SYNTHESIS AND MASS SPECTRA OF SOME TRI-AND TETRA-SUBSTITUTED ADAMANTANES

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The 1,3-dimethyl- and 1,3,5-trimethyladamantanes react under mild conditions with chlorosulfonic acid with the formation of chlorides [1]. Here, due to the stepwise character of the reaction, both the monochloride and the dichloride can be obtained from 1,3-dimethyladamantane. In the present paper are presented some experimental data on the synthesis of the starting alkyladamantanes, their chlorination, and also on some of the transformations of the chlorides. It should be mentioned that the formation of the chlorides proceeds only in the temperature range from -10 to 25° .

Previously, the obtained alkylchloroadamantanes were synthesized only by starting with other functional derivatives of the alkyladamantanes, like the bromides, alcohols, etc. The reactivity of such chlorides had hardly been studied. In the present paper, employing carboxylation by the Koch method and the Ritter reaction, the carboxy and acetamido derivatives were synthesized from the indicated chlorides in good yield



Thus, from dichloride (IV) were obtained dicarboxylic acid (V) and diacetamide (VI), which were previously available only via 1,3-dimethyl-5,7-dihydroxyadamantane, while from chloride (IX) were obtained acid (X) and acetamide (XI), the synthesis of which was described only from 1,3,5-trimethyl-7-bromoadamantane [4, 7, 8].

We studied the mass spectra of compounds (II)-(VI) and (VIII)-(XI), and of some of the substituted adamantanes (XII)-(XV) that we had obtained from them previously [1, 2]



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Data are lacking in the literature on the mass spectra of adamantane derivatives that are di-, tri-, and tetra-substituted in the nodal positions. According to [3], based on the character of the decomposition of the molecular ion of 1-monosubstituted adamantanes under the influence of electron impact, it proves possible to effect separation into a group of derivatives where the substituent is cleaved as a neutral fragment (halogen, alkyl, NO_2), and into a group of derivatives where the substituent (phenyl, OH, NH_2) enters into the structure of the ions of the principal peak in the mass spectrum.

Based on the type of fragmentation of the molecular ion, the compounds studied by us can also be separated into two groups. To the first group belong compounds with the substituents CH_3 , CI, COOH; to the second group belong the adamantanes which, besides methyl groups, contain either OH or NHCOCH₃ groups. The decomposition of the molecular ions of dimethyladamantane (II) and trimethyladamantane (VIII) is similar to the fragmentation of the ion of 1-methyladamantane [3], i.e., additional methyl groups fail to exert noticeable effect on the decomposition. The ions of the principal peak are formed by the removal of one methyl, followed by the ejection of the fragments C_3H_6 and $C_3H_5CH_3$, and C_4H_8 and $C_4H_7CH_3$. Only a slightly greater probability is observed in the processes of eleminating $C_3H_5CH_3$ and $C_4H_7CH_3$ when compared with C_3H_6 and C_4H_8 .

An examination of the mass spectra of dichloride (XII) and trichloride (XIII), taking into account the metastable peaks, discloses that together with the processes that are observed in the mass spectrum of 1-chloroadamantane



there occurs the process

$$\begin{array}{c} \mathrm{M}^{+} \cdot \stackrel{-\mathrm{Gl}^{*}}{\longrightarrow} (\mathrm{M}\mathrm{-Cl})^{+} \stackrel{-\mathrm{HGl}}{\longrightarrow} (\mathrm{M}\mathrm{-HCl}\mathrm{-Cl})^{+} \\ & \downarrow \\ & \downarrow \\ \hline \downarrow \\ -\mathrm{C}_{a}\mathrm{H}_{a} \downarrow \\ -\mathrm{C}_{a}\mathrm{H}_{a} \downarrow \\ -\mathrm{C}_{b}\mathrm{H}_{a} \downarrow \\ -\mathrm{C}_{b}\mathrm{H}_{a} \downarrow \\ \end{array}$$

The successive cleavage of Cl and two HCl occurs in trichloride (XIII). Naturally, together with the processes of eliminating $C_{3}H_{6}$ and $C_{4}H_{3}$, there occurs the elimination of $C_{3}H_{5}Cl$ and $C_{4}H_{7}Cl$.

