Photochemical Behaviour of Bicyclo[6.3.1]dodec-1(11)-en-10-one. Crystal and Molecular Structure of 9,11-Dibromotricyclo[6.3.1.0^{1,5}]-dodecan-10-one

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Bicyclo[6.3.1]dodec-1(11)-en-10-one undergoes photocyclization to give mainly tricyclo[6.3.1.0^{1,5}]dodecan-10-one. The crystal and molecular structure of 9,11-dibromotricyclo[6.3.1.0^{1,5}]dodecan-10-one (6) was determined by direct methods from diffractometer data and refined by least-squares techniques to R 0.067 for 3 204 independent reflections.

In recent years, α,β-unsaturated ketone photochemistry has received a great deal of attention.[1] The most widely investigated group of compounds possessing this chromophore are substituted cyclohexenones, for which the type of reactions found are strictly related to the substitution pattern.[2]

Although 4,4-disubstituted cyclohexenones mainly photoisomerize to give bicyclo[3.1.0]cyclohexan-2-ones,[3] the most frequently observed photochemical reaction is the formation of cyclobutane dimers.[4]

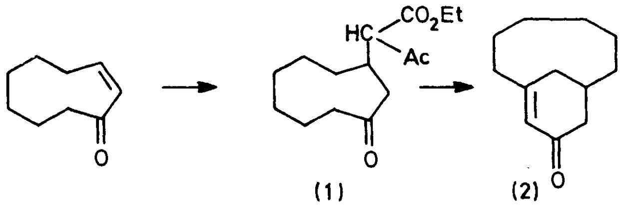
Double-bond shifts due to intermolecular H-abstraction, solvent incorporation, photoreduction,[5] and intramolecular H-abstraction by the ketone oxygen,[6] are also frequently observed. Direct H-transfer to the α-carbon of the enone system has recently been found in certain cyclohexenone derivatives.[7] The photoisomerization of taxinine and some of its derivatives follows a formally similar H-transfer, but a concerted addition has been envisaged as the most likely mechanism.[8]

We have reported[9] the photochemical behaviour of bicyclo[9.3.1]pentadec-1(14)-en-13-one, and explained this reaction as being the result of a H-transfer from the polymethylene chain to the β-carbon of the enone system. We now report the photochemistry of bicyclo-[6.3.1]dodec-1(11)-en-10-one (2), and show that this

[1] For recent reviews, see *e.g.* Chem. Soc. Specialist Periodical Reports, Photochemistry, vols. I—V.
[2] W. G. Dauben, G. W. Shaffer, and N. D. Wetmeyer, *J. Org. Chem.*, 1968, **33**, 4060.
[3] For a review, see P. J. Kropp, *Org. Photochem.*, 1967, **1**, 67.
[4] For a review, see D. J. Trecker, *Org. Photochem.*, 1969, **2**, 71.
[5] D. Bellus, D. R. Kearns, and K. Schaffner, *Helv. Chim. Acta*, 1969, **52**, 971.
[6] A. B. Smith and W. C. Agosta, *J. Org. Chem.*, 1972, **37**, 1259.
[7] J. Gloor and K. Schaffner, *Helv. Chim. Acta*, 1974, **57**, 1815.
[8] T. Kobayashi, M. Kurono, H. Sato, and K. Nakanishi, *J. Amer. Chem. Soc.*, 1972, **94**, 2863.
[9] A. Marchesini, U. M. Pagnoni, and A. Pinetti, *Tetrahedron Letters*, 1973, 4299.

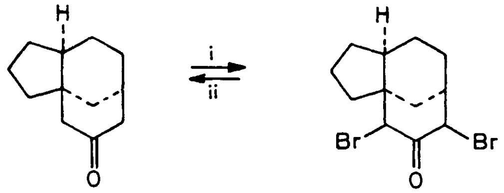
photoisomerization is an entry of synthetic utility to the tricyclo[6.3.1.0^{1,5}]dodecane system.

The title compound was prepared from cyclonon-2-enone [10] in 65% overall yield as shown in Scheme 1.



