# ADAMANTANE AND ITS DERIVATIVES

### COMMUNICATION 1. PREPARATION AND CHEMICAL PROPERTIES

# OF 1,3,5,7-TETRABROMO-2,6-ADAMANTANEDIONE

I. K. Moiseev, P. G. Belyaev, T. A. Mratkhuzina, N. P. Tkacheva, and S. S. Novikov

A study of the chemical properties of polyfunctional derivatives of adamantane and the possibility of synthesizing compounds on their basis are of undoubted interest. In our opinion, the most valuable for study is 1,3,5,7-tetrabromo-2,6-adamantanedione (I), which can be obtained from the readily available 2,6-adamantanedionetetracarboxylic acid (II) [1] by the Hunsdiecker reaction. The literature contains descriptions of the preparation of the bromo derivatives of adamantane from the silver salts of the 1,3-adamantane-dicarboxylic [2], 1,3,5,7-adamantanetetracarboxylic [3], 2,6-adamantanedione-1-carboxylic [4], and 2,6-adamantanedione-1,3-dicarboxylic [5] acids by treatment with bromine in  $CCl_4$ . An analysis of the reaction conditions for the mentioned acids makes it possible to conclude that their reactivity decreases with increase in the number of carboxyl groups. An even lower reactivity could be expected for (II).

In its reactivity, acid (II) is close to the perfluoro carboxylic acids [6], the conversion of which to the perfluoroalkyl bromides requires the use of drastic reaction conditions (pressure, temperature). And, actually, (I) was obtained in 23% yield only by treating the tetrasilver salt of 2,6-adamantanedione-1,3,5,7-tetracarboxylic acid with bromine under pressure. The optimum reaction conditions were found by the factor planning method, which made it possible to increase the yield of (I) up to 80%.

The chemical properties of (I), which has two types of reaction centers, were studied in the reactions of the nucleophilic replacement of the bromine atom at the tertiary carbon atom and of addition to the carbonyl group. In order to ascertain the lability of the bromine atom, (I) was reacted with a number of reducing agents (LiAlH<sub>4</sub>, NaBH<sub>4</sub>, zinc amalgam). An attempt to convert (I) to 2,6-adamantanedione by treatment with zinc amalgam proved unsuccessful, although this reaction proceeds smoothly for 1,3-dibromo-2,6-adamantanedione [5]. Instead of the expected 2,6-adamantanedione, 1,3,5,7-tetrabromo-2,6adamantanediol (III) was obtained when treatment was with NaBH<sub>4</sub>, which makes it possible to suggest that the carboxyl group displays a heightened reactivity toward nucleophilic reagents. In order to identify (III) we prepared its dinitrate (IV). The reduction of (I) and (III) with LiAlH<sub>4</sub> gave 2,6-adamantanediol (V), while the treatment of (V) with a mixture of HNO<sub>3</sub> and acetic anhydride gave its dinitrate (VI). The reduction of the dioxime of diketone (I) with LiAlH<sub>4</sub> to 2,6-diaminoadamantane also proceeds easily.

The high reactivity of the keto group is also corroborated by the ease with which the hydrates of (I) are formed. The IR spectrum of (I) contains an intense band at 1740 cm<sup>-1</sup>, which is characteristic for the keto group. However, after short standing in the air, this band becomes less intense, while on long standing it disappears completely. Simultaneously with its disappearance there appear bands that are characteristic for the hydroxy group (1100 and 3500 cm<sup>-1</sup>). Here the color changes from white to light pink. When a benzene solution of (I) was kept overnight over  $P_2O_5$  a band, characteristic for the keto group, again appeared in its IR spectrum.

The ability of aldehydes and ketones, containing several halogen atoms  $\alpha$  to the carbonyl group, to easily form stable hydrates is described in [7]. Apparently, the same equilibrium also exists for (I):

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Under alkaline hydrolysis conditions, (I) is converted to the dibromobisnoradamantanedicarboxylic acid (IX), which corroborates the possibility of the Favorskii rearrangement



Replacement of the halogen by the hydroxy group fails to occur under acid hydrolysis conditions. The use of 98% H<sub>2</sub>SO<sub>4</sub> and silver sulfate led to obtaining a difficultly identifiable mixture of products, which apparently represented a mixture of fragmentation and hydrolysis products.

As is known [8], a direct replacement of halogen is possible only for ketones of type Ar'COCBrAr'' $\cdot Ar'''$ . For (I) a cleavage of the C-Br bond is complicated by the unfavorable polar effect of the keto group, which destabilizes the formed carbonium ion, and by the steric hindrance to its formation [9, 10].

#### EXPERIMENTAL

<u>Tetrasilver Salt of 2,6-Adamantanedione-1,3,5,7-tetracarboxylic Acid (IIa).</u> With vigorous stirring 5.16 g of (II) was made weakly alkaline with 5% KOH solution, followed by the dropwise addition of a warm solution of 12 g of AgNO<sub>3</sub> in 25 ml of water. The obtained suspension was stirred for 1 h, and then it was filtered, washed in succession with water, methanol and ether, and dried in vacuo. The yield of salt (II) was 85%. Found: Ag 53.0%.  $C_{14}H_8Ag_4O_{10}$ . Calculated: Ag 56.0%.

