

SYNTHESIS OF DIAMANTANEDICARBOXYLIC ACIDS WITH THE CARBOXY GROUPS BONDED AT TERTIARY CARBON ATOMS

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Dedicated to the 50th anniversary of adamantane discovery and his author Prof. Dr Stanislav Landa, corresponding member of the Czechoslovak Academy of Sciences.

The preparation of diamantanedicarboxylic acids with the carboxy groups at the tertiary carbon atoms of the adamantane skeleton is described. The procedure comprises bromination or oxidation of 1- and 4-diamantanedicarboxylic acids and Koch-Haaf carboxylation of the reaction products. Of the four diamantanedicarboxylic acids synthesized, two — 1,4- and 1,7-diamantanedicarboxylic acids — have not been so far described.

Diamantane — pentacyclo[7,3,1,4[·]12,0^{2·7},0^{6·11}]tetradecane — can give rise to three monosubstituted derivatives, two with the substitution at a tertiary carbon atom of the adamantane skeleton — 1- (medial) or 4- (apical) — and one with the substitution at some of the secondary carbon atoms. By introducing an additional substituent the number of derivatives increases considerably; a survey of the conceivable disubstituted derivatives of adamantane containing two identical substituents is given in Table I, presenting for the various constitutional isomers the type of substitution, number of possible configurational isomers, and number of optically active isomers (racemates). Apparently, there are 16 constitutional isomers, 23 configurational isomers, and of them, 14 racemates.

Only one general method is available for the preparation of carboxylic acids derived from adamantoid hydrocarbons, *viz.* Koch-Haaf carboxylation of suitable derivatives (*i.e.*, their reaction with HCOOH in concentrated H₂SO₄ solutions). The reaction is associated with isomerizations; this can be suppressed by carrying out the reaction at high dilutions (with the H₂SO₄-to-adamantane derivative molar ratio exceeding 300). Dihalogen derivatives, dihydroxy derivatives, halogen acids, and hydroxy acids can serve as suitable starting derivatives. Of the six possible diamantanedicarboxylic acids with the carboxy groups at the tertiary carbon atoms (1,2-, 1,4-, 1,6-, 1,7-, 1,9-, and 4,9-, see Table I), only two have been so far described, *viz.* 1,6- and 4,9-diamantanedicarboxylic acids, prepared by Koch-Haaf carboxylation of adamantane-1,6-diol and adamantane-4,9-diol, respectively^{1,2}. The starting substances for these

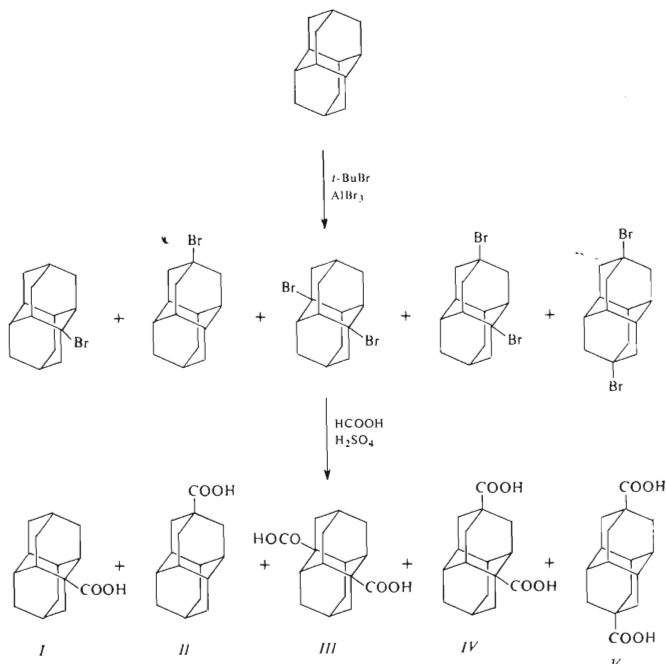
two acids are the major products of diamantane bromination carried out under various conditions: 1,6-dibromodiamantane, which is the major product of diamantane bromination with bromine without using any catalyst³, and 4,9-dibromodiamantane, formed if the bromination is catalyzed by a small amount of AlBr_3 (ref.³). In the reaction mixtures, however, are present also other dibromo derivatives in small quantities, and their isolation is rather difficult. For this reason, we chose to use 1- and 4-diamantanecarboxylic acids as the starting substances and to introduce bromine or hydroxy group to the other tertiary carbon atom by bromination or oxidation. This idea was supported by the diamantane and monobromodiamantane bromination pathways³ as well as by the course of oxidation of 1-adamantanecarboxylic acid with KMnO_4 (ref.⁴). 1-Diamantanecarboxylic acid can be prepared by Koch