SCHEME 1

When the enone (2) was irradiated in benzene solution with a high-pressure Hg lamp through Pyrex, two photoproducts, (3) and (4), were formed in *ca.* 1 : 6 ratio. The yields of these materials were high (80% at 1.87 10^{-4}M concentration) and decreased with increasing concentration, owing to the formation of dimeric products. The two products were isolated by silica gel column chromatography. Details of procedures and weights of chromatographic fractions are given in the Experimental section. A study of product distribution *vs.* extent of irradiation established that the ratio (3) : (4) was constant as a function of time. The spectral data of (3) and (4) are very similar, elemental analysis and mass spectrum indicate the composition $C_{12}H_{18}O$, isomeric



SCHEME 2
Reagents: i, Br_2; ii, Zn–AcOH

with the starting material. The n.m.r. spectrum shows absence of olefinic hydrogens, hence (3) and (4) must be tricyclic compounds.

Irradiation was also carried out for different solvents, and considering the time required for completion of reaction, the reactivity decreases as follows: propan-2-ol, acetone, methanol, benzene, cyclohexane.

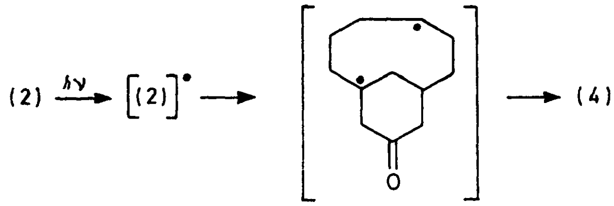
The ratio of the major product (4) to the minor (3) showed a slight solvent dependence. Ratios were 6 : 1 for reactions in cyclohexane, benzene, and acetone, 8 : 1 for propan-2-ol, and 9 : 1 for methanol.

Bromination of (4) affords a dibromoketone (6). I.r. and n.m.r. data suggest an αα′-dibromo-ketone structure with the two bromine atoms axial.

Reduction of the dibromide (6) with Zn in AcOH affords the parent ketone (4). These data establish the presence in (4) of $-CH_2-CO-CH_2-$ system and suggest that the tricyclic system in (4) arises from bond formation between C(1) and either C(4), C(5), or C(6). The exact structure was determined by an *X*-ray diffraction analysis of (6).

If one assumes a stepwise reaction, hydrogen abstraction by the ketone oxygen and directly by the α-carbon of the enone system are possible primary photochemical processes.

One possible mechanism of cyclization, H-abstraction by carbonyl oxygen, was eliminated by the observation that the irradiation in CH_3OD solution did not afford deuteriated (4). Also, examination of models showed considerable strain for this abstraction. For the formation of (4) from (2) we therefore suggest Scheme 3.



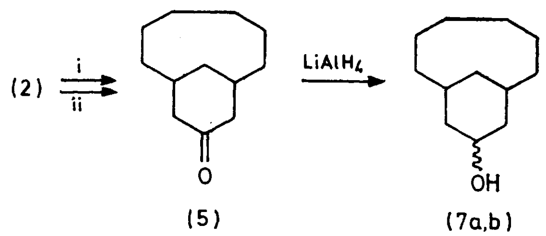
SCHEME 3

The structure of (3) is still under examination. Spectral data suggest it may be a stereoisomer of (4). Bromination affords a non crystalline mixture of *cis*- and *trans*-α,α′-dibromoketones.

The formation of both the photoketones (3) and (4) was found to be completely quenched in the presence of oxygen. This fact, together with the previously reported solvent effects, suggests that a triplet excited state of (2) is involved.

In propan-2-ol another product (5) was formed (25%) and was identified as bicyclo[6.3.1]dodecan-10-one on the basis of analytical and spectral data; it was identical with the dihydro-derivative of (2) obtained by catalytic hydrogenation. The ring junction was proved to be *cis* by reduction with $LiAlH_4$: from (5) two isomeric alcohols, (7a) and (7b) in a 5 : 1 ratio, were obtained.

Molecular Geometry of 9,11-*Dibromotricyclo*[6.3.1.0^{1,5}]-*dodecan*-10-*one* (6).—The Figure shows the projection of the structure on (100) and the numbering system used in the crystal structure analysis. There are two independent molecules in the asymmetric unit and the corresponding bond distances and angles (Table 1) and the conformation are not significantly different.



SCHEME 4
Reagents: i, H_2–Pd: ii, *hν*, propan-2-ol

A similar tricyclic system has already been found in

[10] N. Heap and G. H. Whitham, *J. Chem. Soc.* (*B*), 1966, 164.

