

(E)-exo,endo-2,5,10-Tribromo-exo-6-methoxy-13-oxa-cis-bicyclo[7.3.1]tridec-4-ene

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Abstract. C₁₃H₁₉Br₃O₂, $M_r = 447.02$, monoclinic, $P2_1/c$, $a = 10.442$ (1), $b = 9.681$ (2), $c = 19.558$ (3) Å, $\beta = 129.42$ (1)°, $V = 1527.3$ (9) Å³, $Z = 4$, $D_x = 1.94$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 7.84$ mm⁻¹, $F(000) = 872$, $T = 296$ K, final $R = 0.037$ for 1427 unique observed reflections. The surprising title compound was obtained as a by-product in the methoxybromination of (*E,Z,Z*)-cyclododeca-1,5,9-triene *via* transannular *O*-heterocyclization. The pyran ring has a chair conformation and the boat-chair-boat conformation of the ten-membered ring is heavily distorted by the *cis* double bond.

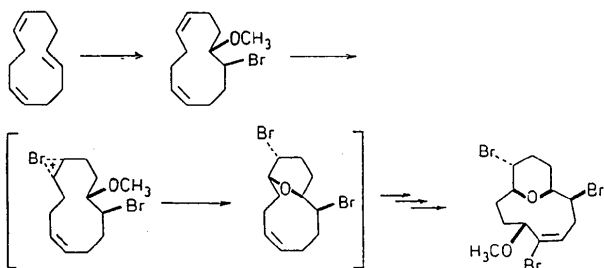
Introduction. Earlier studies have established that bromo-substituted oxabicyclic and oxatricyclic compounds can be synthesized by means of a methoxybromination procedure starting from medium- or large-sized dienes or trienes by treatment with *N*-bromosuccinimide in methanol. In this way isomeric 2,9-dibromo-13-oxabicyclo[8.2.1]tridecanes are obtained from (*E,E*)- and (*E,Z*)-cyclododeca-1,5-dienes (Graefe, Haufe & Mühlstädt, 1976). (*Z*)-*exo,exo*-2,9-Dibromo-13-oxabicyclo[8.2.1]tridec-4-ene and a by-product are formed from (*E,E,Z*)-cyclododeca-1,5,9-triene (Haufe & Mühlstädt, 1984). However, the course of this kind of reaction (transannular *O*-heterocyclization) is strongly directed by the conformational arrangement of the cyclic system in the transition state leading to transannular *O*-bridging, which in turn is dependent on the configuration and conformation of the starting diene or triene. As a result of this conformational dependence the methoxybromination procedure starting from (*E,E,E*)-cyclododeca-1,5,9-triene does not produce bicyclic tetrahydrofuran derivatives but three tetrahydropyran derivatives, namely *endo,endo,exo*-2,6,10-tribromo-*exo*-5-methoxy-13-oxa-*trans*-bicyclo[7.3.1]tridecane, *anti,exo,exo*-5,10,12-tribromo-*exo*-13-oxabicyclo[7.3.1.0^{2,6}]tridecane and *anti,exo*-5,10-dibromo-*exo*-13-oxatricyclo[7.3.1.0^{2,6}]tridecane (Rissanen & Haufe, 1988; Haufe, 1987; Haufe, Faure & Loiseleur, 1987). The tricyclic compound is

formed by transannular π -cyclization and subsequent transannular *O*-heterocyclization. In the reaction of (*E,Z,Z*)-cyclododeca-1,5,9-triene under the conditions described, *endo,endo*-5,9-dibromo-*cis-transoid-cis*-13-oxatricyclo[8.2.1.0^{2,6}]tridecane (15%) was formed by the same mechanism (Rissanen, Valkonen & Haufe, 1987); now an oxabicyclic compound (11%), one π -cyclization product and minor amounts of simple addition products have been isolated as well. To establish the composition, configuration and conformation of this unknown oxabicyclic product, we determined its crystal and molecular structure.