TABLE I
Survey of the possible types of diamantane derivatives

Constitutional isomer	Carbon atom combination			Number of configurational isomers	Of them, optically active
	medial (belt)	apical	secondary		
1,2	2	—	—	1	—
1,3	1	—	1	2	2
1,4	1	1	—	1	—
1,5 (3,11) ^a	1	—	1	1	1
1,6	2	—	—	1	—
1,7	2	—	—	1	—
1,8 (3,6) ^a	1	—	1	2	2
1,9 (2,4) ^a	1	1	—	1	—
1,13 (2,3) ^a	1	—	1	1	1
3,3	—	—	1	1	—
3,4	—	1	1	1	1
3,5	—	—	2	3	1
3,8	—	—	2	3	3
3,9 (4,8) ^a	—	1	1	1	1
3,10	—	—	2	2	2
4,9	—	2	—	1	—
<i>Total (16)</i>				23	14

^a The numbering given in parentheses may be correct in the case of two different substituents, with respect to their mutual priority.

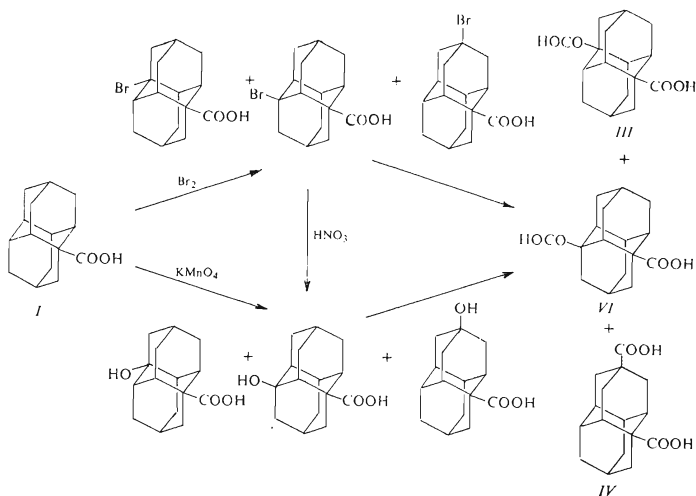
-Haaf carboxylation of diamantane, 1-bromodiamantane, or diamantan-1-ol (refs^{5,6}), 4-diamantanecarboxylic acid is synthesized by Koch-Haaf carboxylation of 4-bromodiamantane at a high dilution⁶. 4-Bromodiamantane is formed invariantly together with 1-bromodiamantane (both on the bromination of diamantane with Br_2 using AlBr_3 for catalysis³ and on the bromination of diamantane with tert-butyl bromide in the presence of AlBr_3 , (ref.³), and the mixture obtained has to be separated, which is a tedious task. With regard to this fact, the reaction mixture from the bromination of diamantane with tert-butyl bromide and AlBr_3 , in addition to 1- and 4-bromodiamantane containing also smaller quantities of three dibromodiamantane derivatives (Scheme 1), was subjected to the carboxylation without



SCHEME 1

preliminary treatment. The obtained mixture of carboxylic acids was more easily separated making use of the substantial difference in the solubilities of their ammonium salts: in contrast to the ammonium salts of the other acids present, the salt of 4-diamantanedicarboxylic acid is practically insoluble in water and can be well separated off by filtration. 1-Diamantanedicarboxylic acid is obtained from the acidified solution of ammonium salts by extraction with pentane, in which diamantanedicarboxylic acids are insoluble. The latter acids then are extracted with ether. A mixture of three diamantanedicarboxylic acids is obtained; by comparing the retention data and the mass spectra of their dimethyl esters with those of standards, the first acid (in the order of elution of the dimethyl esters in the GLC on XF-1150 stationary phase) was identified to be 1,6-diamantanedicarboxylic acid, the second, 1,4-diamantanedicarboxylic acid, and the third, 4,9-diamantanedicarboxylic acid. The 1,6- and 4,9-diamantanedicarboxylic acids standards were prepared according to^{1,2}, the starting dibromodiamantanes were hydrolyzed to the corresponding diamantane-diols with concentrated nitric acid⁷.