In methylchloroadamantanes (III), (IV), and (IX), and methyladamantylcarboxylic acids (V) and (X), the principal ion $C_{10}H_{15-n}(CH_3)n^+$, formed as the result of cleaving either the Cl or the COOH group, subsequently decomposes in the same manner as the $C_{10}H_{15}^+$ ion [3]. At the same time are observed the processes

 $\begin{array}{c} M^{+} \cdot \xrightarrow{-CH_{3}} & (M - CH_{3})^{+} & \xrightarrow{-HX} & (M - CH_{3} - HX)^{+} \\ & \downarrow \\ & \downarrow \\ \hline & & \downarrow \\ \hline & & \downarrow \\ \hline & & -C_{4}H_{4} \downarrow - C_{4}H_{7} \end{pmatrix} & \downarrow \\ \hline & & \downarrow \\ \hline & & \downarrow \\ \hline & & -C_{4}H_{4} \downarrow - C_{5}H_{4} \\ \hline & & X = Cl. COOH \end{array}$

The intensity of the peak of the $(M-CH_3)^+$ ions is 8-10 times less than the intensity of the principal peak. The mass spectra of the second group of compounds testify to the fact that the most probable process during the molecular ionization of compounds containing either OH or NHCOCH₃ groups is the elimination of either the C₄H₉ or C₄H₈CH₃ fragments, with the formation of an ion having a structure of the **a** type [3]



In the molecules of acetamide (XI) and hydroxyadamantane (XV) the formation of an ion with an **a** structure occurs only with the ejection of $C_4H_8CH_3$, while the processes of ejecting $C_4H_8CH_3$ and C_4H_9 are equally probable for hydroxyadamantane (XIV). We will mention that in the second group of compounds the methyls exert an effect on the fragmentation of the molecular ion, and here processes are observed that are characteristic for the fragmentation of the first group of molecules. However, the intensity of the signals of the ions that a reformed by these processes is slight (5-10% of the principal peak).



Fig.1. Mass spectra of compounds (IX) and (XI).

 $\begin{array}{c} \mathbf{M}^{+} \cdot \xrightarrow{-\mathbf{C}\mathbf{H}_{3}} & (\mathbf{M} - \mathbf{C}\mathbf{H}_{3})^{+} & \xrightarrow{-\mathbf{H}\mathbf{X}} & (\mathbf{M} - \mathbf{C}\mathbf{H}_{3} - \mathbf{H}\mathbf{X})^{+} \\ & & & | \\ & & & | \\ & & & | \\ & & & | \\ \hline & & -\mathbf{C}_{4}\mathbf{H}_{s} \Big| - \mathbf{C}_{3}\mathbf{H}_{s} \Big| \stackrel{\cdot}{\cdot} - \mathbf{C}_{5}\mathbf{H}_{s} & & & \int -\mathbf{C}_{4}\mathbf{H}_{s} \Big| - \mathbf{C}_{5}\mathbf{H}_{s} \end{array}$

For example, in Fig.1 are shown the mass spectrum of acetamide (XI), the molecular peak of which is one of the most intense (47%), and the mass spectrum of chloride (IX), with a small relative intensity of the peak of the molecular ion (~1.5%).

EXPERIMENTAL METHOD

The mass spectra were taken on an MKh-1303 mass spectrometer under standard conditions, in an ion source with an energy of the ionizing electrons of ~70 eV. The NMR spectra were recorded on a Varian A-56-60A spectrometer in CCl_4 solution (using HMDS as the internal standard).

The chromatographic analysis was run on a Tswett-3-66 chromatograph, equipped with a flame-ionization detector, at 150°; the column was $3 \text{ mm} \times 3 \text{ m}$, the solid support was Chromosorb W, the stationary phase was Carbowax 15M (10%), and the carrier gas was nitrogen.

Perhydroacenaphthene (I) and perhydrofluorene (VII) were respectively obtained by the hydrogenation of acenaphthene and fluorene over Raney nickel at 150° and an H₂ pressure of 150 atm, and were purified by chromatographing over ShSM silica gel.

<u>1,3-Dimethyladamantane (II)</u>. To a mixture of 66 g of AlBr₃ and 47 g of perhydroacenaphthene was added 8.5 ml of tert-butyl chloride at such a rate that the temperature did not exceed 70°. The mixture was stirred at 50-60° for 6 h. Then the liquid was decanted, while the solid residue was washed with several portions of petroleum ether. The combined solution was washed with water and then dried over MgSO₄. After removal of the solvent and vacuum-distillation we obtained 31.9 g (68%) of (II) with bp 91.3° (22 mm); n_D^{20} 1.4792; see [4].

<u>1,3,5-Trimethyladamantane (VIII)</u>. The isomerization of perhydrofluorene was run for 30 min, in the same manner as described for the preparation of (II). From 60 g of perhydrofluorene, 82 g of AlBr₃ and 9 g of tert-butyl chloride we obtained 40.0 g (66.5%) of 1,3,5-trimethyladamantane, bp 90.5° (20 mm); n_D^{20} 1.4752; see [4].