TABLE 1

Bond distances (Å) and angles (°) in (6)

	Molecule (1)	Molecule (2)
(*a*) Distances		
Br(1)–C(2)	1.988(7)	1.989(7)
Br(2)–C)6)	1.971(7)	1.990(7)
O(1)–C(1)	1.214(9)	1.211(8)
C(1)–C(2)	1.535(10)	1.515(9)
C(1)–C(6)	1.506(10)	1.504(10)
C(2)–C(3)	1.516(10)	1.525(9)
C(3)–C(4)	1.513(10)	1.523(9)
C(3)–C(9)	1.561(10)	1.565(10)
C(3)–C(12)	1.546(10)	1.520(9)
C(4)–C(5)	1.546(9)	1.562(9)
C(5)–C(6)	1.501(11)	1.519(11)
C(5)–C(7)	1.562(10)	1.545(11)
C(7)–C(8)	1.506(12)	1.525(10)
C(8)–C(9)	1.541(9)	1.525(9)
C(9)–C(10)	1.504(11)	1.504(10)
C(10)–C(11)	1.570(12)	1.543(9)
C(11)–C(12)	1.517(11)	1.497(10)
(*b*) Angles		
O(1)–C(1)–C(2)	120.4(11)	120.3(10)
O(1)–C(1)–C(6)	120.9(12)	120.9(11)
C(2)–C(1)–C(6)	118.5(11)	118.8(10)
Br(1)–C(2)–C(1)	102.8(6)	104.2(6)
Br(1)–C(2)–C(3)	112.6(7)	112.1(7)
C(1)–C(2)–C(3)	117.0(11)	117.8(10)
C(2)–C(3)–C(4)	111.0(10)	110.1(9)
C(2)–C(3)–C(9)	109.3(10)	108.5(10)
C(2)–C(3)–C(12)	112.4(10)	112.9(10)
C(4)–C(3)–C(9)	109.9(10)	110.0(10)
C(4)–C(3)–C(12)	115.4(10)	117.2(10)
C(9)–C(3)–C(12)	98.2(8)	97.2(8)
C(3)–C(4)–C(5)	108.1(9)	108.5(9)
C(4)–C(5)–C(6)	111.4(10)	109.6(10)
C(4)–C(5)–C(7)	111.7(10)	111.8(10)
C(6)–C(5)–C(7)	110.0(11)	109.5(11)
Br(2)–C(6)–C(1)	107.0(7)	106.9(7)
Br(2)–C(6)–C(5)	110.9(8)	110.2(7)
C(1)–C(6)–C(5)	114.0(11)	114.6(11)
C(5)–C(7)–C(8)	113.1(11)	114.6(11)
C(7)–C(8)–C(9)	110.1(11)	109.3(10)
C(3)–C(9)–C(8)	111.7(9)	112.8(10)
C(3)–C(9)–C(10)	106.1(10)	105.3(9)
C(8)–C(9)–C(10)	120.9(12)	120.5(11)
C(9)–C(10)–C(11)	103.3(10)	104.3(9)
C(10)–C(11)–C(12)	106.5(11)	105.5(9)
C(3)–C(12)–C(11)	104.6(10)	106.6(9)

TABLE 2

Equations of least-squares planes in the tricyclododecane system of compound (6), in the form $lX + mY + nZ = p$ where X, Y, and Z are related to the crystallographic orthogonal axes by the transformation matrix:

$$\begin{pmatrix} 1 & 0 & \cos\beta \\ 0 & 1 & 0 \\ 0 & 0 & \sin\beta \end{pmatrix}$$

Distances (Å × 10³) of relevant atoms from the planes are given in square brackets; values for molecule (2) follow those for molecule (1)

Plane (*A*): C(9)—(12)

$$0.9586X + 0.2010Y - 0.2019Z = -3.3479$$
$$-0.9618X - 0.1621Y - 0.2207Z = -2.1019$$

[C(3) 701, 695; C(9) −7, −8; C(10) 13, 12; C(11) −13, −12; C(12) 7, 8]