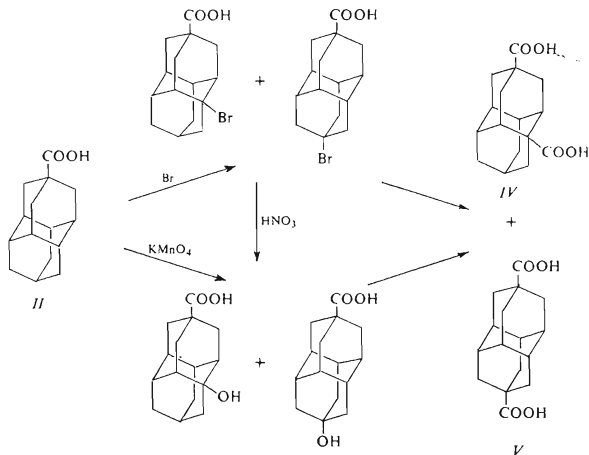
The two diamantanemonocarboxylic acids prepared were either brominated with liquid bromine under boil, or oxidized with an aqueous solution of KMnO_4 at room temperature. In order to make the results of the two reactions mutually



SCHEME 2

comparable, samples of the reaction mixtures from the brominations were hydrolyzed with nitric acid. Another reason for the hydrolysis of the bromo-acids consisted in the fact that their methyl esters decompose partly during the gas chromatographic analysis, and so the results of analysis are ill-reproducible. The structure of the hydroxy-acids was not determined directly, but was suggested based on the results of the carboxylation at high dilutions assuming that under such conditions isomerization does not take place at all or is very low indeed.

Bromination (or oxidation) of 1-diamantanecarboxylic acid can result in the formation of five bromo- (or hydroxy-) acids, *viz.* 2-bromo-, 4-bromo-, 6-bromo-, 7-bromo-, and 9-bromodiamantane-1-carboxylic acids. In reality, however, only three hydroxy-acids are actually formed during the oxidation; their ratio is 28 : 32 : 40. During bromination, a mixture of three bromo acids is formed which on hydrolysis are transformed into the same hydroxy-acids in the ratio 51 : 42 : 7 (Scheme 2). 4-Diamantanecarboxylic acid can theoretically give rise to three bromo- (or hydroxy-) acids, *viz.* 1-bromo-, 2-bromo-, and 9-bromodiamantane-4-carboxylic acids, but in fact only two of them appear, in the ratios 91 : 9 on the bromination and 51 : 49 on the oxidation (Scheme 3). Of the two ways, oxidation is inferior to bromination in that it is more time-consuming and a great deal of the starting acid remains un-



SCHEME 3

reacted. Koch-Haaf carboxylation of a mixture of the bromodiamantane-1-carboxylic acids in high dilution afforded a mixture of three diamantanedicarboxylic acids, *viz.* 1,6-, 1,7-, and 1,4-diamantanedicarboxylic acids in the proportions 44, 46, and 10% wt., respectively. The compounds were transformed into the corresponding diesters with diazomethane, and separated by elution chromatography on silica gel. Obtained were pure dimethyl 1,6-diamantanedicarboxylate and a concentrate of dimethyl 1,7-diamantanedicarboxylate, which then was purified by preparative high performance liquid chromatography. Its structure was confirmed by NMR spectrometry measurements using shift reagents. Koch-Haaf carboxylation of a mixture of bromodiamantane-4-carboxylic acids in high dilution afforded 1,4- and 4,9-diamantanedicarboxylic acids in the proportions 93 and 7% wt., respectively. Pure 1,4-diamantanedicarboxylic acid was obtained by crystallization of the crude product, the crystallization residue was transformed into a mixture of diesters and separated by elution chromatography on silica gel to give pure dimethyl 1,4- and 4,9-diamantanedicarboxylates.

