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A Novel Elimination of Bromine by Ethoxide Ion

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There are examples in the literature[1,2] of dehalogenation by alkoxide ion. In every case, however, there has been a driving force to a conjugated or an aromatic product. This paper reports the first elimination of molecular halogen from a saturated compound by alkoxide ion.

1, 2-Dibromo-tetrafluoroethane (Ⅰ) was mixed with a three-fold molar excess of potassium ethoxide in ethanol. The reaction yielded starting material and two products identified as the saturated fluorinated alkyl ether (Ⅴ) and 1-bromo-2-ethoxy-tetrafluoroethane (Ⅵ) isolated in 31% and 8% conversions respectively.

$$CF_2Br\text{-}CF_2Br \xrightarrow{-OEt} \left[CF_2Br\text{-}\overset{\ominus}{C}F_2 \right] \xrightarrow{-Br^-} CF_2{=}CF_2 \xrightarrow{-OEt}$$
Ⅰ　　Ⅱ　　Ⅲ

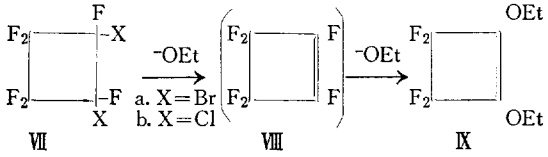
$$EtO\text{-}CF_2\text{-}\ddot{C}F_2^{\ominus} \xrightarrow{EtOH} EtO\text{-}CF_2CF_2Br\ (Ⅴ) + {}^-OEt$$
Ⅳ

$$EtO\text{-}CF_2\text{-}CF_2Br\ (Ⅵ) + CF_2Br\text{-}CF_2^{\ominus}$$

A possible explanation might be similar to that proposed by Miller[3]. Ethoxide ion attacked the bromine leaving the carbanion Ⅱ which expells bromide ion to yield Ⅲ. It is interesting to note, however, that no tetrafluoroethylene was detected during the reaction. Ⅲ then reacted with ethoxide ion to form the carbanion Ⅳ which either abstracted a proton from solvent ethanol to yield Ⅴ or a bromine from Ⅰ to yield Ⅵ.

Ⅵ could have also been formed by a reaction of Ⅳ with ethyl hypobromite. In addition, the idea that the formation of Ⅵ by an Sn^2 attack of ethoxide on Ⅰ cannot be ruled out.

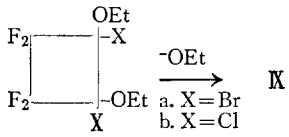
1, 2-Dibromo-hexafluorocyclobutane (Ⅶa) was treated with a five fold molar excess of ethoxide ion. A slow reaction at room temperature resulted in a quantitative yield of 1, 2-diethoxy-tetrafluorocyclobutene (Ⅸ) presumably through the in situ production of hexafluorocyclobutene (Ⅷ). Ⅷ is known to react with ethoxide ion to give Ⅸ[4].



Ⅶ　　Ⅷ　　Ⅸ

1, 2-Dichloro-hexafluorocyclobutane (Ⅶb) was similarly mixed with an excess of ethoxide ion at 40°C. for 18 hrs. No reaction took place.

When 1, 2-Dibromo-1, 2-diethoxy-3, 3, 4, 4-tetrafluorocyclobutane (Ⅹa) was mixed with an excess of ethoxide ion, an immediate exothermic reaction took place to give Ⅸ in 71% yield.



Ⅸ

When 1, 2-Dichloro-1, 2-diethoxy-3, 3, 4, 4-tetrafluorocyclobutane was mixed with ethoxide ion at 75°C. for 9 hrs., only starting material was found.

Both alpha-halo-ethers, Xa and Xb, proved to be remarkably stable to heat and hydrolysis. Xa started to decompose to a tar at 160°C. Xb boiled at 184°C. with no decomposition. Both compounds were subjected to conc. (95-98%) sulfuric acid at 95°C. Only starting material was recovered.