Plane (*B*): C(3), C(5), C(7), C(9)

$$0.7284X + 0.5151Y - 0.4518Z = -1.4072$$
$$-0.7396X - 0.4306Y - 0.5173Z = -2.1538$$

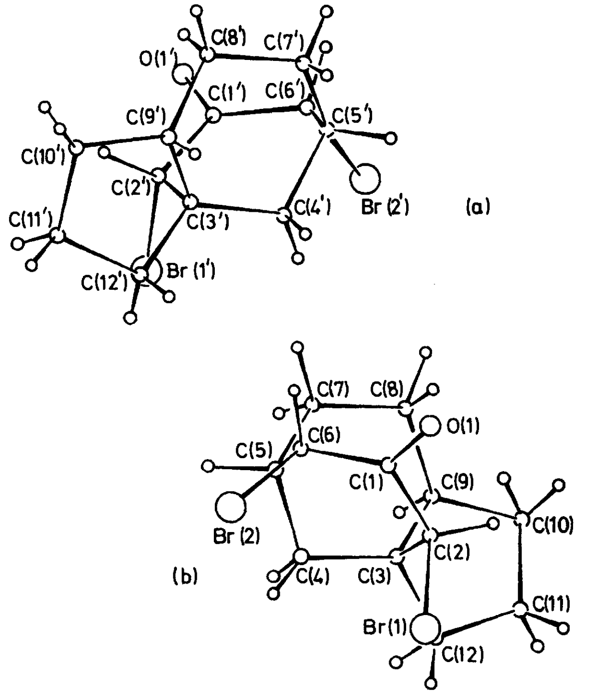
[C(3) 19, 20; C(4) −724, −710; C(5) −24, −24; C(7) 26, 29; C(8) 647, 644; C(9) −21, −24]

Plane (*C*): C(2), C(3), C(5), C(6)

$$-0.3728X + 0.4936Y - 0.7858Z = -0.3096$$
$$0.3688X - 0.3581Y - 0.8578Z = -0.9269$$

[C(1) 301, 296; C(2) 25, 28; C(3) −27, −29; C(4) −746, −756; C(5) 29, 32; C(6) −27, −31]

pseudoclovene-A-diol,[11] a rearrangement product of caryophyllene, but while in compound (6) the fusion between the five- and six-membered rings is *trans*, in the case of pseudoclovene it is *cis*. The cyclohexane ring adopts a chair and the cyclopentane ring an envelope



Projection of the structure on (100): (a) molecule (1) and (b) molecule (2)

TABLE 3

Torsion angles (°)

	Molecule (1)	Molecule (2)
C(6)–C(1)–C(2)–C(3)	23.6	23.5
C(2)–C(1)–C(6)–C(5)	−27.4	−27.8
C(1)–C(2)–C(3)–C(4)	−40.3	−40.1
C(1)–C(2)–C(3)–C(9)	81.0	80.3
C(1)–C(2)–C(3)–C(12)	−171.2	−173.1
C(2)–C(3)–C(4)–C(5)	60.3	60.8
C(9)–C(3)–C(4)–C(5)	−60.6	−58.7
C(12)–C(3)–C(4)–C(5)	−170.4	−168.4
C(2)–C(3)–C(9)–C(8)	−61.3	−59.9
C(2)–C(3)–C(9)–C(10)	72.8	73.4
C(4)–C(3)–C(9)–C(8)	60.6	60.6
C(4)–C(3)–C(9)–C(10)	−165.7	−166.2
C(12)–C(3)–C(9)–C(8)	−178.5	−177.1
C(12)–C(3)–C(9)–C(10)	−44.9	−43.8
C(2)–C(3)–C(12)–C(11)	−72.4	−70.9
C(4)–C(3)–C(12)–C(11)	159.1	159.6
C(9)–C(3)–C(12)–C(11)	42.4	42.7
C(3)–C(4)–C(5)–C(6)	−65.9	−66.1
C(3)–C(4)–C(5)–C(7)	57.6	55.5
C(4)–C(5)–C(6)–C(1)	48.4	48.4
C(7)–C(5)–C(6)–C(1)	−76.2	−74.6
C(4)–C(5)–C(7)–C(8)	−54.2	−52.8
C(6)–C(5)–C(7)–C(8)	70.2	68.9
C(5)–C(7)–C(8)–C(9)	51.2	50.7
C(7)–C(8)–C(9)–C(3)	−54.4	−54.1
C(7)–C(8)–C(9)–C(10)	179.7	−179.5
C(3)–C(9)–C(10)–C(11)	29.5	29.0
C(8)–C(9)–C(10)–C(11)	158.0	157.9
C(9)–C(10)–C(11)–C(12)	−2.0	−2.0
C(10)–C(11)–C(12)–C(3)	−26.2	−26.8