Great differences were found in the reactivity of carboxy groups bonded at the medial and at the apical carbon atoms: while a carboxy group in the position 4 is readily esterified, a carboxy group in the position 1 virtually is not esterified at all. This can form a basis for the separation of 1- and 4-diamantanecarboxylic acids from their mixtures. Esterification of 1,4-diamantanedicarboxylic acid, containing carboxy groups of both types in a molecule, results in the formation of a mono ester. *viz.* 4-methyl ester of 1,4-diamantanedicarboxylic acid. Hydrolysis of the dimethyl ester of this acid concerns the ester group in the position 4, whereupon the other mono ester is formed. A carboxy group at a medial carbon atom can be esterified quantitatively only with diazomethane.

EXPERIMENTAL

Analytical and Separation Techniques

The chromatographic analyses were performed on a CHROM 4 apparatus fitted with a flame ionization detector. A glass column 1 200 mm long, i.d. 3 mm, packed with Chromaton N-AW-DMCS wetted with 3% XF 1150 was used. Nitrogen served as the carrier gas, the column temperature was 160–180°C. The composition of the mixture was evaluated from the chromatograms. Diamantanecarboxylic acids and substituted diamantanecarboxylic acids as well as diamantanedicarboxylic acids were analyzed in the form of their methyl esters, obtained by esterification with diazomethane.

The mass spectra of the compounds prepared were measured on an LKB 9000 instrument (GC/MS combination). The spectra of the pure compounds were measured by the heated inlet or direct inlet techniques, the spectra of the compounds from the mixtures were run after a preliminary gas chromatographic separation. Their detailed analysis will be the subject of a forthcoming paper.

The ^{13}C NMR spectra were measured on a Varian XL 101 spectrometer. CDCl_3 served as the solvent, $\text{Eu}(\text{FOD})_3$ as the shift reagent. The analysis of the spectra will also be given in a forthcoming paper.

The separations were carried out on a Jobin-Yvon Chromatospac Prep 100 liquid chromatograph. The column length was 270 mm, i.d. 40 mm, the packing was 200 g of SILASORB 600 silica gel supplied as particles of irregular shape, size 10–20 μm (Lachema, Brno), Pentane containing 10% wt. diethyl ether was used as the mobile phase; its flow rate was 25 ml/min. A differential refractometer served for the detection. The sample was introduced into the column in the solid state.

The melting points of acids III and V were determined on a Perkin-Elmer 1B differential scanning calorimeter in nitrogen, for the other substances the melting points were determined in a capillary and their values have been corrected.

1,6-Dibromodiamantane

Bromine (5 ml) was added portionwise to diamantane (5 g, 26.7 mmol) stirred at room temperature. After the major part had reacted, the mixture was boiled under reflux for 18 h preventing access of air moisture. The excess bromine was distilled off and its residues were removed with an air stream. The reaction product was taken up in chloroform, the solution was washed with NaHSO_3 solution and water and dried, and chloroform was distilled off to give the crude product (8.9 g). The latter was boiled with hexane (50 ml), and after cooling, crystals of 1,6-dibromodiamantane were collected (2.8 g).

For $\text{C}_{14}\text{H}_{18}\text{Br}_2$ (346.1) calculated: 46.18% Br, found: 45.88% Br. M.p. 270.8–272.7°C (ref.³ 272–273°C).

