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Synthesis and structures of 1,4-bis(chloromethyl)- and 1,4-bis(bromomethyl)cubanes

***A. V. Shastin,*[a]* *L. B. Romanova,*[a] *L. T. Eremenko,*[a] *V. V. Zakharov,*[a] *G. V. Lagodzinskaya,*[a]**
***G. G. Aleksandrov,*[b] *and I. L. Eremenko*[b]**

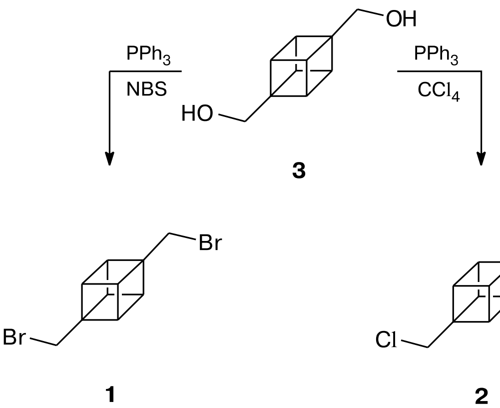
[a]*Institute of Problems of Chemical Physics, Russian Academy of Sciences,*
1 prosp. Akad. Semenova, 142432 Chernogolovka, Moscow Region, Russian Federation.
Fax: +7 (496) 515 5420. E-mail: shastin@icp.ac.ru
[b]*N. S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences,*
31 Leninsky prosp., 119991 Moscow, Russian Federation.
Fax: +7 (495) 952 1279. E-mail: ilerem@igic.ras.ru

1,4-Bis(chloromethyl)- and 1,4-bis(bromomethyl)cubanes were synthesized by the reactions of triphenylphosphine with CCl_4 and NBS, respectively. The structures of the compounds were studied by X-ray diffraction analysis.

Key words: cubane derivatives, diols, alkyl chlorides, alkyl bromides, X-ray diffraction analysis.

1,4-Bis(halomethyl)cubanes, of which only 1,4-bis(bromomethyl)cubane (**1**) has been described,[1] can be of interest for the preparation of cubane-containing compounds. In the present work, we synthesized dibromide **1** using a new procedure and, for the first time, 1,4-bis(chloromethyl)cubane (**2**) from 1,4-bis(hydroxymethyl)cubane (**3**) (Scheme 1) and studied their molecules by X-ray diffraction analysis.

Scheme 1



The CCl_4—PPh_3 system has been well recognized in the chlorodehydroxylation of alcohols that readily undergo isomerization under standard conditions of hydroxyl group substitution for halogen.[2,3] In the case of compound **3**, which is poorly soluble in CCl_4 being the medium for chlorodehydroxylation, the reaction occurs rather slowly and the yield of dichloride **2** does not exceed 50%. Dibromide **1** was synthesized by the reaction of diol **3** with a PPh_3—NBS complex according to an earlier described procedure.[4] A similar synthesis of related diiodide was also attempted using a PPh_3—NIS system; however, we failed to isolate the compound in the pure state.

Attempts to substitute bromine and chlorine in compounds **1** and **2** for iodine using a $LiI \cdot H_2O$ system in acetone gave a complex mixture of products containing no cubane cage (IR and NMR spectroscopic data). This indicates that the reaction proceeds, most likely, through the intermediate formation of carbocationic intermediates (cationic rearrangements of halomethylcubanes and hydroxymethylcubanes to the corresponding homocubanes have been described[1,5,6]).

According to the X-ray diffraction data, the crystals of dichloride **2** contain so-called non-classical hydrogen bonds (chlorine—hydrogen) of the halomethyl groups (the distances between the atoms are shorter than the sum of their van der Waals radii). Interactions of this type stabilizing the crystal structure are rather abundant for compounds containing only carbon, hydrogen, and halogen atoms.[7]

Experimental

IR spectra were recorded on a Specord M-82 spectrophotometer, and ^1H and ^{13}C NMR spectra were obtained on Bruker WM-250 and Bruker AM-300 instruments using Me_4Si as internal standard and $CDCl_3$ as the solvent. X-ray diffraction studies

