe & Mühlstädt, 1984; Rissanen, Valkonen & Haufe, 1987). The reaction pathway is determined by the ring size, the configuration of the double bonds and the conformation of the unsaturated carbocycle.

The reaction of (*E,E,E*)-cyclododeca-1,5,9-triene with *N*-bromosuccinimide and methanol yields a mixture of simple *anti*-1,2-addition products, two oxatricyclic compounds and one oxabicyclic compound. The structure of the latter compound, a tribromomethoxy-13-oxabicyclo[7.3.1]tridecane, could not be determined completely from spectroscopic data (Haufe, 1987).

To establish the exact composition, configuration and conformation of the compound, we determined its crystal and molecular structure. The title compound is presumably formed by the following mechanism.



The first step, a typical methoxybromination, yields the *cis*-1,2-addition product. Repeated attack of the electrophilic bromonium species leads to a cation from which, through transannular *O*-participation of the methoxy group and subsequent demethylation, *endo,exo*-2,10-dibromo-13-oxabicyclo[7.3.1]tridec-(*E*)-5-ene is formed. This compound could not be isolated. The *E* double bond of the oxacyclodecene system, which contains a medium-sized ring, is likely more strained and hence more reactive than the *E* double bonds in the starting triene. Thus another attack of a brominium species from the *endo* side and nucleophilic attack of methanol on carbon C(5) can be presumed to take place, leading to the final product, *endo,endo,exo*-2,6,10-tribromo-*exo*-5-methoxy-13-oxa-*trans*-bicyclo[7.3.1]tridecane.

Experimental. Colourless crystals, synthesized according to Haufe (1987), $0\cdot15 \times 0\cdot12 \times 0\cdot25$ mm, mounted on a glass fibre, Enraf–Nonius CAD-4 diffractometer, graphite-monochromatized Mo $K\alpha$, ω–2θ method, lattice parameters from 25 reflections with $6 < \theta < 12°$, two standard reflections measured every hour, linear 15% loss of intensity; corrected, 2675 independent reflections (h: $0\rightarrow9$, k: $0\rightarrow17$, l: $0\rightarrow26$) with $\theta < 30°$,

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Table 1. *Fractional coordinates and equivalent isotropic temperature factors with e.s.d.'s in parentheses*

$$B_{eq} = \tfrac{4}{3}[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)].$$

	x	*y*	*z*	B_{eq} (Å^2)
Br(1)	0·5682 (2)	0·52969 (9)	0·68550 (5)	5·29 (2)
Br(2)	1·3335 (2)	0·68967 (9)	0·88986 (6)	5·76 (2)
Br(3)	0·7702 (2)	0·16895 (7)	0·92430 (5)	4·67 (2)
O(1)	0·8744 (8)	0·4081 (4)	0·8516 (2)	3·1 (1)
O(2)	0·943 (1)	0·7845 (4)	0·8448 (3)	4·6 (1)
C(1)	0·701 (1)	0·4409 (6)	0·8132 (4)	2·9 (2)
C(2)	0·779 (1)	0·4620 (7)	0·7397 (4)	3·3 (2)
C(3)	0·972 (1)	0·5308 (7)	0·7346 (4)	3·5 (2)
C(4)	0·964 (2)	0·6493 (7)	0·7595 (4)	4·2 (2)
C(5)	0·934 (1)	0·6696 (6)	0·8371 (4)	3·6 (2)
C(6)	1·082 (1)	0·6062 (7)	0·8843 (4)	3·9 (2)
C(7)	1·013 (1)	0·5805 (7)	0·9572 (4)	3·9 (2)
C(8)	0·822 (1)	0·5094 (7)	0·9613 (4)	3·9 (2)
C(9)	0·849 (1)	0·3970 (6)	0·9254 (4)	3·3 (2)
C(10)	0·676 (1)	0·3198 (7)	0·9406 (4)	3·7 (2)
C(11)	0·492 (1)	0·3420 (8)	0·8972 (4)	4·3 (2)
C(12)	0·547 (1)	0·3554 (7)	0·8196 (4)	3·7 (2)
C(13)	0·843 (2)	0·8297 (8)	0·9004 (5)	7·0 (3)