Bromination of Diamantane with Bromine in the Presence of AlBr_3

Diamantane (15 g, 79.8 mmol) was placed in a 250 ml flask fitted with a stirrer and a calcium chloride trap and accommodated in a cooling bath at 0°C, and to the stirred substance was added dry bromine (40 ml). After the reaction the mixture was cooled to –7°C and a portion (0.4 g) of anhydrous AlBr_3 was added. A reaction associated with a vigorous evolution of hydrogen bromide took place. After the reaction (3 min) the contents of the flask were poured onto an ice– NaHSO_3 mixture. The products were extracted with ether and the extract was washed with water and dried with anhydrous Na_2SO_4 , and ether was distilled off. The crude product (28.5 g) was boiled with hexane (50 ml), and after cooling down, the separated substance was collected (22.9 g) and analyzed gas chromatographically. It was found to contain 1,4-, 1,6-, and 4,9-dibromodiamantanes in the proportions 24.2, 12.3, and 63.3% wt., respectively. By elemental analysis, 49.3% bromine was found (for dibromodiamantane calculated: 46.18% Br).

Bromination of Diamantane with tert-Butyl Bromide in the Presence of AlBr_3

Diamantane (12 g, 63.8 mmol) was dissolved in cyclohexane (100 ml) in a flask accommodated in a cooling bath at 0°C (part of the substance remained undissolved). tert-Butyl bromide (12 g) and anhydrous AlBr_3 (0.5 g) were added and the mixture was stirred at 0°C for 2 h; the reaction was terminated by adding water (10 ml). The cyclohexane solution was drawn off, washed with water and dried with anhydrous Na_2SO_4 , and cyclohexane was distilled off. The product (18.6 g) contained 85.4% wt. 1- and 4-bromodiamantanes, the remaining part was 1,4-, 1,6- and 4,9-dibromodiamantanes in the mutual ratio 1 : 0.66 : 1.76.

Diamantane-1,6-diol

1,6-Dibromodiamantane (0.8 g, 2.32 mmol) was stirred with 65% HNO_3 (10 ml) on water bath heated at 70°C until bromine ceased to evolve (20 min). The reaction mixture was diluted with water, the product separated was collected, washed with water to a neutral reaction, and dried to give diamantane-1,6-diol in a 68% yield (0.35 g). For $\text{C}_{14}\text{H}_{20}\text{O}_2$ (220.3) calculated: 82.30% C, 9.87% H; found: 82.33% C, 9.96% H. M.p. 225.0–226.8°C.

Diamantane-4,9-diol

The dibromodiamantane mixture from the diamantane bromination in the presence of AlBr_3 (27.5 g, 72.5 mmol) was stirred with 65% HNO_3 (100 ml) on water bath at 70°C until bromine ceased to evolve (20 min); bromine vapours were removed with an air stream. The reaction mixture was diluted with water to 500 ml, the product separated was filtered out, washed with water to a neutral reaction, and dried to give diamantane-4,9-diol (9.8 g); m.p. 289.4–291.1°C (ref.⁸ 290–292°C). An additional portion (5.2 g, 53%) of diamantanediols (2% of 1,6-, 61% of 1,4-, and 37% of 4,9-diols) was obtained by extracting the filtrate and the washing waters with ether.

1,6-Diamantanedicarboxylic Acid (*III*)

To 96% H_2SO_4 (100 ml) cooled to 0°C were added several drops of HCOOH and a portion (1.0 g, 3.27 mmol) of 1,6-dibromodiamantane in CCl_4 (50 ml), and 98% HCOOH (25 ml) was added dropwise to the stirred mixture within 4 h. The reaction mixture was poured into water, the product was extracted with ether, and the extract was washed with 5% aqueous solution of ammonia. The ammoniacal solution was made acidic with HCl , and the acid separated was extracted with ether. The extract was washed with water and dried with anhydrous Na_2SO_4 , and ether was distilled off to give acid *III* in a yield of 87% (0.7 g). For $\text{C}_{16}\text{H}_{20}\text{O}_4$ (276.3) calculated: 69.54% C, 7.29% H; found: 69.47% C, 7.31% H. M.p. 410°C (DSC measurements).

To 96% H_2SO_4 (25 ml) was added diamantane-1,6-diol (0.20 g, 0.91 mmol), and within 15 min, 98% HCOOH (5 ml) was added dropwise to the stirred mixture. The reaction system was poured onto ice and extracted with ether. The extract was washed with water and dried, and ether was distilled off. Yield 80% (0.20 g) of acid *III*.