[11] D. M. Hawley, G. Ferguson, T. F. W. McKillop, and J. M. Robertson, *J. Chem. Soc.* (*B*), 1969, 599.

conformation. The cyclohexanone ring adopts a chair arrangement but deviates from the ideal conformation, the ring being flattened because of the sp^2 character of atom C(1). The two bromine atoms are *cis* and axial. The reciprocal orientation of the ring in the two molecules can be deduced from an analysis of planarity and from the torsion angles (Tables 2 and 3). The dihedral angles between planes (*A*) and (*B*), and (*C*) and (*D*) are 153.3 and 153.0, and 109.7 and 109.0° in molecules (1) and (2) respectively. Carbon–hydrogen bonds are in the range 0.95(7)—1.09(7) Å, mean 1.02(1) Å. Packing is consistent with van der Waals interactions.

EXPERIMENTAL

Methods and Materials.—I.r. spectra were recorded on a Perkin-Elmer 377, ^{1}H n.m.r. spectra in [^{2}H]chloroform solution with a Varian HA 100 or A 60 A spectrometer. Chemical shifts are given in δ from tetramethylsilane as internal standard and refer to the centre of the signal. U.v. spectra were recorded for 96% ethanolic solutions on a Beckmann DB GT spectrometer. Mass spectra were obtained with a Perkin-Elmer 270 GC Ms system, at an ionizing potential of 70 eV, using the gas chromatographic inlet. G.l.c. analyses were run on a Pye series 104 chromatograph [dual glass column; (*A*) 2 m × 3 mm, packed with 5% EAS on 100—120 mesh silanized Chromosorb W, nitrogen flow 40 ml min^{-1}; (*B*) 1.7 m × 3 mm, packed with 5% QF1 on 100—120 mesh silanized Chromosorb W, nitrogen flow 40 ml min^{-1}]. Column chromatography was performed on Merck Kieselgel 60, 0.063—0.200 mm. T.l.c. was carried out using Merck Kieselgel F_{254}. Magnesium sulphate was used as drying agent. Evaporation was carried out *in vacuo* (rotary evaporator). Irradiation was carried out with a 125 W HPK Philips high-pressure Hg lamp.

Immersion-well apparatus. This consists of a water-jacketted Pyrex well housing a 125 W lamp. The well fits into a cylindrical 400 ml reaction vessel equipped with an inlet for gas and an outlet for the removal of aliquot portions.

Irradiation. In a typical irradiation experiment, ketone was dissolved in the appropriate solvent, and the solution placed in the reaction vessel, which was held in place around the immersion-well apparatus. Nitrogen was bubbled through the solution for 15 min before irradiation. Aliquot portions were periodically withdrawn to ascertain the extent of reaction.

Ethyl 2-(3-*Oxocyclononyl)acetoacetate* (1).—To a mixture of cyclonon-2-enone [10] (20 g) and ethyl acetoacetate (20.7 g) a solution of EtONa in EtOH [from Na (300 mg) and EtOH (5 ml)] was added. After 12 h at room temperature, the reaction mixture was diluted with Et_2O (200 ml), washed with water (2 × 50 ml), and dried. *In vacuo* distillation of the residue from the solvent evaporation afforded (1), b.p. 144—146 °C at 0.5 mmHg (34 g, 87.5%), $\nu_{max.}$ (film) 1 740 and 1 705 cm^{-1}; δ 4.2 (2 H, q, CO_2CH_2Me), 3.44 [0.5 H, d, *J* 7 Hz, $-CH(CO_2Et)COMe$], 3.48 [0.5 H, d, *J* 8 Hz, $-CH(CO_2Et)COMe$], 2.4 (4 H, m, $-CH_2COCH_2-$), 2.26 (3 H, s, $-COCH_3$), and 1.28 (3 H, t, $-COOCH_2CH_3$).

Bicyclo[6.3.1]*dodec*-1(11)-*en*-10-*one* (2).—Ethyl 2-(3-oxocyclononyl)acetoacetate (1) (34 g) was added to a mixture of AcOH (170 ml), H_2O (100 ml), and H_2SO_4 (25 ml). The solution was heated under reflux for 4 h. After cooling, water (500 ml) was added and the mixture extracted with n-pentane (3 × 100 ml). The organic layer was dried. The residue from the solvent evaporation was distilled *in vacuo* affording (2) (16.9 g, 74.7%), b.p. 110 °C at 0.5 mmHg, $\nu_{max.}$ (film) 1 675 and 1 625 cm^{-1}; $\lambda_{max.}$ 242 (ε 12 630) 322 (ε 51), 5.88 (1 H, s, =C*H*CO–).