Table 2. *Bond distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

Br(1)—C(2)	1·950 (8)	C(3)—C(4)	1·532 (12)
Br(2)—C(6)	1·984 (9)	C(4)—C(5)	1·526 (11)
Br(3)—C(10)	1·981 (8)	C(5)—C(6)	1·554 (12)
O(1)—C(1)	1·437 (9)	C(6)—C(7)	1·511 (12)
O(1)—C(9)	1·437 (9)	C(7)—C(8)	1·561 (13)
O(2)—C(5)	1·420 (9)	C(8)—C(9)	1·554 (11)
O(2)—C(13)	1·379 (12)	C(9)—C(10)	1·529 (12)
C(1)—C(2)	1·529 (10)	C(10)—C(11)	1·521 (12)
C(1)—C(12)	1·483 (11)	C(11)—C(12)	1·545 (11)
C(2)—C(3)	1·549 (12)		

Br(1)—C(2)—C(3)	110·1 (5)	Br(1)—C(2)—C(1)	108·4 (5)
Br(2)—C(6)—C(7)	108·6 (6)	Br(2)—C(6)—C(5)	108·6 (5)
Br(3)—C(10)—C(11)	109·9 (6)	Br(3)—C(10)—C(9)	107·8 (5)
O(1)—C(1)—C(2)	104·0 (6)	O(1)—C(1)—C(12)	109·2 (6)
O(1)—C(9)—C(8)	111·6 (6)	O(1)—C(9)—C(10)	109·7 (6)
O(2)—C(5)—C(4)	105·0 (6)	O(2)—C(5)—C(6)	114·2 (7)
C(1)—O(1)—C(9)	116·0 (6)	C(1)—C(2)—C(3)	116·0 (6)
C(1)—C(12)—C(11)	108·9 (7)	C(2)—C(1)—C(12)	116·0 (6)
C(2)—C(3)—C(4)	117·9 (7)	C(3)—C(4)—C(5)	117·7 (6)
C(4)—C(5)—C(6)	114·0 (7)	C(5)—O(2)—C(13)	117·4 (7)
C(5)—C(6)—C(7)	116·8 (7)	C(6)—C(7)—C(8)	114·6 (7)
C(7)—C(8)—C(9)	112·0 (7)	C(8)—C(9)—C(10)	111·9 (7)
C(9)—C(10)—C(11)	114·0 (7)	C(10)—C(11)—C(12)	110·7 (7)

1085 with $I > 3\sigma(I)$, Lp correction, empirical absorption correction (Walker & Stuart, 1983); correction factors: max. = 1·104 and min. = 0·816, direct methods, refinement by full-matrix least-squares method using *F*'s, all non-H atoms anisotropic, H atoms calculated (C—H distance 1·05 Å) and used as riding atoms with fixed isotropic temperature factor (B_{eq} = 5·0 Å^2), 263 parameters, max. shift/σ < 0·01 on final cycle, $R = 0{\cdot}028$, $wR = 0{\cdot}038$, $w = 1/[(\sigma F)^2 + (0{\cdot}035F)^2]$, σF from counting statistics, $S = 0{\cdot}97$, final difference map max. 0·30 (7) and min. −0·24 (6) e Å^{-3}, scattering factors from *International Tables for X-ray Crystallography* (1974), computer programs *MULTAN*11/82 (Main *et al.*, 1982), *SDP* (Frenz, 1978), *PLUTO* (Motherwell & Clegg, 1978).

Discussion. The atomic coordinates and isotropic temperature factors are listed in Table 1, and the bond distances and angles are given in Table 2.[*] A view of the molecule and the numbering scheme are shown in Fig. 1. A stereoscopic view of the packing is presented in Fig. 2.

The bond distances and angles are normal. There are some intermolecular contacts (keeping in mind the calculated C—H distances, 1·05 Å) shorter than the sums of the van der Waals radii[†] (d_w), *viz.* 3·546 (1) for Br(1)···Br(3) [d_w(Br↔Br) = 3·90], 2·831 and 2·926 for Br(2)···H20 and Br(3)···H14, respectively [d_w(Br↔H) = 3·15], and 2·293 Å for H3···H19 [d_w(H↔H) = 2·40 Å]. The conformation occasions some short intramolecular contacts: 3·003 (6) [Br(2)···O(2)] [d_w(Br↔O) = 3·35], 2·841 [Br(1)···H1], 2·849 [Br(1)···H5], 2·928 [Br(1)···H18], 2·990 [Br(2)···H9], 2·794 [Br(3)···H13], 2·122 [O(1)···H8] [d_w(O↔H) = 2·60], 1·984 [H1···H7], 2·148 [H1···H11], 2·002 [H7···H11] and 2·284 Å [H12···H14].