4,9-Diamantanedicarboxylic Acid (*V*)

To 96% H_2SO_4 (70 ml) cooled to 0°C and containing several drops of HCOOH was added diamantane-4,9-diol (1.0 g, 4.54 mmol), and 98% HCOOH (15 ml) was added dropwise with stirring within 4 h. The reaction mixture was decomposed by pouring it onto ice. The product was collected, washed with water to a neutral reaction, and dried to afford acid *V* in a 96% yield (1.20 g). For $\text{C}_{16}\text{H}_{20}\text{O}_4$ (276.3) calculated: 69.54% C, 7.29% H; found: 69.50% C, 7.23% H. M.p. 404°C (by DSC) (ref.² 456°C, determined in a capillary).

Synthesis of 1- and 4-Diamantanedicarboxylic Acids (*I*, *II*)

The mixture from the diamantane bromination with tert-butyl bromide and AlBr_3 (18.6 g), CCl_4 (1 000 ml), 98% HCOOH (110 ml), and 96% H_2SO_4 (1 000 ml) were taken to the reaction. To sulfuric acid cooled to 0°C and containing several drops of HCOOH was added, in one portion, the solution of the bromide mixture in CCl_4 , and formic acid was added dropwise to the stirred and cooled (0°C) system within 6 h. The reaction mixture was poured onto ice and extracted

with ether. The ethereal extract together with the insoluble part was washed with 5% ammonia solution. The precipitate formed was collected and washed with water and ether and taken up in a mixture of ether and 10% aqueous HCl. The ethereal extract was washed with water and dried, and ether was distilled off. The crude diamantane-4-carboxylic acid (*II*) obtained (5.0 g) was recrystallized from benzene. For $C_{15}H_{20}O_2$ (232.2) calculated: 77.55% C, 8.68% H; found: 77.50% C, 8.71% H. M.p. 278.7–281°C (ref.⁶ 278.5–279.9°C). The ammoniacal aqueous solution was separated from the organic (ether- CCl_4) layer, the latter was washed with water and dried, and the solvent mixture was distilled off. In this manner, unreacted dibromodiamantane (5.6 g) was reclaimed. The ammoniacal aqueous solution was made acidic with HCl and extracted with pentane. The precipitate formed was filtered out, washed with pentane and water to a neutral reaction, and dried to yield acids *III*, *IV* and *V* in a ratio 8 : 22 : 70 (total of 1.7 g).

The pentane solution was washed with water and dried, and pentane was distilled off to give acid *I* (5.0 g); m.p. 200–201.8°C (ref.⁵ 201–202.2°C).

The crystallization residues of acid *II* (2.1 g) were dissolved in methanol (100 ml), concentrated H_2SO_4 (2 ml) was added, and the mixture was refluxed for 10 h. Methanol was distilled off and the residue was taken up in pentane. The pentane solution was washed with 10% K_2CO_3 solution and water and dried, and pentane was removed by distillation. Methyl ester of acid *II* contaminated by 2% of methyl ester of acid *I* (1.4 g) was obtained. The alkaline waters were acidified and extracted with ether to give acid *I* contaminated by 5% of acid *II* (0.5 g).

The above mixture of diamantanedicarboxylic acids *III*, *IV*, and *V* (10.2 g) was dissolved in methanol (300 ml), concentrated H_2SO_4 (5 ml), was added, and the system was refluxed for 8 h. Methanol was removed by distillation and the residue was taken up in ether. The ethereal solution was washed with water, 3% aqueous ammonia, and water, dried with Na_2SO_4 , and ether was distilled off to give dimethyl ester of acid *V* (7.6 g); m.p. 188.5–190°C (ref.² 189 to 190°C). The mass spectrum exhibits the ions M^+ (13%), $[M-58]^+$ (21%), $[M-59]^+$ ($COOCH_3$, 100%), and in addition, *m/e* 217 (2%), 213 (6%), 185 (27%). ^{13}C chemical shifts in the FT NMR spectrum (δ): 177.9 (2C), 151.5 (2C), 39.3 (6C), 38.9 (2C), 26.5 (6C).

The ammoniacal aqueous solutions were acidified and extracted to give "acid" fraction" (3.4 g), which was esterified with CH_2N_2 and gas chromatographically analyzed. Only dimethyl esters of acids *III* and *IV* were present in the ratio 21 : 79.