Experimental. Colourless crystals were synthesized according to Haufe (1987). A crystal 0.05 × 0.10 × 0.20 mm was mounted on a glass fibre. Enraf-Nonius CAD-4 diffractometer was used with graphite-monochromatized Mo *K* α radiation, ω - 2θ method. Lattice parameters were determined from 25 reflections with $8 < \theta < 13^\circ$. Two standard reflections were measured every hour during the intensity-data collection, no loss of intensity. The data set consisted of 2864 independent reflections ($h: 0 \rightarrow 12$, $k: 0 \rightarrow 11$, $l: -22 \rightarrow 17$) with $\theta < 25^\circ$, 1427 of which had $I > 3\sigma(I)$. *Lp* correction, empirical absorption correction (Walker & Stuart, 1983); correction factors: max = 1.351 and min = 0.696. The structure was solved with direct methods and refined by full-matrix least-squares method using *F*'s and all non-H atoms anisotropic. The positions of the H atoms were calculated (C—H distance 1.03 Å) and used as riding atoms with a fixed isotropic temperature factor ($B_{eq} = 5.0$ Å²). 163 parameters and max. shift/ $\sigma < 0.01$ in final cycle, $R = 0.037$, $wR = 0.050$ with $w = 1/[(\sigma F)^2 + (0.035F)^2]$, σF from counting statistics; $S = 1.15$, final difference map max. 0.55 (10) and min. -0.50 (10) e Å⁻³. Scattering factors were taken from *International Tables for X-ray Crystallography* (1974). The computer programs used were *MULTAN*11/82 (Main *et al.*, 1982), *SDP* (Frenz, 1978) and *PLUTO* (Motherwell & Clegg, 1978).

Discussion. The atomic coordinates and equivalent isotropic temperature factors are listed in Table 1, the bond distances and angles 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. The double bond causes shortening of the Br—C bond distance from the normal average value of 1.968 (9) Å (Br—C_{sp³}) found in this type of compound (Rissanen *et al.*, 1987; Haufe, Faure & Loiseau, 1987; Rissanen & Haufe, 1988; this work) to 1.909 (7) Å (Br—C_{sp²}). Also the conformation of the ten-membered ring is changed from slightly to heavily distorted boat-chair-boat conformation (Rissanen & Haufe, 1988). Owing to the conformational change the bond angle in the methoxy group situated next to bromine is decreased from 117.4 (7)° in the aliphatic bicyclic ether (Rissanen & Haufe, 1988) to 113.5 (4)°, although there are no changes in bond distances.



The formation of the double bond in the oxacyclodecane ring is surprising, but the overall formation of the compound can be presumed to proceed by the following mechanism. In the first step the more reactive *E* double bond of the starting triene will be attacked yielding a normal bromomethoxycyclohexadiene with *cis* configuration of the substituents in the 1- and 2-positions. Repeated attack of the electrophilic bromonium species at one of the *Z* double bonds yields a more-or-less bridged bromonium ion from which (*E*)-*exo,endo*-dibromo-13-oxa-*cis*-bicyclo[7.3.1]tridec-4-ene should be formed by transannular *O*-participation and subsequent demethylation of the intermediately occurring oxonium ion. From that compound, which could not be isolated, the final product, (*E*)-*exo,endo*-2,5,10-tribromo-*exo*-6-methoxy-13-oxa-*cis*-bicyclo[7.3.1]tridec-4-ene, must be formed by an additional

