SYNTHESIS OF 2,2′-(ADAMANTYLENE-1,3)-DIETHANOIC ACIDS

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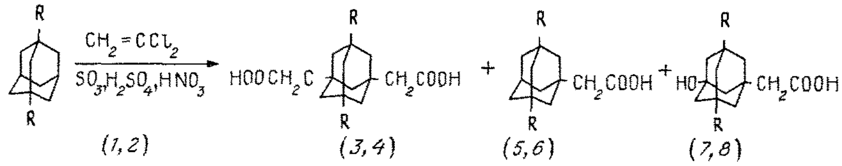
Via direct oxidative addition of 1,1-dichloroethylene to adamantane or 1,3-dimethyladamantane one obtains diethanoic acids of the adamantane series, which are useful in themselves or for preparation of other functional derivatives. Optimal reaction conditions were found by mathematical modeling.

Keywords: synthesis, adamantane, dimethyladamantane, 1,1-dichloroethylene, 1,3-bis(carboxymethyl)adamantane, 1,3-bis(carboxymethyl)-5,7-dimethyladamantane, mathematical planning.

Improvement of the physicochemical characteristics and chemical resistance of a series of industrial condensation polymers can be achieved by their modification with small amounts of aromatic or alicyclic compounds. In this respect bifunctional derivatives of adamantane are of interest, particularly diethanoic acids which can be used directly for modification as well as for preparing other compounds, for example, diamines, used for the same purpose.

It is known that for obtaining diethanoic acids the most expedient method is oxidative addition of 1,1-dichloroethylene to the adamantane cation, readily formed in an acidic medium, followed by hydrolysis of the product [1]. The direct preparation of 2,2-(adamantylene-1,3)diethanoic acid in the presence of boron fluoride and *tert*-butyl alcohol has been described [2]. Earlier authors obtained in a mixture of nitric and sulfuric acids with oleum the monoethanoic [3] and dicarboxylic [4] acids of the adamantane series, suggesting the possibility of obtaining diethanoic acids from adamantane (**1**) and dimethyladamantane (**2**) under the same conditions.

Synthesis of diethanoic acids of the adamantane series was carried out by the reaction:



where R = H (for **1**, **3**, **5**, **7**); R = CH_3 (for **2**, **4**, **6**, **8**).

The products were analyzed as their esters by GLC. The results of analysis are shown in Tables 1 and 2.

It was established that besides diethanoic acids the products contain monoethanoic and hydroxymonoethanoic acids, which are intermediates in the synthesis.

In the preliminary experiments with adamantane the synthesis conditions varied within the following ranges: volumetric ratio of oleum to sulfuric acid of 0.51:0.55 (here and below, 60% oleum), 12-14 moles of nitric acid per mole of starting adamantane, and temperature of 27-37°C. It was determined that under these conditions only small amounts of 2-(adamantylene-1)ethanoic acid (**5**) are formed.

For the next experiments we used a mathematical planning method. The data were processed and the corresponding equation was obtained which indicated that the most significant factors in this reaction are the temperature and the amount of nitric acid added. In order to increase the yield of adamantylenediethanoic acid it is necessary to increase the temperature and amount of nitric acid in the system. Adamantane conversion is 87-100%.

For prevention of secondary reactions and increase of the dispergation degree it was proposed to use trichloromethane and hexane as solvents. As follows from data of Table 1, it was possible to decrease the reaction temperature and increase the yield of diethanoic acid to 74%. Decrease of oleum content leads to decrease of both the yield and purity of the product.

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TABLE 1. Composition of Reaction Products **1-3** as a Function of Conditions*

$\frac{V_{ol}}{V_{ol}+V_{H_2SO_4}}$	Solvent †	Yield of (3), %	Composition of ester mixture according to GLC, %		
			5	**7**	**3**
0.32	Hexane	91.3	0.5	12.9	86.6
0.32	Trichloromethane	75.7	0.9	8.4	90.0
0.29	Hexane	57.3	6.0	29.0	64.4
0.27	Hexane	74.4	0.9	12.2	86.3
0.25	Hexane	42.8	0.3	40.7	57.6

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*In the presence of HNO_3 (2 moles per mole of starting **1**, concentration of added HNO_3 solution 56%; reaction time 4.5 h; process temperature 25 ± 3°C).

†Ratio of added solvent volume to acid mixture volume 0.18.

