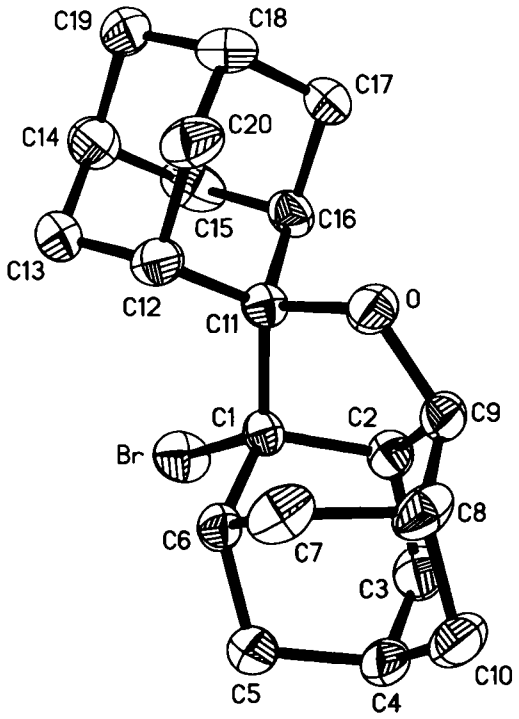
Crystal structure of 2,4′-oxa-2′-bromo-2,2′-bisadamantane, $C_{20}H_{27}BrO$

Carsten Wattenbach[I], Dieter Lenoir[II], Cinzia Chiappe[III] and Ulrich Müller*,[IV]

[I] Technische Universität München, Lehrstuhl für Chemisch-Technische Analyse und Chemische Lebensmitteltechnologie, D-85350, Freising, Germany
[II] Institut für Ökologische Chemie, GSF-Forschungszentrum für Umwelt und Gesundheit, Postfach 1129, D-85778 Neuherberg, Germany
[III] Universita di Pisa, Dipartimento Chimica Bioorganica e Biofarmacia, Via Bonanno 33, I-56126 Pisa, Italy
[IV] Universität Marburg, Fachbereich Chemie, D-35032 Marburg, Germany

Received November 12, 2001, accepted February 11, 2002; CCDC-No. 1267/723



Abstract

$C_{20}H_{27}BrO$, monoclinic, *I*12/*a*1 (No. 15), $a = 24.359(3)$ Å, $b = 6.9025(6)$ Å, $c = 19.369(3)$ Å, $\beta = 99.76(1)°$, $V = 3209.5$ Å^3, $Z = 8$, $R_{gt}(F) = 0.055$, $wR_{ref}(F^2) = 0.162$, $T = 193$ K.

Source of material

A solution of 0.2 g (0.07 mmol) (1*R**,2*R**)-2-hydroxy-4-(tricyclo[3.3.1.1^{3,7}]decylidene)-tricyclo[3.3.1.1^{3,7}]decane in 40 mL dichloromethane was cooled in an ice bath and treated dropwise with bromine until the solution remained slightly coloured. After 1 min the solvent was evaporated under reduced pressure. The residue was recrystallized from methanol to yield an almost white solid (0.216 g, 85 %; mp 381 K – 384 K).

Discussion

The mechanism of bromination of adamantylidene-adamantane was studied recently [1]. Now we have studied the bromination of 4-eq substituted adamantylidene-adamantanes in aprotic polar solvents like dichloromethane and tetrachloroethane [2]. Stable bromonium ions were obtained in solution with 4-eq halogen substituted compounds. However, the 4-eq OH derivative yields an addition- elimination product, whose structure is presented in this paper.

Table 1. Data collection and handling.

Crystal:	colourless, irregular
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	25.62 cm^{-1}
Diffractometer, scan mode:	Stoe IPDS-II, $\Delta\omega = 1°$
$2\theta_{max}$:	52.04°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	13182, 2999
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 2424
$N(param)_{refined}$:	200
Program:	SHELX-97 [3]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{iso}
H(2)	8*f*	0.1823	0.2601	0.3165	0.051
H(3A)	8*f*	0.2137	0.3566	0.4329	0.067
H(3B)	8*f*	0.1497	0.3095	0.4239	0.067
H(4)	8*f*	0.1676	0.6084	0.4833	0.065
H(5A)	8*f*	0.0967	0.7833	0.4119	0.063
H(5B)	8*f*	0.0802	0.5631	0.4082	0.063
H(6)	8*f*	0.0663	0.6991	0.2934	0.049
H(7A)	8*f*	0.1391	0.9320	0.3238	0.066
H(7B)	8*f*	0.1425	0.8318	0.2517	0.066
H(8)	8*f*	0.2323	0.8250	0.3173	0.064
H(9)	8*f*	0.2494	0.4965	0.3094	0.059
H(10A)	8*f*	0.2460	0.6906	0.4320	0.074
H(10B)	8*f*	0.2043	0.8656	0.4277	0.074
H(12)	8*f*	0.0862	0.7091	0.1802	0.056
H(13A)	8*f*	0.0157	0.5739	0.0992	0.069
H(13B)	8*f*	0.0202	0.4567	0.1694	0.069
H(14)	8*f*	0.0129	0.2391	0.0731	0.073
H(15A)	8*f*	0.0916	0.0458	0.1201	0.075
H(15B)	8*f*	0.0630	0.1300	0.1806	0.075
H(16)	8*f*	0.1609	0.1780	0.2088	0.055
H(17A)	8*f*	0.2053	0.3658	0.1315	0.063
H(17B)	8*f*	0.1768	0.1840	0.0917	0.063
H(18)	8*f*	0.1553	0.4644	0.0220	0.063
H(19A)	8*f*	0.0579	0.4236	–0.0022	0.073
H(19B)	8*f*	0.0869	0.2199	0.0092	0.073
H(20A)	8*f*	0.1029	0.7144	0.0634	0.065
H(20B)	8*f*	0.1602	0.6904	0.1139	0.065