<u>1,3,5,7-Tetrabromo-2,6-adamantanedione (I)</u>. An ampule containing 5 g of salt (IIa), dried at 120°, and 23 ml of dry bromine, was heated in an autoclave for 6 h at 120 ± 5° (temperature of reaction mixture  $\leq$  98°, pressure 7 atm). After cooling the autoclave (residual pressure 1.5-2 atm) the bromine was vacuum-distilled, while the dry residue was extracted with CCl<sub>4</sub>. The obtained product (yield 70-80%) was recrystallized from toluene and then sublimed at 220° (3-5 mm of Hg). The melting point of (I) was 292° (in a sealed capillary). Found: C 24.70; H 1.61; Br 67.11%. C<sub>10</sub>H<sub>8</sub>Br<sub>4</sub>O<sub>2</sub>. Calculated: C 25.00; H 1.60; Br 66.66%. The IR spectrum contains a band at 1740 cm<sup>-1</sup> (C = O).

Dioxime (VII), mp 340°. Found: C 20.47; H 2.00; N 5.55; Br 61.50%.  $C_{10}H_{10}Br_4N_2O_2$ . Calculated: C 23.52; H 1.96; N 5.49; Br 62.74%.

1,3,5,7-Tetrabromo-2,6-adamantanediol (III). A solution of 1 g of (I) in 12 ml of methanol was mixed at 20-25° with a solution of 0.4 g of NaBH<sub>4</sub> in 13 ml of water. The mixture was kept at ~20° for 1 h. The precipitate was filtered and washed with water. The yield of (III) was 0.54 g, mp 208-210° (from heptane). Found: C 24.54; H 2.47; Br 56.50%.  $C_{10}H_{12}Br_4O_2$ . Calculated: C 24.60; H 2.46; Br 66.11%. The IR spectrum contains a band at 3500 cm<sup>-1</sup> (OH). The absorption band of C =O bonds was not detected.

 $\frac{1,3,5,7-\text{Tetrabromo-2,6-adamantanediol Dinitrate (IV).}{\text{of a cetic anhydride and 0.3 g of (III)}.}$  The mixture was stirred at 0° for 3 h and then poured into ice water. The obtained precipitate was filtered, washed well with water, and dried. The yield of (IV) was 0.2 g, mp 135°. Found: Br 53.89; N 4.63%. C<sub>10</sub>H<sub>10</sub>Br<sub>4</sub>N<sub>2</sub>O<sub>6</sub>. Calculated: Br 55.55; N 4.87%. The IR spectrum confirms the presence of the ONO<sub>2</sub> group (1660 cm<sup>-1</sup>).

<u>2,6-Adamantanediol (V).</u> a) From (I). To a mixture of 1.5 g of LiAlH<sub>4</sub> and 200 ml of absolute dioxane was added 1 g of (I), and the mixture was refluxed for 3 h. Then the mixture was cooled and 3-5 ml of water was added cautiously. The precipitate was filtered, and the product was extracted with dioxane and evaporated. The yield of (V) was 0.23 g (60%), mp 170° (after sublimation in vacuo at 150-160°, based on the TLC and GLC, a mixture of conformers). From [11]: mp 344°. Found: C 71.80; H 9.49%. C<sub>10</sub>H<sub>16</sub>O<sub>2</sub>. Calculated C 71.42; H 9.25%. b) From (III). To 0.7 g of LiAlH<sub>4</sub> in 100 ml of absolute dioxane was added 0.5 g of (III), and the mixture was refluxed for 3 h. Then it was cooled and 2 ml of water was added cautiously. The precipitate was filtered, and the product was extracted with dioxane and evaporated. The residue was sublimed in vacuo. We obtained (V), mp 165-170°. Found: C 69.28; H 9.49%. C<sub>10</sub>H<sub>16</sub>O<sub>2</sub>. Calculated: C 71.42; H 9.52%.

2,6-Adamantanediol Dinitrate (VI). To a mixture of 7 ml of acetic anhydride and 7 ml of 97.7% HNO<sub>3</sub> at 0° was added 0.5 g of (V). The mixture was kept at ~20° for 1 h and then poured over ice. The obtained precipitate was filtered, and the product was washed with water, dried, and sublimed in vacuo. The yield of (VI) was 50-60\%, mp 44°. The IR spectrum confirms the presence of ONO<sub>2</sub> groups (1600 and 1280 cm<sup>-1</sup>).

<u>2,6-Diaminoadamantane (VIII)</u>. To 0.8 g of LiAlH<sub>4</sub> in 100 ml of absolute dioxane was added 0.3 g of (VII) and the mixture was refluxed for 3 h. The solution was filtered, and the precipitate was washed with warm dioxane. The dioxane was evaporated, while the solid residue was sublimed at 120° in vacuo. The yield of (VIII) was 50-60%, mp 135°. Found: C 67.10; H 9.01; N 13.32%.  $C_{10}H_{18}N_2$ . Calculated: C 72.28; H 10.84; N 16.85%. Infrared spectrum ( $\nu$ , cm<sup>-1</sup>): 3500, 1590, 670.

Bisnoradamantanedicarboxylic Acid (IX). To a solution of 0.8 g of KOH in 2 ml of ethanol and 2 ml of water was added 0.5 g of (I), and the mixture was heated for 4 h and then acidified with dilute HCl solution, in which connection a precipitate was obtained. The solution was evaporated to dryness and the residue was extracted with acetone. The yield of (IX) was 0.3 g, mp 282-288°. Found: C 32.03; H 2.80; Br 39.71%.  $C_{10}H_{10}Br_2O_4$ . Calculated: C 32.91; H 2.74; Br 43.98%. The IR spectrum confirms the presence of COOH groups (1720, 2960, 2930 cm<sup>-1</sup>).

# CONCLUSIONS

1,3,5,7-Tetrabromo-2,6-adamantanedione was obtained and its chemical properties were studied.

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