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were carried out on a Bruker AXS SMART automated diffractometer equipped with a CCD detector (graphite monochromator, 110 °C, ω scan mode with an increment of 0.3°, frame exposure 30 s, $2\theta_{max}$ = 42 and 60° for compounds **1** and **2**, respectively) using a standard procedure.[8] The structures of the both compounds were determined by direct methods and refined in the full-matrix anisotropic approximation for the Br atom, in the isotropic approximation for all other atoms in structure **1**, and in the anisotropic approximation for all non-hydrogen atoms in structure **2**. Hydrogen atoms were geometrically revealed and refined isotropically in the riding model. The calculations were performed using the SHELX97 program package.[8,9] The crystallographic data and selected refinement parameters for compounds **1** and **2** are given in Table 1. Compounds **1** and **2** have similar structures. Bond lengths and bond angles are presented only for more exact structure **2** in Table 2.

Table 1. Crystallographic parameters of compounds **1** and **2**

Parameter	1	2
Molecular formula	$C_{10}H_{10}Br_2$	$C_{10}H_{10}Cl_2$
Space group	*P*2(1)/*c*	*P*2(1)/*c*
a/Å	6.035(12)	5.332(3)
b/Å	7.365(17)	11.074(7)
c/Å	11.49(3)	7.787(4))
β/deg	104.67(10)	105.83(4)
V/Å^3	494(2)	442.3(4)
Z	2	2
ρ_{calc}/g cm^{-3}	1.950	1.510
μ/cm^{-1}	8.146	0.668
Radiation	Mo-Kα (λ = 0.71073 Å)	Mo-Kα (λ = 0.71073 Å)
Number of independent reflections	400	993
Number of reflections with $I > 2\sigma$	268	917
R_1	0.0803	0.0428
wR_2 (for observed reflections)	0.1878	0.1293

Table 2. Selected geometric characteristics of compound **2**

Bond	*d*/Å	Bond	*d*/Å
Cl(1)—C(5)	1.804(2)	C(2)—C(4)	1.574(2)
C(1)—C(2)	1.560(3)	C(3)—C(4)	1.572(3)
C(1)—C(4)	1.572(2)	C(3)—C(1)	1.574(2)
C(1)—C(3)	1.574(2)	C(4)—C(5)	1.494(3)
C(2)—C(3)	1.568(2)	C(4)—C(2)	1.574(2)
Angle	ω/deg	Angle	ω/deg
C(2)—C(1)—C(4)	90.17(13)	C(4)—C(3)—C(1)	89.45(13)
C(2)—C(1)—C(3)	90.53(13)	C(5)—C(4)—C(3)	126.68(15)
C(4)—C(1)—C(3)	89.81(11)	C(5)—C(4)—C(1)	124.67(14)
C(1)—C(2)—C(3)	90.25(13)	C(3)—C(4)—C(1)	89.66(13)
C(1)—C(2)—C(4)	89.89(12)	C(5)—C(4)—C(2)	124.57(15)
C(3)—C(2)—C(4)	90.00(10)	C(3)—C(4)—C(2)	90.13(12)
C(2)—C(3)—C(4)	89.92(13)	C(1)—C(4)—C(2)	90.01(11)
C(2)—C(3)—C(1)	90.17(11)	C(4)—C(5)—Cl(1)	108.95(13)

Diol **3** was synthesized according to a described procedure[10]; its melting point and spectral characteristics coincided with literature data.

Chromatography was conducted on a short (5 cm) column packed with silica gel L 5/40 using hexane as the eluent. Reagents NIS and NBS (Aldrich) were used as purchased, and solvents (Khimmed) were distilled before use (THF was refluxed over LiH and then distilled).