Bromination of Diamantanecarboxylic Acids

A mixture of a diamantanecarboxylic acid with bromine was boiled under reflux condenser with stirring for 1 h, bromine was then removed by distillation, and the residue was taken up in a mixture of an aqueous solution of $NaHSO_3$ and ether. The ethereal solution was washed with water and dried with anhydrous Na_2SO_4 , and ether was distilled off.

1-Diamantanecarboxylic acid: 2.32 g (10 mmol) of the acid and 10 ml of dry bromine were taken; 3.05 g of a bromo acid mixture was obtained.

4-Diamantanecarboxylic acid: 1.2 g (5.2 mmol) of the acid and 5 ml of dry bromine were taken, 2.3 g of a bromo acid mixture was obtained.

Oxidation of Diamantanecarboxylic Acids with $KMnO_4$

To a solution of KOH in water was added the diamantanecarboxylic acid of interest and $KMnO_4$ and the mixture was allowed to stand at room temperature with occasional stirring until the violet colour of the permanganate disappeared. The MnO_2 formed was sucked off and washed with hot water. The filtrate was made acidic with H_2SO_4 and extracted with ether; the extract was washed with water and dried, and ether was distilled off.

1-Diamantanecarboxylic acid: The amounts taken were 2.32 g (10 mmol) of the acid, 1.7 g of KOH in 150 ml of distilled water, and 1.55 g of KMnO_4 . The reaction period was 50 h. The product (1.7 g) contained, in addition to the unreacted acid (8% wt.), two hydroxy acids in the ratio 28 : 32 : 40.

4-Diamantanecarboxylic acid: To the reaction were taken 2.32 (10 mmol) of the acid, 1.7 g of KOH in 150 ml of distilled water, and 1.55 g of KOH. The reaction period was 90 h. The product (1.2 g) contained, besides 17% of the unreacted acid, two hydroxy acids in the ratio 51 : 49.

Hydrolysis of Bromodiamantanecarboxylic Acids

The bromo acid mixture in 65% HNO_3 was stirred on water bath at 80°C until bromine vapours ceased to evolve (15–20 min), the vapours being removed by means of air stream. During the reaction the suspension transformed into a clear solution. The reaction mixture then was diluted with water and extracted with ether. The extracts were washed with a solution of NaHSO_3 and water and dried, and ether was removed by distillation.

Bromodiamantane-1-carboxylic acids: The reaction was carried out using 0.5 g of the bromo acid mixture and 5 ml of 65% HNO_3 . A mixture (0.35 g) was obtained of three hydroxy-acids in the ratio 51 : 42 : 7, their methyl esters exhibited the same retention times as those of the hydroxy acids formed on the oxidation of 1-diamantanecarboxylic acid with KMnO_4 .

Bromodiamantane-4-carboxylic acids: 1.0 g of the bromo acid mixture and 10 ml of 65% HNO_3 were taken. Obtained was 0.75 g of a mixture of two hydroxy acids (in the ratio 91 : 9) whose methyl esters displayed retention times identical with those of methyl esters of the hydroxy acids resulting from the oxidation of 4-diamantanecarboxylic acid with KMnO_4 .

Koch-Haaf Carboxylation of Bromodiamantane-1-carboxylic Acids

The procedure using the reaction product from the bromination of diamantane-1-carboxylic acid (0.80 g, 2.58 mmol), CCl_4 (50 ml), 98% HCOOH (25 ml), and 96% H_2SO_4 (100 ml) was the same as that employed for the synthesis of 1,6-diamantanedicarboxylic acid. The reaction period was 10 h. The reaction mixture was decomposed by pouring it onto ice and extracted with ether. The extract was worked up as usual to yield 98% (0.70 g) of a mixture of acids *III*, *VI*, and *IV* in the ratio 44 : 46 : 10.