Irradiation of Bicyclo[6.3.1]*dodec*-1(11)-*en*-10-*one* (2).—(*a*) *In benzene*. In a typical run the ketone (2) (1 g) was dissolved in benzene (300 ml) and irradiation carried out for 5 h. Solvent was removed by rotary evaporation. The residue from three runs, distilled *in vacuo*, afforded 2.4 g, b.p. 94—100 °C at 0.5 mmHg. G.l.c. [(*A*), 150 °C] showed two products: (3) 14.3% and (4) 85.7%. Silica gel (70 g) column chromatography (eluant n-hexane to n-hexane–Et_2O 10 : 1 v/v) afforded a mixture (857 mg) of (3) and (4) (42 and 58% respectively), and (4) (1.40 g), b.p. 98—100 °C at 0.6 mmHg; $\nu_{max.}$ (film) 1 710 cm^{-1}; δ 2.3 (4 H, m) and 1.95 (2 H, m); *m/e* 178 (M^+) (59), 149(24), 135(49), 134(75), 122(17), 121(100), 120(56), 109(8), 108(21), 107(22) 95(27), 94(23), 93(49), 92(22), 91(40), 81(28), 79(62), 77(28), 67(38), 55(26), 53(24), 41(49), and 39(34).

Column chromatography of the mixture of (3) and (4) on silica gel (50 g) (eluant n-hexane to n-hexane–Et_2O 10 : 1 v/v) afforded (3) (150 mg), b.p. 87—90 °C at 0.4 mmHg; $\nu_{max.}$ (film) 1 710 cm^{-1}; n.m.r. spectrum inconclusive; *m/e* 178 (M^+)(76), 149(7), 135(89), 134(58), 122(24), 121(100), 120(74), 109(29), 108(18), 107(26), 95(60), 94(23), 93(51), 92(18), 91(36), 81(24), 79(62), 77(24), 67(53), 55(29), 53(24), 41(60), and 39(45).

(*b*) *In propan-2-ol*. Irradiation was carried out for 3 h, as previously described. The residue from three runs, distilled *in vacuo*, afforded 2.8 g, b.p. 90—95 °C at 0.4 mmHg. G.l.c. [(*A*), 150 °C] showed three products: (3) 8.3%, (4) 66.7%, and (5) 25%. Silica gel (80 g) column chromatography (eluant n-hexane to n-hexane–Et_2O, 10 : 1 v/v) afforded a mixture (1.8 g) of (4) and (5) (69 and 31% respectively). Compound (5) (320 mg), b.p. 92—94 °C at 0.4 mmHg, was obtained by preparative g.l.c. (2 m × 6 mm glass column, QF1 5%, silanized Chromosorb W 60—80 mesh, 185°, nitrogen flow 180 ml min^{-1}); $\nu_{max.}$ (film) 1 708 cm^{-1}; n.m.r. spectrum was inconclusive; *m/e* 180 (M^+) (7), 137(4), 109(7), 95(100), 81(5), 68(11), 67(14), 55(20), and 41(22).

Irradiation in the Presence of Oxygen.—Bicyclo[6.3.1]-dodec-1(11)-en-10-one (2) (40 mg) was dissolved in benzene (10 ml), in a Pyrex test tube, and oxygen bubbled through the solution for 5 min. The solution was then photolysed for 2 h. A probe in benzene, degassed with nitrogen, was also photolysed simultaneously. Product analysis by g.l.c. showed only a trace of (4) [<0.1%].

Bicyclo[6.3.1]*dodecan*-10-*one* (5).—Hydrogenation of bicyclo[6.3.1]dodec-1(11)-en-10-one (2) was carried out with 5% Pd–C as catalyst. In a typical run the ketone (2) (356 mg) was dissolved in AcOMe (30 ml) and 5% Pd–C catalyst (30 mg) added to the solution. Hydrogenation was then carried out at room temperature under atmospheric pressure until all the ketone (2) had disappeared as shown by g.l.c. (*ca*. 30 min). Catalyst was then filtered off and solvent evaporated. Vacuum distillation afforded (5) (330 mg) identical with a sample obtained from (2) by irradiation in propan-2-ol.