<u>1,3-Dimethyl-5-chloroadamantane (III)</u>. To 10 ml of $ClSO_3H$, cooled to 0°, was added 2.5 g of 1,3dimethyladamantane in drops, after which the ice-cooled mixture was stirred for 1 h and then poured on ice. The product was extracted with $CHCl_3$. After distilling off the $CHCl_3$ and vacuum-distillation we obtained 2.25 g (75%) of (III), bp 80° (4 mm); n_D^{20} 1.4964; see [5].

<u>1,3-Dimethyl-5,7-dichloroadamantane (IV)</u>. The reaction was run under the same conditions as described for (III), keeping the mixture at 0-5° for 60 h. From 2.5 g of (II) we obtained 3.2 g of a product that, based on the GLC data, contained 83% of 1,3-dimethyl-5,7-dichloroadamantane. The product was purified by chromatographing on Al_2O_3 (hexane), and was recrystallized from methanol, mp 92-93°; see [6]. Found:

C 61.6; H 7.8; Cl 30.3%. $C_{12}H_{18}Cl_2$. Calculated: C 61.78; H 7.77; Cl 30.41%. NMR spectrum: singlet of CH_3 groups at 0.90 ppm, and singlets of methylene groups at 1.10, 1.68, and 2.23 ppm; the ratio in the intensities of the signals was 6:2:8:2.

1,3,5-Trimethyl-7-chloroadamantane (IX). To 5.0 g of 1,3,5-trimethyladamantane, cooled to 5°, was added 30 ml of $CISO_3H$. The mixture was stirred for 1 h, poured on ice, and extracted with $CHCl_3$. After removal of the $CHCl_3$ we obtained 5.43 g (92%) of (IX). The product was purified by chromatographing on Al_2O_3 (hexane), and was recrystallized from methanol, mp 85-86°; see [6]. NMR spectrum: singlet of CH_3 groups at 0.83 ppm, and singlets of protons of methylene groups at 1.04 and 1.63 ppm. The ratio in the intensities of the signals was 9:6:6.

<u>1,3-Dimethyladamantane-5,7-dicarboxylic Acid (V)</u>. To 12.3 ml of 100% H_2SO_4 , cooled to 10°, was added 0.45 g of 1,3-dimethyl-5,7-dichloroadamantane, and then 2.0 ml of 95% formic acid was added in drops. The mixture was stirred for 2 h and then poured on ice. The obtained crystals were filtered, washed with water, and dried. The yield of acid (V) was 0.44 g (91%). After reprecipitation from saturated caustic solution and recrystallization, mp 267-268°; see [7].

<u>1,3-Dimethyl-5,7-diacetamidoadamantane (VI)</u>. To a mixture of 0.5 g of 1,3-dimethyl-5,7-dichloroadamantane and 1.8 g of actonitrile at 60° was added 1.4 g of 100% H_2SO_4 in drops, after which the reaction mass was stirred for 2 h at 60° and then poured on ice. The crystals were filtered, washed with water, and dried. We obtained 0.43 g (80%) of (VI). After purification by sublimation, mp 312-315°C; see [8].

1,3,5-Trimethyladamantane-7-carboxylic Acid (X). To 6.5 ml of 100% H₂SO₄, cooled to 10° , was added 0.22 g of (IX), and then 1 ml of 95% formic acid was added in drops (10 min). The mixture was stirred for 2 h and then poured on ice. The obtained crystals were filtered, washed with water, and dried. We obtained 0.19 g (82%) of (X), mp 139-140° (after reprecipitation from saturated caustic solution and recrystallization from aqueous methanol); see [4].

 $\frac{1,3,5-\text{Trimethyl-7-acetamidoadamantane (XI).}{\text{of acetonitrile and } 3.8 \text{ g of } 100\% \text{ H}_2\text{SO}_4.}$ The yield of (XI) was 1.08 g (83%). After purification and sublimation, mp 176-178°. Found: C 76.51; H 10.72; N 5.93%. C₁₅H₂₅NO. Calculated: C 76.54; H 10.70; N 5.95%.

CONCLUSIONS

1. A new and convenient method was developed for the preparation of mono- and difunctional derivatives of alkyladamantanes from the chlorides of the corresponding hydrocarbons.

2. A study was made of the behavior of the di-, tri-, and tetra-substituted adamantanes under the influence of electron impact, and the relation between their fragmentation and the type of substituents was established.

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