Experimental

Reaction of 1, 2-Dibromo-tetrafluoroethane (Ⅰ) with Ethoxide Ion. -75g. (0.29 mole) of 1, 2-dibromotetrafluoroethane and 56g. (0.85 mole) of 85% pure potassium hydroxide in 125 ml. of ethanol were mixed at room temperature. After one minute an extensive bright yellow precipitate formed instantaneously which turned dark and did not seem to increase with time. The reaction mixture was stirred for 45 hrs. at room temperature and 5 hrs. at 50°C. The precipitate was then filtered out as product mixture was poured into water. The organic layer that separated out was

washed twice with water. The aqueous washings were then 3 times with diethyl ether. The precipitate in filter paper was also washed with ether. The ether extracts were then washed once with water. The product and ether extracts were dried over anhyd. $CaCl_2$ and distilled on a 4-ft. Todd colum to yield 30g. (0.115 mole) of starting material and 11.79 (0.09 mole) $HCF_2CF_2OC_2H_5$, b. p. 50°C/625mm., n_D^{25} 1.295 (lit.[5] b. p. 50.7°C/622mm n_D^{25} 1.2961). Infrared spectrum identical to literature[5]. Analysis by gas-liquid chromatography showed this material to be 100% pure.

The n. m. r. spectrum contained three equal intensity triplets attributed to the single proton on the fluorinated carbon centered at 4.39 τ (ref. T. M. S.) with J'_{HF} of 53.6 cps. and J^2_{HF} of 2.8 cps. and a methylene quartet at 5.95 τ and methyl triplet at 8.67 τ.

The distillation also yielded 5.2g. (0.023 moles) of 1-bromo-2-ethoxy-tetrafluorethane, b. p. 76.5°C/624mm n_D^{25} 1.3433; d_4^{25} 1.593. Molar refraction: calcd. 30.08, obsd. 29.86.

Anal. Calcd. for $C_4H_5F_4BrO$: C, 21.35; H, 2.24; F, 33.78; Br, 35.52. Found: C, 21.44; H, 2.32; F, 33.96; Br, 35.29.

Analyeis by gas-liquid chromatography showed this material to be 100% pure.

The n. m. r. spectrum showed a methylene quartet centered at 5.90 τ and methyl triplet at 8.63 τ.

1, 2-Dibromohexafluorocyclobutane (VIIa). 79.0g. (0.339 mole) of 1, 2-dichlorohexafluorocyclobutane was added slowly through an addition funnel to a 250 ml. 3-necked flask charged with 32g. (0.5 mole) of zinc dust stirred in dibutoxy-tetraglycol at 80°C. The product hexafluorocyclobutene was conducted through a water reflux condenser to a dry-ice trap.

The contents of the trap was emptied into an autoclave with 80g. (0.5 mole) of molecular bromine. The autoclave heated at 140°C. for 12 hrs., then at 240° for 2 hrs. After cooling the contents of the autoclave was washed with aqueous sodium bisulfite solution to remove excess bromine, then poured into water in a separatory funnel. The organic layer was drawn off and dried overnight over anhyd. $MgSO_4$, then distilled on 2-foot glasshelice column to yield 73.0g. (0.227 mole) of the pure dibromo product, b. p. 90.0°C/630mm., n_D^{25} 1.3856 (lit.[6] b. p. 90~90.5°C/638mm., n_D^{20} 1.3838). The infrared spectrum is similar to that of 1, 2-dichlorohexafluorocyclobutane with the exception of two new peaks at 760cm^{-1} and 840 cm^{-1}. Analysis by gas-liquid chromatography showed this material to be 100% pure.

Reaction of 1, 2-Dibromohexafluorocyclobutane with Ethoxide Ion. 12.1g. (0.0387 mole) of 1, 2-dibromo-hexafluorocylobutane was mixed with 13g. of 85% pure KOH pellets (0.20 mole) dissolved in 85 ml. of absolute ethanol at room temperature. After 30 minutes a white precipitate started to form. Reaction was complete after 30 hrs. The reaction mixture was poured into water in separatory funnel and product layer drawn off. Product layer was washed twice with water. The aqueous washings were extracted with methylene chloride three times. The methylene chloride extracts in turn were washed twice with water again before being added to the product layer. The product and methylene chloride extracts were dried over anhyd. $MgSO_4$ and vacuum distilled on six-inch spiral column to yield 8.0g. (0.0373 mole) of 1, 2-diethoxy-3, 3, 4, 4-tetrafluorocyclobutene, b. p. 73°/20mm., n_D^{25} 1.3813 (lit.[4] b. p. 52.8°C/10.3mm., n_D^{25} 1,3790, Infrared spectrum and g. l. c. retention time were identical with those obtained from an authentic sample.