The diamantanedicarboxylic acids mixture was esterified with diazomethane, and a portion (3.8 g) of the mixture obtained was separated by elution chromatography on silica gel (250 g of silica gel; eluent: hexane-ether mixture with increasing content of ether). Yield: 0.75 g of a concentrate of acid *IV* dimethyl ester (purity about 95%) and 0.60 g of pure acid *III* dimethyl ester. M.p. 191–191.5°C. The mass spectrum exhibits the ions M^+ (7%), $[\text{M}-32]^+$, (CH_3OH , 4%), $[\text{M}-58]^+$ (19%), $[\text{M}-59]^+$ (COOCH_3 , 100%), $[\text{M}-60]^+$ (46%), and additional *m/e* 217 (21%), 213 (7%), 187 (21%), 185 (54%). ^{13}C chemical shifts (δ): 177.3 (2C), 51.4 (2C), 46.9 (2C), 41.8 (2C), 37.6 (4C), 34.7 (4C), 25.8 (2C). The remainder was constituted by fractions with different proportions of the three compounds present. The concentrate was subjected to preparative liquid chromatography separation, which afforded 0.55 g of pure dimethyl ester of acid *VI*. M.p. 95.0–97.0°C. The mass spectrum displays the ions M^+ (14%), $[\text{M}-32]^+$ (CH_3OH , 5%), $[\text{M}-58]^+$ (21%), $[\text{M}-59]^+$ (COOCH_3 , 100%), and, in addition, *m/e* 217 (18%), 213 (7%), 187 (23%), 185 (44%). The ^{13}C chemical shifts in the FT NMR spectrum were (δ): 177.0 (2C), 51.4 (2C), 47.8 (2C), 41.7 (2C), 37.4 (2C), 36.9 (3C), 35.0 (2C), (32.4 (1C), 26.9 (1C) 24.7 (1C).

Koch-Haaf Carboxylation of Bromodiamantane-4-carboxylic Acids

The reaction comprising the reaction product from the bromination of diamantane-4-carboxylic acid (0.60 g, 1.9 mmol), CCl_4 (50 ml), 98% HCOOH (25 ml), and 96% H_2SO_4 (100 ml) was conducted in the same manner as in the preceding case. Yield 91% (0.50 g) of a product consisting of diamantanecarboxylic acids *IV* and *V* in the ratio 93 : 7. Crystallization of the product from benzene afforded pure acid *IV*, m.p. 306.3–309.5°C.

The crystallization residue was converted to a mixture of the dimethyl esters by means of diazomethane, and separated by elution chromatography on silica gel (3.1 g of the dimethyl ester mixture, 220 g of silica gel; eluent: hexane-ether). Yield: 0.9 g of pure dimethyl ester of acid *IV*, m.p. 90.1–90.8°C. Mass spectrum: M^+ (16%), $[\text{M}-32]^+$ (CH_3OH , 7%), $[\text{M}-58]^+$ (19%), $[\text{M}-59]^+$ (COOCH_3 , 100%), $[\text{M}-60]^+$ (41%); *m/e* 217 (3%), 213 (6%), 185 (50%). ^{13}C chemical shifts (δ): 177.8 (1C), 177.0 (1C), 51.5 (2C), 46.5 (1C), 41.4 (1C), 39.7 (1C), 38.6 (1C), 37.2 (2C), 37.0 (2C), 36.9 (2C), 36.7 (2C), 26.7 (1C), 26.2 (1C).

A mixture of methanol (100 ml), acid *IV* (2.0 g), and concentrated H_2SO_4 (2 ml) was refluxed for 8 h, the excess methanol was removed by distillation, and the residue was dissolved in ether. The ethereal solution was washed with water and dried, and ether was distilled off. The residue was recrystallized from a benzene-hexane mixture. Yield: 1.50 g of 4-methyl ester of 1,4-diamantanedicarboxylic acid, m.p. 146.5–148.0°C.

Solution of dimethyl ester of acid *IV* (0.50 g) and KOH (2.0 g) in a methanol-water mixture (70 : 30) was refluxed for 3 h, poured into water, and extracted with ether. The extract was washed with water and dried, and ether was distilled off. The residue was recrystallized from benzene to give 1-methyl ester of 1,4-diamantanedicarboxylic acid (0.33 g), m.p. 209.0–210.3°C.

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