TABLE 2. Composition of Reaction Products **2-4** as a Function of Reaction Conditions

Sample No.	$\frac{V_{ol}}{V_{ol}+V_{H_2SO_4}}$	HNO_3, mole per 1 mole	$\frac{V_{CHCl_3}}{V_{acid.\,mix.}}$	T°. C	Yield 4, %	Content in reaction products, %			
						6	**8**	unidentified products	**4**
1	0	1.57	0.5	64	12.2	33.7	15.5	12.2	38.3
2	0.40	3.16	1.0	42	15.4	69.2	1.3	3.0	28.2
3	0.46	2.20	0	64	54.9	2.5	6.4	12.0	89.0
4	0.46	2.56	0	64	43.5	2.0	2.0	6.0	86.5
5	0.20	2.36	0.1	53	7.5	71.0	2.8	1.0	25.8

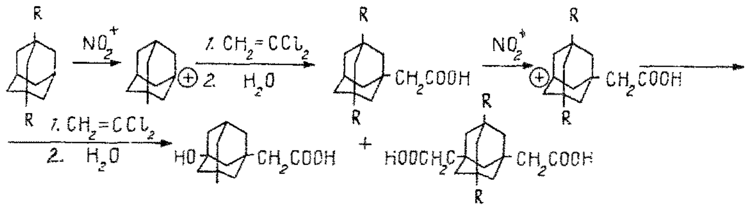
From the theoretical and practical points of view it was of interest to study the use of dimethyladamantane, which is a liquid within a wide temperature range. Considering the results obtained with adamantane, we investigated the direct preparation of 2,2-(5,7-dimethyladamantanylene-1,3)diethanoic acid (**4**) from 1,3-dimethyladamantane.

As seen from Table 2, the content of diethanoic acid in the reaction products reached 70%.

Processing the data led to the conclusion that the yield of diethanoic acids obtained from 1,3-dimethyladamantane increases with increase of temperature and the amount of added oleum and with decrease of amount of trichloromethane. By changing the volumetric ratio of oleum to sulfuric acid and using no solvent, one can obtain under normal conditions a product containing 80-90% of diethanoic acid in a yield of 52-55%.

Comparing the results of Tables 1 and 2 one can conclude that the reactivity of 1,3-dimethyladamantane is lower than that of adamantane. Thus, for obtaining **4** with sufficiently high yield and purity, higher temperatures and oleum concentrations are necessary. The higher stability of 1,3-dimethyladamantane in comparison with adamantane permits one to choose reaction temperature as the controlling factor, since increasing the oleum amount will lead to sharp increase of acidic waste.

As a result of our investigations the following reaction mechanism can be proposed, in which the hydride ion acceptor is the nitronium cation:



Our investigations testify that diethanoic acids of the adamantane series can be obtained by direct oxidative addition of 1,1-dichloroethylene to adamantane and dimethyladamantane. With adamantane it is expedient to use a nonpolar solvent in order to improve dispergation and to prevent decomposition and secondary processes.

EXPERIMENTAL

Analysis of a mixture of adamantane carboxylic esters were carried out by GLC on a Tsvet-100 chromatograph with a 2 m × 2 mm column with 5% SE-30 on a Chromaton N-AW with a column temperature of 170°C, flame-ionizing detector, and argon as carrier gas.

2,2′-(Adamantylene-1,3)diethanoic Acid (3). Into a reactor 12.7 ml of HNO_3, 87.5 ml of concentrated H_2SO_4, and 42 ml of 60% oleum was added so that the temperature did not rise above 40°C, then cooled to 25°C and maintaining this temperature 10 g of adamantane was added, 25 ml of hexane was poured in, and at 25°C 50 ml of 1,1-dichloroethylene was added dropwise for 4.5 h. Then the reaction mixture was poured into ice, the residue was filtered, reprecipitated from an alkaline solution, and dried. The weight of the obtained product was 13.4 g, with composition according to GLC analysis (%) of: **3** 86.6, **5** 0.5, **7** 12.9. The yield of **3** was 91.3% of theory. Mp 132-135°C. IR spectrum (ν, cm^{-1}): 945, 1140-1190, 1280, 1325, 1380, 1420, 1460-1475, 1720, 2800-3000.

2,2′-(5,7-Dimethyladamantylene-1,3)diethanoic Acid (4). Into a four-necked reactor (reflux condenser, thermometer) 6.5 ml of 56% HNO_3, 17 ml of concentrated H_2SO_4, and 13 ml of 60% oleum was added such that the temperature did not exceed 45°C. Then 5 g of dimethyladamantane and 7.1 ml of trichloromethane was added, the mixture was heated to 64°C, and 40 ml of 1,1-dichloroethylene was added dropwise for 3.5 h. After the end of the process the reaction mixture was poured into water with vigorous stirring. The precipitate was filtered and reprecipitated from an alkaline solution, and dried at 100°C. The weight of the obtained product was 4.7 g with the composition according to a GLC analysis (%) of: **4** 84.2, **6** 3.3, **8** 3.7, unidentified compounds 8.8. The yield of **4** was 4-46% of theory. Mp 200-225°C (mp of pure **4** 224-226°C). IR spectrum (ν, cm^{-1}): 945, 1055, 1140-1190, 1245, 1285, 1325, 1385, 1420, 1465-1480, 1720, 2800-3000.

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