1, 2-Dichloro-1, 2-diethoxy-3, 3, 4, 4-tetrafluorocyclobutane. Chlorine gas was bubbled through 29.0g. (0.135 mole) of 1, 2-diethoxy-3, 3, 4, 4-tetrafluorocyclobutene kept at salt-ice-bath temperature and in the dark for 25 hrs. The progress of the reaction was followed by the increase in volume of the liquid in the reaction vessel. The reaction mixture was first washed with a cold aqueous solution of sodium bisulfite, followed by a water wash and then dried over anhyd. calcium sulfate. Distillation yielded 17.0g. (0.596 mole) of the dichloro product, b. p. 184°C/624mm., n_D^{25} 1.4049, d_4^{25} 1.375. Molar refraction: cacd. 50.44; obsd. 50.81.

Anal. Calcd. for $C_8H_{10}F_4Cl_2O_2$: C, 33.70; H, 3.54; Cl, 24.90. Found: C, 33.90; H, 3.53; Cl, 24.74.

Analysis by gas-liquid chromatography showed the heart cut to be greater than 95% pure. The other 5% were higher boiling compounds presumably due to chlorine substitution on the ethoxy groups.

1, 2-Dibromo-1, 2-diethoxy-3, 3, 4, 4-tetrafluorocyclobutane. To a stirred solution of 25.0g. (0.117 mole)

of 1, 2-diethoxy-3, 3, 4, 4-tetrafluorocyclobutene and 30 ml. of methylene chloride was added 19.0g. (0.119 mole) of liquid bromine. The mixture was heated to reflux with a 100 watt incandescent light bulb under approximately 1000 mm. Hg pressure for 24 hrs. The reaction mixture was washed with cold aqueous sodium bisulfite to remove excess bromine. After separation, the aqueous layer was extracted with methylene chloride. The methylene chloride extracts and product were dried over magnesium sulfate overnight and vacuum distilled to yield 32.7g. (0.0874 mole) of the dibromo adduct, b. p. 215°C/627mm., n_D^{25} 1.4474, d_4^{25} 1.7393. Molar refraction: calcd. 56.24; obsd. 57.47.

Anal. Calcd. for $C_8H_{10}F_4Br_2O_2$: C, 25.70; H, 2.70; F, 20.34; Br, 42.70. Found: C, 25.92; H, 2.84; F, 20.29; Br, 42.68.

Analysis by gas-liquid chromatography showed this material to be 100% pure.

Reaction of 1, 2-Dibromo-i1, 2-dethoxy-3, 3, 4, 4-tetrafluorocyclobutane with Ethoxide Ion. About 20 g. (0.054 mole) of 1, 2 dibromo-1, 2-diethoxy-3, 3, 4, 4-tetrafluorocyclobutane was mixed with 12g. (85% pure) of KOH (0.18 mole) dissolved in 30ml. of 95% ethanol at room temperature. The temperature of the pot mixture rose to 60°C. After 6 hrs., when the reaction mixture had cooled to room temprature, the products were washed with water several times and separated. The aqueous washings were extracted methylene chloride, and the combined extracts were dried over magnesium sulfate. Vacuum distillation on a six-inch spiral column yielded 5.2g. (0.0139 mole) of starting material and 8.2 g. (0.0383 mole) of 1, 2-diethoxy-3, 3, 4, 4-tetrafluorocyclobutene, b. p. 163.5°C /624mm., n_D^{25} 1.3795. Infrared spectrum and g. l. c. retention time were identical with those obtained from an authentic sample.

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