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

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

| | x | y | z | B _{eq} (Å ²) |
|-------|-------------|-------------|-------------|-----------------------------------|
| Br(1) | 0.01931 (9) | 0.05398 (9) | 0.30208 (4) | 4.43 (2) |
| Br(2) | 0.32772 (9) | 0.03727 (9) | 0.65257 (4) | 4.19 (2) |
| Br(3) | 0.81979 (9) | 0.2934 (1) | 0.53535 (5) | 5.72 (2) |
| O(1) | 0.3623 (4) | 0.2170 (5) | 0.4642 (2) | 2.6 (1) |
| O(2) | 0.3832 (5) | 0.3676 (6) | 0.6756 (2) | 4.0 (1) |
| C(1) | 0.2506 (7) | 0.2838 (8) | 0.3804 (3) | 3.0 (2) |
| C(2) | 0.0788 (7) | 0.2454 (7) | 0.3451 (4) | 3.0 (2) |
| C(3) | 0.0509 (7) | 0.2687 (8) | 0.4132 (4) | 3.4 (2) |
| C(4) | 0.1260 (6) | 0.1652 (8) | 0.4868 (3) | 2.8 (2) |
| C(5) | 0.2613 (6) | 0.1807 (7) | 0.5690 (3) | 2.8 (2) |
| C(6) | 0.3801 (7) | 0.3024 (8) | 0.6091 (3) | 2.8 (2) |
| C(7) | 0.5656 (7) | 0.2695 (8) | 0.6583 (4) | 3.4 (2) |
| C(8) | 0.6090 (6) | 0.1974 (8) | 0.6058 (3) | 3.1 (2) |
| C(9) | 0.5278 (6) | 0.2641 (8) | 0.5162 (3) | 2.8 (2) |
| C(10) | 0.5938 (7) | 0.2260 (8) | 0.4688 (4) | 3.3 (2) |
| C(11) | 0.4850 (7) | 0.2876 (8) | 0.3762 (4) | 3.7 (2) |
| C(12) | 0.3034 (8) | 0.2497 (9) | 0.3255 (4) | 3.9 (2) |
| C(13) | 0.2371 (7) | 0.438 (1) | 0.6418 (4) | 4.4 (2) |

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

| | | | | | |
|------------------|------------|-------------------|------------|-------------|------------|
| Br(1)—C(2) | 1.965 (7) | C(1)—C(2) | 1.504 (10) | C(7)—C(8) | 1.528 (12) |
| Br(2)—C(5) | 1.909 (7) | C(1)—C(12) | 1.522 (13) | C(8)—C(9) | 1.524 (9) |
| Br(3)—C(10) | 1.946 (6) | C(2)—C(3) | 1.551 (12) | C(9)—C(10) | 1.510 (12) |
| O(1)—C(1) | 1.428 (6) | C(3)—C(4) | 1.502 (9) | C(10)—C(11) | 1.521 (8) |
| O(1)—C(9) | 1.413 (7) | C(4)—C(5) | 1.310 (6) | C(11)—C(12) | 1.525 (10) |
| O(2)—C(6) | 1.427 (10) | C(5)—C(6) | 1.519 (9) | O(2)—C(13) | 1.395 (9) |
| C(6)—C(7) | 1.553 (9) | | | | |
| Br(1)—C(2)—C(1) | 113.0 (5) | Br(1)—C(2)—C(3) | 109.0 (5) | | |
| Br(2)—C(5)—C(4) | 119.3 (6) | Br(2)—C(5)—C(6) | 112.8 (3) | | |
| Br(3)—C(10)—C(9) | 109.9 (4) | Br(3)—C(10)—C(11) | 109.7 (5) | | |
| O(1)—C(1)—C(2) | 106.3 (6) | O(1)—C(1)—C(12) | 108.3 (5) | | |
| O(1)—C(9)—C(8) | 102.9 (6) | O(1)—C(9)—C(10) | 107.8 (5) | | |
| O(2)—C(6)—C(5) | 110.7 (7) | O(2)—C(6)—C(7) | 103.2 (4) | | |
| C(1)—O(1)—C(9) | 114.5 (5) | C(1)—C(2)—C(3) | 113.0 (5) | | |
| C(1)—C(12)—C(11) | 110.3 (5) | C(2)—C(1)—C(12) | 119.0 (5) | | |
| C(2)—C(3)—C(4) | 117.2 (6) | C(3)—C(4)—C(5) | 126.8 (7) | | |
| C(4)—C(5)—C(6) | 127.8 (6) | C(5)—C(6)—C(7) | 116.7 (6) | | |
| C(6)—O(2)—C(13) | 113.5 (4) | C(6)—C(7)—C(8) | 117.6 (4) | | |
| C(7)—C(8)—C(9) | 113.2 (6) | C(8)—C(9)—C(10) | 117.7 (6) | | |
| C(9)—C(10)—C(11) | 110.4 (6) | C(10)—C(11)—C(12) | 111.1 (7) | | |

