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Halogen Migration of 2,2-Dihaloadamantane Induced by Aluminum Halides

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We reported on the halogen migration in the reaction of organic dihalides with aluminum halide.[1] McKervey and coworkers have shown the formation of 1,3-dichloroadamantane (IVa) from 2,2-dichloroadamantane (Ia) when Ia was treated with aluminum chloride in carbon tetrachloride.[2] When the reaction of Ia was effected in nitromethane, they could identify a mixture of *trans*- and *cis*-1,4-dichloroadamantanes (Va) (VIa) from the reaction mixture. However, no experimental details were given. As an effective means for the synthesis of new haloadamantane,[3] we have reinvestigated the reaction in more detail under slightly different conditions.

When a solution of 2,2-dichloroadamantane[2] (Ia) was treated with anhydrous aluminum chloride at a low temperature, six compounds IIa—VIIa (conversion 100%) could be separated by a combination of column chromatography and preparative glc (Scheme 1; % ratio in brackets). Compounds IIa, IIIa, and IVa were identified by comparison with the corresponding authentic samples. The structure of stereoisomers (Va) and (VIa) were assigned to *trans*- and *cis*-1,4-dichloroadamantanes, respectively, mainly by spectroscopic

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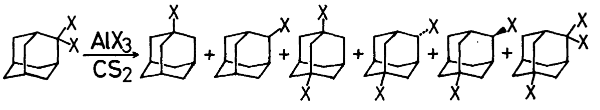
[2] M. A. McKervey, D. Grant, and H. Hamill, *Tetrahedron Lett.*, 1975 (1970).

[3] *Cf.* R. Keese and E.-P. Krebs, *Angew. Chem.*, **83**, 254 (1971).



I II III IV V VI VII

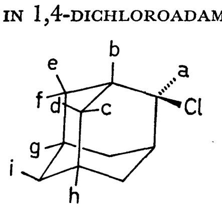
a X = Cl a(0.3) a(6.4) a(1.8) a(22.9) a(62.7) a(5.9)

b X = Br b(3.9) b(16.0) b(0.3) b(22.9) b(40.1) b(16.8)

Scheme 1

methods. The fragmentation patterns of mass spectra of Va and VIa were very similar. NMR spectrum of Va showed the existence of one proton due to CH–Cl at δ 4.26, and that of VIa at δ 4.19. When these shift values were compared with those of a mixture of Va and VIa derived from 1,4-dihydroxyadamantane[4) a very good coincidence was observed (Table 1). The product (VIIa) was assigned to 1,4,4-trichloroadamantane, since VIIa was identical with the compound obtained by the reaction of 1-hydroxyadamantan-4-one[4) with a mixture of phosphorus trichloride and phosphorus pentachloride. 2,2-Dibromoadamantane (Ib)[5) being more reactive than Ia, its reaction with aluminum bromide was carried out at lower concentration and temperature. Six products (IIb—VIIb) were obtained (conversion 100%; % ratio in brackets in Scheme 1) and each was identified similarly, Vb, VIb, and VIIb being new compounds.

Table 1. Chemical shift values (δ) of the secondary protons in 1,4-dichloroadamantanes



Proton	Calcd for[a) 1,4-*ax.* (h=Cl)	Found for[b) VIa (h=Cl)	Calcd for[a) 1,4-*eq.* (g=Cl)	Found for[b) Va (g=Cl)
a	4.31	4.19 (4.23)[c)	4.31	4.26 (4.33)[c)
c	2.60	2.67 (2.66)	2.19	
d	1.90		1.49	1.50 (1.50)
e,f	1.78	1.84 (1.82)	2.19	
i	2.09	2.13 (3.13)	2.09	2.17 (2.13)

a) Values calculated by using the substituent shift data of 1- and 2-chloroadamantanes.[4)

b) Observed values.

c) Values estimated from the mixture of 1,4-dichloroadamantanes.[4)

The reactions of VIa and IIIa were also investigated. A solution of VIa was treated with aluminum chloride at −15—−20°C. The formation of IIa—Va was confirmed by glc method (conversion 38.3%) (Scheme 2). A similar reaction of IIIa was conducted at −35—−40°C, and adamantane, IIa, Va, and VIa were produced (conversion 61.6%).

$$\text{VIa} \xrightarrow[\text{CS}_2]{\text{AlCl}_3} \text{IIa}(1.2) + \text{IIIa}(5.6) + \text{IVa}(18.5) + \text{Va}(74.4)$$

$$\text{IIIa} \xrightarrow[\text{CS}_2]{\text{AlCl}_3} \text{Adamantane}(21.9) + \text{IIa}(71.1) + \text{Va}(1.0) + \text{VIa}(5.4)$$

Scheme 2

Experimental

All mp are uncorrected. IR spectra were obtained in nujol mull on a Shimadzu IR-27 spectrophotometer. MS spectra were taken using a Hitachi RMS-4 mass spectrometer. NMR spectra were obtained on a JEOL C-60H spectrometer in CCl_4 solution, TMS being chosen as an internal standard.

Authentic Samples. 1-Chloroadamantane (IIa),[6) 2-chloroadamantane (IIIa),[7) 1,3-dichloroadamantane (IVa),[8) 1-bromoadamantane (IIb),[6) 2-bromoadamantane (IIIb),[7) and 1,3-dibromoadamantane (IVb)[9) were prepared according to the reported methods.