9,11-*Dibromotricyclo*[6.3.1.$0^{1.5}$]*dodecan*-10-*one* (6).—To a solution of (4) (400 mg) in CH_2Cl_2 (40 ml), Br_2 (380 mg) in CH_2Cl_2 (10 ml) was added during 5 min. After solvent evaporation, the residue was crystallized from n-pentane–

Et_2O and shown to be (6), 520 mg, m.p. 107 °C; $\nu_{max.}$ (Nujol) 1 715, (CCl_4) 1 720 cm^{-1}; δ 4.1 (2 H, m), 2.95 (1 H, d, *J* 13 Hz), 2.5 (1 H, m), 2.3 (1 H, m); *m/e* 338(5), 336(10), 334(5), 257(24), 255(25), 175(30), 147(12), 133(11), 121(100), 119(20), 91(23), 79(19), 67(13), 41(13).

Tricyclo[6.3.1.0^{1,5}]*dodecan*-10-*one* (4) *from the Dibromide* (6).—Zinc powder (400 mg) was added to a solution of the dibromide (6) (200 mg) in AcOH (10 ml). After 30 min at 80 °C, water (30 ml) was added and the mixture extracted with n-hexane (3 × 50 ml). Usual work-up afforded (4) (74 mg).

Bicyclo[6.3.1]*dodecan*-10-*ol* (7a and b).—To a solution of bicyclo[6.3.1]dodecan-10-one (5) (250 mg) in dry Et_2O (40 ml), $LiAlH_4$ (53 mg) was added during 3 min. After 1 h at room temperature, water was added (1 ml) and the organic layer dried. Silica gel (20 g) column chromatography (eluant n-hexane to n-hexane–Et_2O, 8 : 1 v/v) of the residue from the solvent evaporation afforded (7a) [181 mg, b.p. 105—110 °C at 0.1 mmHg, m.p. 62 °C; $\nu_{max.}$ (Nujol) 3 360 cm^{-1}; δ 4.16 (1 H, m, -C*H*OH)] and (7b) [45 mg, b.p. 105—110 °C at 0.1 mmHg, m.p. 70 °C; $\nu_{max.}$ (Nujol) 3 280 cm^{-1}; δ 4.03 (1 H, m, -C*H*OH)].

Crystal Structure of 9,11-*Dibromotricyclo*[6.3.1.0^{1,5}]-*dodecan*-10-*one* (6).—Crystals are colourless prisms, elongated on [100]. Preliminary cell dimensions and space-group data were obtained from oscillation and Weissenberg photographs. Lattice parameters were refined by a least-squares fit of 14 $(\theta,\chi,\varphi)_{hkl}$ measurements taken on a Siemens single-crystal diffractometer.

Crystal data. $C_{12}H_{16}Br_2O$, M = 336.1. Monoclinic, a = 7.24(1), b = 14.90(1), c = 22.61(1) Å, β = 93.0(2)°, Z = 8, D_m = 1.83 g cm^{-3}, U = 2 435.7 Å^3. Cu-K_α radiation, λ = 1.541 8 Å; μ(Cu-K_α) = 91.3 cm^{-1}. Space group $P2_1/c$ from systematic absences.

Intensity data were collected on a Siemens single-crystal diffractometer up to θ 70° by use of the ω—2θ scan method and the five-points technique [12] (nickel-filtered Cu-K_α radiation). Of 4 577 independent reflections measured, 3 204 were used in the crystal analysis, having intensities $\geqslant 2[\sigma^2(I) + 10^{-4} I^2]^{1/2}$, where I is the relative intensity and $\sigma^2(I)$ its variance. The dimensions of the crystal used in the analysis were 0.3 × 0.4 × 0.8 mm in the *x, y, z* directions. Absorption was ignored.

