
REACTION OF 5-OXO-4-OXAHOMOADAMANTANE WITH THIONYL CHLORIDE

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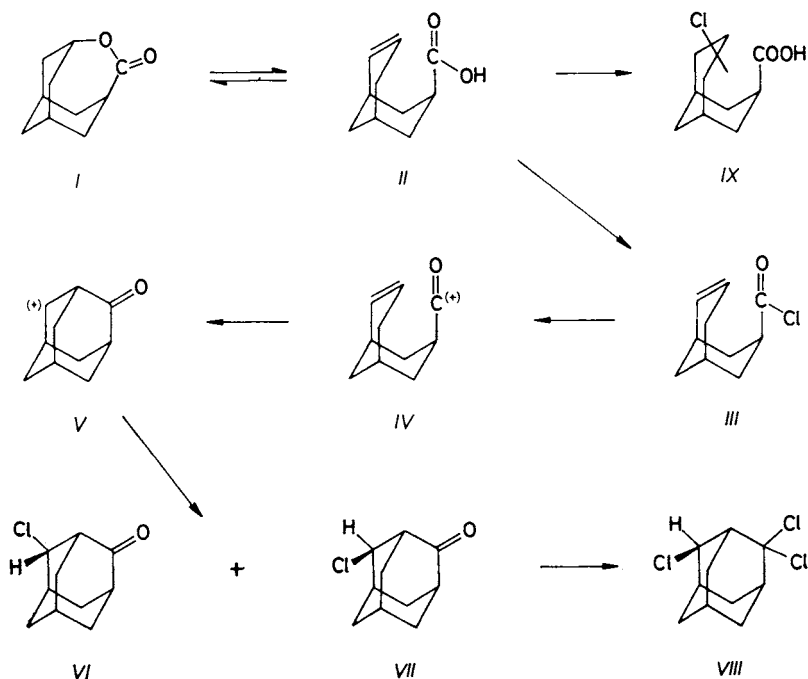
On reaction with thionyl chloride 5-oxo-4-oxahomoadamantane gives rise to a mixture of 4^a-chloro- and 4^e-chloro-2-adamantanone. The carbonyl group of chloroadamantane further reacts with thionyl chloride under formation of 2,2,4^e-trichloroadamantane. In the same way adamantanone reacts with thionyl chloride, giving rise to 2,2-dichloroadamantane.

On reaction with 80% sulfuric acid 5-oxo-4-oxahomoadamantane gives a mixture of 4^a-hydroxy and 4^e-hydroxy-2-adamantanone¹ in a 5 : 1 ratio. A similar reaction also takes place in thionyl chloride. As the main products of this reaction 4^a-chloro-2-adamantanone (*VI*), 4^e-chloro-2-adamantanone (*VII*) and 2,2,4^e-trichloroadamantane (*VIII*) are formed. The reaction probably takes place according to Scheme 1. The first reaction step is the formation of the unsaturated acid *II*. Chloride *III* is formed from it on reaction with thionyl chloride, which by splitting off of the chloride anion and cyclization of *IV* affords the cation *V*. A mixture of chloroadamantanones *VI* and *VII* is formed from it on reaction with Cl⁻. 2,2,4^e-Trichloroadamantane (*VIII*) is formed only on further reaction of chloroadamantanones with thionyl chloride. The correctness of this assumption is supported by the reaction of chloroadamantanones *VI* and *VII* and adamantanone with thionyl chloride. Under similar conditions as in the reaction of lactone (*I*) an exchange of the carbonyl group oxygen for two chlorine atoms takes place and 2,2,4-trichloroadamantanes or 2,2-dichloroadamantane are formed, respectively.

The observed ratio of the axial and the equatorial isomer (*VI* : *VII* = 2 : 3) is probably close to the equilibrium ratio of both isomers. As is evident from the results of the reaction of individual compounds *VI* and *VII* with thionyl chloride, the isomerization rate of 4-chloroadamantanones is at least one order of magnitude higher than the rate of the reaction of chloroadamantanones to 2,2,4-trichloroadamantanes.

The chlorobicyclo[3,3,1]nonane-3-carboxylic acid (*IX*; 7%) was also found in the reaction mixture. It is formed presumably by the addition of hydrogen chloride to

the double bond of acid *II*. The position of the chlorine atom has not yet been determined.



SCHEME 1

EXPERIMENTAL

Analytical Methods

Gas chromatographic analyses were carried out on a Chrom 5 instrument (Laboratorní přístroje, Prague) using a glass column of 1 200 mm length and 3 mm internal diameter, packed with Chromaton N-AW-DMCS wetted with 3% of XF-1 150. FID detector was used, nitrogen as carrier gas, column temperature 150°C. The relative elution times of the compounds (t_r) are referred to adamantanone. The mass spectra were measured on an LKB 9 000 instrument and the infrared spectra on a Perkin-Elmer 325 spectrophotometer in KBr pellets.

5-Oxo-4-oxahomoadamantane (*I*)

Adamantanone (6.8 g; 45 mmol) was dissolved in 100 ml of glacial acetic and 10 g of sodium acetate were added to the solution. After dissolution 50 ml of 40% peracetic acid were added over 15 min under permanent stirring. The reaction mixture was allowed to stand at room temperature for 24 h and then poured into water. The excess of the acid was neutralized with solid potassium hydrogen carbonate and the product was extracted with ether. The extract was washed with water, dried over sodium sulfate and the ether evaporated. Yield, 7.4 g (98%) of lactone *I*. M.p. 284.5–287.5°C (hexane–benzene), ref.¹ gives 286–289°C.