* Correspondence author (e-mail: mueller@chemie.uni-marburg.de)

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Br	8*f*	0.05806(2)	0.28082(7)	0.30513(3)	0.0544(3)	0.0592(3)	0.0632(4)	–0.0217(2)	0.0274(2)	–0.0007(2)
O	8*f*	0.1872(1)	0.5435(4)	0.2266(2)	0.041(2)	0.064(2)	0.039(2)	–0.010(1)	0.010(1)	0.005(1)
C(1)	8*f*	0.1179(1)	0.4585(5)	0.2883(2)	0.028(2)	0.035(2)	0.040(2)	–0.003(1)	0.010(2)	0.003(1)
C(2)	8*f*	0.1736(2)	0.3910(6)	0.3310(2)	0.042(2)	0.045(2)	0.040(2)	0.008(2)	0.008(2)	0.013(2)
C(3)	8*f*	0.1770(2)	0.3974(8)	0.4100(2)	0.050(2)	0.078(3)	0.041(3)	0.006(2)	0.011(2)	0.019(2)
C(4)	8*f*	0.1656(2)	0.6034(8)	0.4324(2)	0.043(2)	0.088(3)	0.033(2)	0.000(2)	0.008(2)	0.000(2)
C(5)	8*f*	0.1067(2)	0.6569(7)	0.3960(2)	0.044(2)	0.065(3)	0.049(3)	0.001(2)	0.012(2)	–0.007(2)
C(6)	8*f*	0.1037(2)	0.6599(6)	0.3161(2)	0.037(2)	0.041(2)	0.044(2)	0.005(2)	0.004(2)	–0.004(2)
C(7)	8*f*	0.1459(2)	0.8102(6)	0.3018(3)	0.073(3)	0.044(2)	0.047(3)	–0.010(2)	0.003(2)	0.003(2)
C(8)	8*f*	0.2044(2)	0.7375(7)	0.3310(3)	0.051(3)	0.067(3)	0.042(3)	–0.028(2)	0.006(2)	0.000(2)
C(9)	8*f*	0.2104(2)	0.5381(7)	0.3015(2)	0.033(2)	0.078(3)	0.039(2)	–0.007(2)	0.010(2)	0.004(2)
C(10)	8*f*	0.2092(2)	0.7353(8)	0.4109(3)	0.050(3)	0.092(4)	0.042(3)	–0.016(2)	0.005(2)	–0.007(2)
C(11)	8*f*	0.1309(2)	0.4609(5)	0.2117(2)	0.034(2)	0.036(2)	0.039(2)	–0.006(1)	0.012(2)	0.002(1)
C(12)	8*f*	0.0937(2)	0.5863(6)	0.1582(2)	0.058(2)	0.041(2)	0.039(2)	0.012(2)	0.007(2)	–0.000(2)
C(13)	8*f*	0.0392(2)	0.4871(7)	0.1306(3)	0.048(2)	0.074(3)	0.051(3)	0.018(2)	0.008(2)	–0.009(2)
C(14)	8*f*	0.0488(2)	0.2998(8)	0.0914(3)	0.042(2)	0.076(3)	0.064(3)	–0.011(2)	0.008(2)	–0.028(2)
C(15)	8*f*	0.0836(2)	0.1640(6)	0.1436(3)	0.077(3)	0.037(2)	0.081(4)	–0.013(2)	0.038(3)	–0.019(2)
C(16)	8*f*	0.1386(2)	0.2653(6)	0.1753(2)	0.046(2)	0.046(2)	0.049(3)	0.014(2)	0.014(2)	0.001(2)
C(17)	8*f*	0.1697(2)	0.3052(7)	0.1140(3)	0.041(2)	0.069(3)	0.049(3)	0.006(2)	0.016(2)	–0.008(2)
C(18)	8*f*	0.1350(2)	0.4384(7)	0.0605(2)	0.064(3)	0.055(2)	0.042(2)	–0.001(2)	0.019(2)	–0.004(2)
C(19)	8*f*	0.0800(2)	0.3403(8)	0.0321(3)	0.049(3)	0.087(3)	0.044(3)	0.009(2)	0.001(2)	–0.020(2)
C(20)	8*f*	0.1249(2)	0.6278(6)	0.0966(2)	0.073(3)	0.049(2)	0.041(2)	0.003(2)	0.009(2)	0.005(2)

References

1. Brown, R. S.: Investigation of the early steps in electrophilic bromination through the study of the reaction with sterically encumbered olefins. Acc. Chem. Res. **30** (1997) 131-137.
2. Chiappe, C.; De Rubertis, A.; Jaber, A.; Lenoir, D.; Wattenbach, C.; Pomelli, C. S.: Reactivity of homoallylic substituted adamantylidene-adamantanes with bromine. In preparation.
3. Sheldrick, G. M.: SHELX-97, a program package for crystal structure solution and refinement. University of Göttingen, Germany 1997.