Structure analysis and refinement. Data were put on an absolute scale by Wilson's method [13] and normalized structure-factor amplitudes were derived. The structure was solved from 499 reflections with $|E| \geqslant 1.59$. The basic set was chosen using the programme MULTAN [14] and an E map, computed by using the most consistent set of signs, revealed the position of four bromine atoms. A structure-factor calculation carried out at this stage gave R 0.30. The remaining non-hydrogen atoms were located from a subsequent Fourier calculation. The structure was refined by block-diagonal least-squares cycles first with isotropic and then with anisotropic thermal parameters, reducing R to 0.085. A difference-Fourier synthesis was then computed and revealed significant residual peaks near the positions where the hydrogen atoms were expected to occur. A few least-squares cycles with unit weights were then

TABLE 4

Fractional co-ordinates (× 10^4; × 10^3 for H atoms) with standard deviations in parentheses

	Molecule (1)			Molecule (2)		
	x	*y*	*z*	*x*	*y*	*z*
Br(1)	171(1)	4 772(1)	3 158(1)	−2 326(1)	1 748(1)	527(1)
Br(2)	664(2)	2 665(1)	2 261(1)	−3 117(1)	4 077(1)	−113(1)
O(1)	286(8)	4 807(4)	1 680(2)	−3 004(7)	2 112(4)	−920(2)
C(1)	−738(11)	4 380(5)	1 982(3)	−1 836(10)	2 457(5)	−591(3)
C(2)	−1 715(10)	4 837(5)	2 488(3)	−703(10)	1 890(4)	−150(3)
C(3)	−3 567(10)	4 453(5)	2 644(3)	1 222(10)	2 225(4)	48(3)
C(4)	−3 541(11)	3 438(5)	2 624(3)	1 190(11)	3 238(5)	138(3)
C(5)	−3 125(12)	3 148(5)	1 988(3)	581(11)	3 691(5)	−464(3)
C(6)	−1 209(11)	3 418(5)	1 836(3)	−1 411(11)	3 442(5)	−634(3)
C(7)	−4 576(12)	3 535(6)	1 520(3)	1 831(11)	3 409(5)	−965(4)
C(8)	−4 780(11)	4 539(6)	1 558(3)	2 044(11)	2 398(5)	−1 040(3)
C(9)	−5 109(11)	4 820(5)	2 200(3)	2 587(11)	1 978(5)	−441(3)
C(10)	−5 369(12)	5 790(6)	2 359(4)	2 875(11)	981(5)	−386(3)
C(11)	−4 855(12)	5 813(6)	3 042(4)	2 613(12)	781(5)	274(3)
C(12)	−4 275(11)	4 867(5)	3 217(3)	2 131(11)	1 663(5)	543(3)
H(1)	−185(8)	549(4)	239(3)	−53(9)	127(4)	−32(3)
H(2)	−239(10)	316(5)	288(3)	29(9)	340(5)	44(3)
H(3)	−466(9)	319(5)	276(3)	248(9)	344(5)	28(3)
H(4)	−101(9)	334(4)	141(3)	−167(9)	365(4)	−109(3)
H(5)	−317(10)	244(5)	197(3)	387(9)	226(4)	−31(3)
H(6)	−642(9)	452(4)	231(3)	72(9)	437(4)	−43(3)
H(7)	−429(9)	338(4)	111(3)	141(9)	367(5)	−136(3)
H(8)	−583(9)	322(4)	158(3)	314(9)	368(4)	−88(3)
H(9)	−582(9)	476(5)	129(3)	86(9)	216(4)	−120(3)
H(10)	−362(9)	484(5)	142(3)	294(9)	225(4)	−135(3)
H(11)	−443(9)	621(4)	213(3)	191(9)	63(5)	−66(3)
H(12)	−663(9)	602(4)	223(3)	403(9)	77(4)	−51(3)
H(13)	−598(9)	604(5)	327(3)	154(9)	34(5)	34(3)
H(14)	−383(9)	627(4)	314(3)	376(9)	52(4)	47(3)
H(15)	−325(9)	488(4)	355(3)	338(9)	197(5)	71(3)
H(16)	−533(9)	454(5)	338(3)	127(9)	159(4)	87(3)

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computed including the hydrogen atoms with isotropic thermal parameters, and giving a final R factor of 0.067. Final positional parameters together with their standard deviations are given in Table 4. Atomic scattering factors used were from ref. 15 for non-hydrogen atoms and from ref. 16 for hydrogen. Observed and calculated structure-factors and thermal parameters are listed in Supplementary Publication No. SUP 21886 (21 pp., 1 microfiche).*

* See Notice to Authors No. 7, in *J.C.S. Perkin II*, 1975, Index issue.

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