Reaction of Lactone *I* with Thionyl Chloride

Lactone *I* (2.0 g; 12 mmol) was dissolved in 5 ml of thionyl chloride and the mixture was allowed to stand at room temperature for 140 h, under exclusion of air humidity. The excess of thionyl chloride was distilled off in a vacuum. The residue was dissolved in chloroform, the solution was washed with 5% potassium hydroxide solution, then water, dried over sodium sulfate and the solvent was distilled off. Yield, 2.05 g of a product containing according to gas chromatography 2,2,4^e-trichloroadamantane (*VIII*) (t_r 1.74; 17.8%), 4^e-chloro-2-adamantanone (*VII*) (t_r 2.19; 36.0%), 4^a-chloro-2-adamantanone (*VI*) (t_r 5.14; 23.6%), an unidentified substance (t_r 6.60; 7.2%), and 5-oxo-4-oxahomoadamantane (t_r 9.02; 15.4%). Elution chromatography on silica gel gave pure compounds *VI*, *VII*, and *VIII*.

4^a-Chloro-2-adamantanone (*VI*): M.p. 217–219°C, ref.² gives 214.5–216°C. The mass spectrum is identical with the spectrum published in ref.³. The elution is the same as that of a standard².

4^e-Chloro-2-adamantanone (*VII*): M.p. 202.5–204°C, ref.⁴ 201–203°C. The mass spectrum is identical with that published in ref.³, the elution time is identical with that of a standard².

2,2,4^e-Trichloroadamantane (*VIII*): M.p. 151.5–154°C. For C₁₀H₁₃Cl₃ (239.6) calculated: 50.13% C, 5.47% H, 44.40% Cl; found: 50.00% C, 5.43% H, 44.17% Cl. Mass spectrum, m/z (%): 238 (0.3, M⁺), 204 (66), 203 (20), 202 (100), 167 (25), 131 (40), 91 (51). IR spectrum: 632, 643, 670, 677, 683, 693, 753, 779, 815, 826, 836, 847 cm⁻¹. ¹³C NMR spectrum: 25.60 (CH), 28.70 (CH₂), 31.46 (CH₂), 33.95 (CH), 34.21 (CH₂), 35.02 (CH₂), 43.81 (CH), 51.12 (CH), 61.95 (CHCl), 98.02 (CCl₂). The measured values are in agreement with those measured in ref.⁵.

The alkaline washing waters were acidified with hydrochloric acid and extracted with chloroform. The extract was washed with water, dried over sodium sulfate and the solvent evaporated. Yield, 0.17 g (7%) of chlorobicyclo[3,3,1]nonane-3-carboxylic acid (*IX*). M.p. 132–134°C (hexane–benzene). For C₁₀H₁₅ClO₂ (202.7) calculated: 59.26% C, 7.46% H, 17.49% Cl; found: 59.18% C, 7.40% H, 17.27% Cl. Mass spectrum, m/z (%): 202 (4, M⁺), 184 (7), 167 (32), 166 (4), 149 (11), 148 (3), 122 (16), 121 (28), 81 (51), 80 (89), 79 (100). Mass spectrum of the methyl ester of *IX*, m/z (%): 216 (4, M⁺), 185 (30), 184 (5), 181 (13), 180 (10), 149 (24), 148 (47), 121 (54), 79 (100). According to gas chromatography of the methyl ester and the mass spectra of both the acid and its methyl ester the product seems pure. However, the ¹³C NMR spectrum showed that it is a mixture of two isomers in a approximately 2 : 1 ratio.

Reactions of Chloroadamantanones with Thionyl Chloride

Chloroadamantanone (50 mg) was dissolved in 0.5 ml of thionyl chloride and the solution was allowed to stand at room temperature under exclusion of air humidity. After 140 h the reaction was terminated by distilling off thionyl chloride in a vacuum. The residue was dissolved in chloroform, the solution was washed with water, and the chloroform evaporated. The reaction product of compound *VI* with thionyl chloride (47 mg) consisted of 2.2% of 2,2,4^e-trichloroadamantane *VIII* (t_r 1.74), 36.8% of chloroadamantanone *VII* (t_r 2.19), 2.7% of 2,2,4^e-trichloroadamantane (t_r 4.21), and 58.3% of chloroadamantanone *VI* (t_r 5.14). The reaction product of compound *VII* (46 mg) with thionyl chloride consisted of 2.3% of 2,2,4^e-trichloroadamantane *VIII*, 89.7% of chloroadamantanone *VII* and 8% of chloroadamantane *VI*. Under the given conditions 2,2,4^e-trichloroadamantane could not be detected in the reaction mixture.

Reaction of Adamantanone with Thionyl Chloride

A solution of 0.5 g (3.3 mmol) of adamantanone in 5 ml of thionyl chloride was allowed to stand

at room temperature and under exclusion of air humidity for 170 h. The excess of thionyl chloride was evaporated in a vacuum and the residue dissolved in chloroform. The solution was washed with water, dried over sodium sulfate and the solvent evaporated. Yield, 0.57 g of a product consisting according to gas chromatography of 53% of 2,2-dichloroadamantane (t_r 0.90) and 47% of adamantanone (t_r 1.00). Elution chromatography on silica gel with hexane gave 0.27 g (40%) of 2,2-dichloroadamantane. M.p. 208.5–209°C (hexane), ref.⁶ gives 203 to 204°C. Mass spectrum, m/z (%): 204 (3, M^+), 169 (92), 168 (67), 133 (63), 91 (100). IR spectrum: 630, 643, 663, 740, 770, 788, 805, 830, 834, 840 cm^{-1} .

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