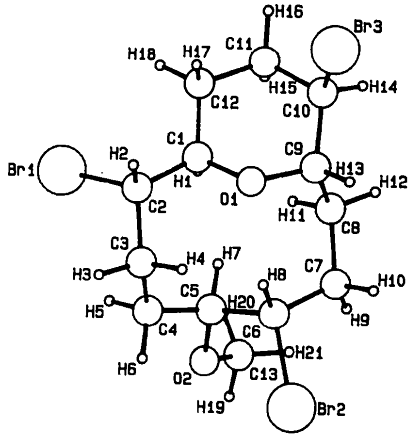

Fig. 1. *PLUTO* plot (Motherwell & Clegg, 1978) and the numbering scheme for the bicyclic ether.

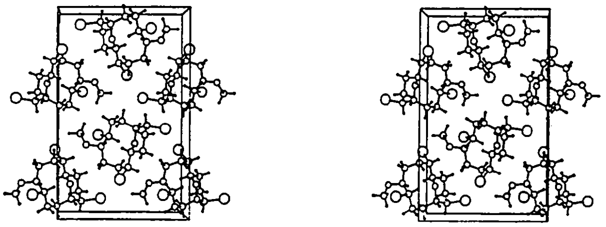

Fig. 2. A stereoscopic view of the packing for the bicyclic ether. The *c* axis is horizontal and the *b* axis vertical.

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[*] Lists of structure factors, H-atom parameters, anisotropic thermal parameters and selected torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51120 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

[†] E.s.d.'s for Br···H are 0·015 and for H···H 0·040 Å.

The tetrahydropyran ring has a chair conformation and the oxacyclodecane part has a distorted boat–chair–boat conformation.

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Structure of (*Z*)-1-*p*-Methoxyphenyltelluro-2-phenylethene

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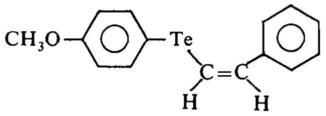
Abstract. $C_{15}H_{14}OTe$, $M_r = 337{\cdot}9$, triclinic, $P\bar{1}$, $a = 7{\cdot}878\,(3)$, $b = 5{\cdot}757\,(2)$, $c = 14{\cdot}853\,(5)$ Å, $\alpha = 90{\cdot}28\,(3)$, $\beta = 92{\cdot}60\,(3)$, $\gamma = 91{\cdot}08\,(3)°$, $V = 672{\cdot}8\,(4)$ Å^3, $Z = 2$, $D_x = 1{\cdot}67$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 2{\cdot}27$ mm^{-1}, $F(000) = 328$, $T = 296$ K, final $R = 0{\cdot}060$ for 2156 unique observed reflections. The average Te—C bond distance is 2·103 (11) Å and the C=C bond distance is 1·317 (7) Å. The Te—C=C—phenyl grouping is nearly planar and rotated approximately 66° from the planar *p*-methoxyphenyl group. Steric effects in the molecule are apparent, with Te—C=C = 130·9 (4)° and C=C—phenyl = 130·4 (5)°. There is a short intermolecular Te···Te′ distance, 3·839 (1) Å.

Introduction. We have determined the structure of a molecule in which Se$^{\rm II}$ is directly bonded to an acetylenic C and to a phenyl C (Husebye, Meyers, Zingaro, Braga, Comasseto & Petragnani, 1986). In that structure, the bond from Se to the acetylenic C is 0·079 Å shorter than that from Se to the phenyl C. In addition, there seems to be some slight indication of secondary bonding between Se atoms, linking the molecules into zigzag chains. We wished to explore the possibility of similar structural features in molecules which have Te attached to phenyl groups and to unsaturated C atoms and have determined the present structure (I) in order to do so.



(I)

Experimental. The preparation of the title compound has been reported previously (Dabdoub, Dabdoub, Comasseto & Petragnani, 1986). The material was recrystallized from ethanol as very-pale-yellow plates. X-ray data were collected by the Molecular Structure Corporation, College Station, Texas. A plate 0·40 × 0·20 × 0·05 mm was used for intensity measurements with graphite-monochromatized Mo $K\alpha$ radiation on an Enraf–Nonius CAD-4 diffractometer. Cell constants were obtained from least-squares refinement of 2θ for 25 reflections in the range $5 < \theta < 12°$. The crystals are triclinic, $P1$ or $P\bar{1}$. At $T = 296$ K, 3097 independent reflections were examined and the intensities were measured ($\theta/2\theta$ scan mode) for 2464 of them for which $I > 0{\cdot}5\sigma(I)$ and $2\theta < 55°$ ($0 \le h \le 10$, $-6 \le k \le 6$,

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