Reaction of Ia with aluminum chloride. To a solution of Ia (3.83 g) in 80 m*l* of carbon disulfide, 4 g of aluminum chloride was added at −40°C. The solution was stirred at −35—−40°C for 3.5 hr. It was then poured onto ice and extracted three times with ether. The extract was washed with dil. aqueous NaOH and dried ($CaCl_2$). Evaporation of the solvent yielded 3.7 g (96%) of a white solid which was separated into six compounds (IIa—VIIa) by silica gel column chromatography with *n*-hexane as an eluent followed by preparative glc (15% HVSG on chromosorb W AW, 3 m, 150°C, 40 m*l* N_2/min). Va: mp 131.5—133.5°C, MS: 204 (M^+), 159 (100%), 133, 91, NMR: δ 4.26 (1H, bs), 1.20—2.95 (13H, adamantyl), IR: 1347 (m), 1231 (m), 1102 (m), 1030 (s), 946 (m), 923 (m), 823 (s), 783 (m), 764 (s) cm^{-1}, Found: C, 58.50; H, 6.85%. Calcd for $C_{10}H_{14}Cl_2$: C, 58.55; H, 6.88%. VIa: mp 157—159°C, MS: 204 (M^+), 169 (100%), 133, 91, NMR: δ 4.19 (1H, bs), 1.43—3.00 (13H, adamantyl), IR: 1350 (m), 1099 (m), 1025 (s), 923 (m), 833 (s), 786 (m), 763 (m) cm^{-1}, Found: C, 58.48; H, 7.01%. Calcd for $C_{10}H_{14}Cl_2$: C, 58.55; H, 6.88%. VIIa: MS: 238 (M^+), 203 (100%), 167, 131, 91, NMR: δ 1.45—3.05 (13H), IR: 1348 (m), 1028 (s), 946 (m), 926 (m), 800 (s) cm^{-1}, mp 152/153°C with no depression when admixed with the authentic specimen described below. Found: C, 50.13; H, 5.53%. Calcd for $C_{10}H_{13}Cl_3$: C, 50.12; H, 5.47%.

Reaction of Ib with Aluminum Bromide. To a solution of Ib (3 g) in 100 m*l* of carbon disulfide, 3 g of aluminum bromide was added at −78°C. The mixture was stirred at −73—−78°C for 2.5 hr. The same treatment as above yielded 2.98 g (98%) of a white solid. This mixture was separated into six compounds (IIb—VIIb) by the same procedure as described above (column temp: 175°C). Vb: mp 143—146°C, MS: 292 (M^+), 213 (100%), 133, 91, NMR: δ 4.55 (1H, bs, CH–Br), 1.40—2.75 (13H, adamantyl), IR: 1342 (m), 1196 (m), 1019 (s), 937 (m), 918 (m), 806 (s), 738 (s) cm^{-1}, Found: C, 40.80; H, 4.85%. Calcd for $C_{10}H_{14}Br_2$: C, 40.85; H, 4.80%. VIb: mp 109/110°C, MS: 292 (M^+), 213 (100%), 133, 91, NMR: δ 4.50 (1H, bs, CH–Br), 1.57—3.31 (13H, adamantyl), IR: 1348 (m), 1258 (m), 1191 (m), 1100 (m), 1018 (s), 939 (m), 918 (m), 817 (m), 808 (m), 773 (m), 738 (s) cm^{-1}, Found: C, 40.76;

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H, 4.92%. Calcd for $C_{10}H_{14}Br_2$: C, 40.85; H, 4.80%. VIIb: mp 120—122°C, MS: 291 (M^+-Br), 211, 131, 91, NMR: δ 1.50—3.50 (13H), IR: 1342 (m), 1290 (m), 1248 (m), 1096 (m), 1023 (s), 936 (m), 914 (s), 812 (s), 757 (s) cm^{-1}, Found: C, 32.26; H, 3.62%. Calcd for $C_{10}H_{13}Br_3$: C, 32.21; H, 3.51%.

Reaction of VIa with Aluminum Chloride. To a solution of VIa (62 mg) in 1 m*l* of carbon disulfide, 134 mg of aluminum chloride was added at −20°C. The mixture was stirred at −15—−20°C for 3 hr. The usual work-up yielded 60 mg (96%) of a white solid which was analyzed by glc (column temp: 120°C).

Reaction of IIIa with Aluminum Chloride. To a solution of IIIa (51 mg) in 1 m*l* of carbon disulfide, 134 mg of aluminum chloride was added at −40°C. The mixture was stirred at −35—−40°C for 3 hr. The usual work-up gave 49 mg (96%) of a white solid which was subjected to glc analysis (column temp: 120°C).

Preparation of a Mixture of Va and VIa. To 1,4-dihydroxyadamantane (100 mg; a mixture of *trans*- and *cis*-isomers),[4] 3 m*l* of PCl_3 and 2 g of PCl_5 were added. The mixture was stirred for 26 hr at 70°C. Hydrolysis followed by extraction (Et_2O) gave 155 mg (95%) of a mixture of Va and VIa, mp 146—149°C (lit.[4] mp 148—151°C).

Preparation of a Mixture of Vb and VIb. This was obtained in 98% yield with a mixture of PBr_3 and PBr_5 by a similar procedure to that mentioned above, mp 99—101°C.

Preparation of VIIa. The authentic sample was obtained in 88% yield by treating 1-hydroxyadamantan-4-one[4] (150 mg) with a mixture of PCl_3 (3 m*l*) and PCl_5 (2 g) and gave correct analysis, mp 151—153°C.

Preparation of VIIb. The authentic specimen was obtained in 88% yield with a mixture of PBr_3 and PBr_5 by a similar procedure to the mentioned above and gave correct analysis, mp 120.5—122.5°C.

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