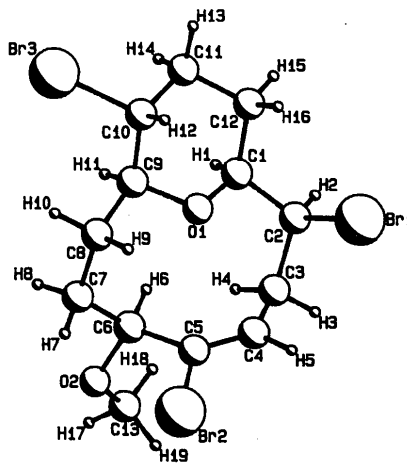


Fig. 1. PLUTO plot (Motherwell & Clegg, 1978) and the numbering scheme for the bicyclic ether.

* Lists of structure factors, H-atom parameters, anisotropic thermal parameters and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52020 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

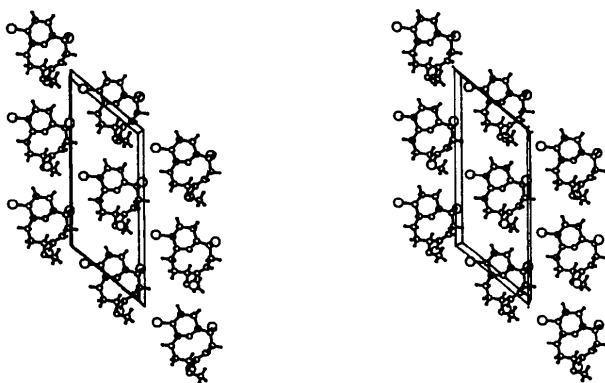


Fig. 2. A stereoscopic view of the packing for the bicyclic ether along the *b* axis.

methoxybromination step and formal loss of hydrogen. The presence of the double bond can be verified from two signals at $\delta = 134.4$ [C(4)] and 128.9 [C(5)] in the ^{13}C NMR spectrum.

The conformation results in some intramolecular contacts (keeping in mind the calculated C—H distances, 1.03 \AA) which are noticeably shorter than the sum of van der Waals radii (d_w): H(6)—O(1) = 2.36 (3), H(9)—O(1) = 2.41 (3), $d_w = 2.60 \text{ \AA}$; H(4)—H(6) = 2.02 (5), $d_w = 2.40 \text{ \AA}$. The molecules are packed in planes parallel to the *ac* plane with two planes in a unit cell and are held together by van der Waals forces. Due to the packing there are also some

intermolecular contacts shorter than the sum of van der Waals radii: Br(2)—O(2) = 3.197 (7), $d_w = 3.35 \text{ \AA}$; Br(1)—H(2) = 2.89 (2), Br(3)—H(19) = 2.85 (2), $d_w = 3.15 \text{ \AA}$.

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Dipotassium Sodium Tris[dicyanoargentate(I)]

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Abstract. $\text{K}_2\text{Na}[\text{Ag}(\text{CN})_2]_3$, $M_r = 580.91$, trigonal, $P\bar{3}1m$, $a = 7.0509$ (7), $c = 8.5766$ (8) \AA , $V = 369.26 \text{ \AA}^3$, $Z = 1$, $D_x = 2.614 \text{ Mg m}^{-3}$, $\lambda(\text{Mo K}\alpha)$

$= 0.71073 \text{ \AA}$, $\mu = 4.375 \text{ mm}^{-1}$, $F(000) = 268$, $T = 298 \text{ K}$. The structure was refined to $R = 0.0504$, $wR = 0.0156$ for 410 absorption-corrected observed reflections. Ag atoms of linear NC—Ag—CN groups are arranged in Kagomé nets parallel to (001). The

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