1,4-Bis(bromomethyl)cubane (1). A solution of NBS (325 mg, 1.83 mmol) in THF (10 mL) was added with stirring and cooling on an ice bath to a solution of PPh_3 (479 mg, 1.83 mmol) in THF (10 mL). Then THF (10 mL) was added to a white precipitate that formed, and after this diol **3** (100 mg, 0.61 mmol) was added in one portion. The reaction mixture was stirred for 24 h at room temperature. An additional portion of NBS (50 mg) was added to the mixture before the final work up. The solvent was evaporated *in vacuo*, the residue was extracted with hot hexane (3×100 mL), and the extract was left to stand for ~14 h. A precipitated $Ph_3P=O$ was filtered off, hexane was distilled off *in vacuo*, and the residue was dissolved in hot hexane (50 mL). After cooling the solution was passed through the short silica gel layer, and the solvent was distilled off. The products were isolated on a chromatographic column using hexane as the eluent. Compound **1** was obtained in a yield of 70 mg (40%) as a viscous oil, whose recrystallization from hexane gave a sample with m.p. 65—66 °C (*cf.* Ref. 1: m.p. 65—66 °C). The ^{1}H NMR spectra of the obtained oil and crystallization product coincided completely and contained no admixture signals. IR (KBr), ν/cm^{-1}: 2989 s, 2953 m, 2924 w, 2850 w, 1462 w, 1434 w, 1420 w, 1377 w, 1329 w, 1273 w, 1225 s, 1205 w, 1188 w, 1162 w, 1140 w, 1075 w, 1029 w, 975 w, 933 w, 840 m, 828 w, 808 w, 758 w, 675 w, 639 m, 593 w, 571 w. ^{1}H NMR, δ: 3.67 (s, 4 H, CH_2); 3.73 (s, 6 H, CH_{cubane}). ^{13}C NMR, δ: 58.47 ($C_{quatern}$); 44.34 (CH); 36.36 (CH_2Br).

1,4-Bis(chloromethyl)cubane (2). A solution of PPh_3 (1.57 g, 6 mmol) and diol **3** (328 mg, 2 mmol) in anhydrous CCl_4 (50 mL) was refluxed for 105 h protected from atmosphere by a tube with $CaCl_2$. Then the solvent was distilled off *in vacuo*, the residue was extracted with hot hexane (3×100 mL), and the extract was left to stand for ~14 h. A precipitated $Ph_3P=O$ was filtered off, hexane was distilled off *in vacuo*, and the residue was dissolved in 50 mL of hot hexane. After cooling the solution was passed through a short silica gel layer, and the solvent was distilled off. The products were isolated on a chromatographic column using at first hexane and then chloroform as eluents. Compound **2** was obtained in a yield of 200 mg (50%) as a viscous oil, whose recrystallization from hexane gave a sample with m.p. 54—55 °C. ^{1}H NMR spectra of the oily product and crystallization product coincided completely and contained no admixture signals. Found (%): C, 59.53; H, 5.25; Cl, 35.30. $C_{10}H_{10}Cl_2$. Calculated (%): C, 59.73; H, 5.01; Cl, 35.26. IR (KBr), ν/cm^{-1}: 2988 s, 2980 s, 2972 s, 2952 m, 2924 w, 2849 w, 1460 w, 1431 w, 1330 w, 1265 s, 1232 w, 1193 w, 1170 w, 1140 w, 1008 w, 934 w, 852 w, 844 m, 824 w, 700 s, 673 m, 622 w, 612 w. ^{1}H NMR, δ: 3.756 (s, 4 H, CH_2); 3.772 (s, 6 H, CH_{cubane}). ^{13}C NMR, δ: 58.38 ($C_{quatern}$); 46.49 (CH); 43.96 (CH_2Cl).

Crystals of compound **2** suitable for X-ray diffraction analysis were obtained by slow evaporation of its hexane solution.

1,4-Bis(iodomethyl)cubane. A solution of NIS (250 mg, 1.1 mmol) in THF (5 mL) was added with stirring and cooling on an ice bath to a solution of PPh_3 (290 mg, 1.1 mmol) in THF

(10 mL). More THF (5 mL) was added to a viscous mixture containing white precipitate that formed (to facilitate stirring), and immediately after this diol **3** (82 mg, 0.5 mmol) was added in one portion. The reaction mixture was stirred for 18 h at room temperature and then treated as in the synthesis of dichloride **2**. A viscous oil (98 mg) obtained consisted of ~80% of the target product (NMR data). An attempt to purify the product by column chromatography or recrystallization failed. ^{1}H NMR, δ: 3.61 (s, 6 H, CH_{cubane}); 3.50 (s, 4 H, CH_2). ^{13}C NMR, δ: 55.65 ($C_{quatern}$); 44.72 (CH); 11.06 (CH_2I).

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