

PREPARATION OF DIAMANTANEDICARBOXYLIC ACIDS WITH CARBOXYL GROUPS ON ONE SECONDARY AND ONE TERTIARY CARBON ATOM

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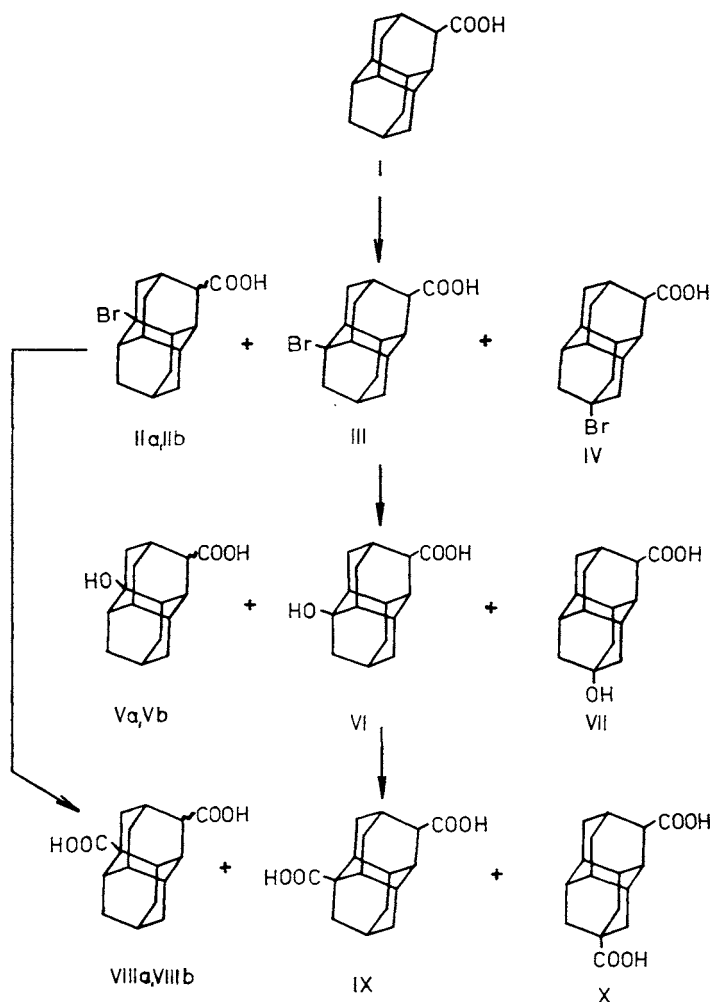
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Bromination of 3-diamantanecarboxylic acid leads to a mixture of bromodiamantanecarboxylic acids which on Koch-Haaf carboxylation at high dilution affords a mixture of diamantanedicarboxylic acids with one carboxyl on the secondary and the other on the tertiary carbon atom of the diamantane skeleton. At low dilution, the Koch-Haaf carboxylation gives predominantly 3,9-diamantanedicarboxylic acid.

In our previous paper¹ we studied the preparation of diamantanedicarboxylic acids with both carboxyl groups on tertiary carbon of the diamantane skeleton. As follows from the Table in the mentioned paper¹, six diamantanedicarboxylic acids are possible which have one carboxyl group on the secondary and the other on the tertiary carbon atom (1,3-, 1,5-, 1,8-, 1,13-, 3,4-, 3,9-), two of them (1,3- and 1,8-) existing as pairs of configurational isomers. Suitable starting compound for the preparation of such compounds appears to be 3-diamantanecarboxylic acid. Uncatalyzed bromination of the acid affords a mixture of bromodiamantane-3-carboxylic acids² containing predominantly 11-bromodiamantane-3-carboxylic acid. This mixture on hydrolysis with concentrated nitric acid gives a mixture of the corresponding hydroxydiamantanecarboxylic acids which on isomerization in concentrated sulfuric acid gives 9-hydroxydiamantane-3-carboxylic acid as the principal product². Both bromodiamantanecarboxylic and hydroxydiamantanecarboxylic acids are immediate precursors for the preparation of diamantanedicarboxylic acids by the Koch-Haaf carboxylation.

The reactions carried out in this study are shown in Scheme 1. Bromination of 3-diamantanecarboxylic acid afforded a mixture of bromodiamantanecarboxylic acids *IIa*, *b*, *III*, and *IV*. A part of the mixture was subjected to Koch-Haaf carboxylation at highly diluted solution, another part was hydrolyzed with nitric acid. The obtained mixture of hydroxydiamantanecarboxylic acids *Va*, *b*, *VI*, and *VII* was then carboxylated at low dilution. In highly diluted solution, bimolecular isomerization of the substituted diamantyl cation is maximally suppressed¹ and the arising

diamantanedicarboxylic acids therefore retain the structure of the starting bromo acids. On the contrary, at low dilution the isomerization should be maximally enhanced. The high dilution-carboxylation gives predominantly the acids *VIIIa, b* and *IX* with one carboxyl group on the medial carbon atoms (95% of the product), the latter



SCHEME 1

acid being the principal product (63% of the product). Low dilution-carboxylation gives acid *X* as the principal product (64% of the product). The acids were separated using the fact that carboxyls on the medial carbon atoms are esterified substantially more slowly than those on the secondary and apical carbon atoms^{1,3}. Thus, acid *X* is

esterified with methanol to give practically quantitatively the dimethyl ester whereas acids *VIIIa*, *b* and *IX* afford only monomethyl esters separable in the form of salts. From a mixture of dimethyl esters of acids *VIIIa*, *b* and *IX* the latter ester was obtained in the pure form by elution chromatography on silica gel. The isomers *VIIIa* and *VIIIb* were separated from each other by preparative gas-liquid chromatography.

EXPERIMENTAL

Analytical and Separation Techniques

Gas-liquid chromatographic analyses were performed on a Chrom 5 chromatograph, equipped with a 3×1200 mm glass column packed with 3% XF 1 150 on Chromaton N-AW-DMCS; temperature 160°C, carrier gas N₂, flame-ionization detector. Diamantanedicarboxylic acids were analyzed as methyl esters prepared by treatment of the sample with diazomethane.

Preparative gas-liquid chromatography was carried out on a Chrom 5 instrument (2300×10 mm stainless steel column, 5% XF 1 150 on Chromaton N-AW-DMCS; 190°C, carrier gas nitrogen).

Mass spectra were taken on an LKB 9000 spectrometer. Spectra of pure compounds were measured using direct inlet, spectra of mixtures after separation on a gas-liquid chromatographic column at the peak maximum.

¹³C NMR spectra were recorded in deuteriochloroform on a Varian XL 1001 instrument. Only methyl esters (prepared by treatment with diazomethane) were measured since the free acids were insoluble. The spectra were interpreted using an additive rule derived from the published data^{4,5}.

Bromination of 3-Diamantanedicarboxylic Acid

A mixture of acid *I* (6.0 g; 25.9 mmol) and dry bromine (40 ml) was refluxed (calcium chloride protecting tube) until hydrogen no longer evolved (1 h). The excess bromine was distilled off, the residue dissolved in ether and the residual bromine removed by washing with 5% aqueous potassium hydrogen sulfite. Removal of the solvent afforded 7.8 g (97%) of a mixture of bromodiamantanedicarboxylic acids.

Hydrolysis of Bromodiamantanedicarboxylic Acids

A stirred mixture of the reaction product (1.5 g; 4.8 mmol) from the bromination of *I* and 65% nitric acid (6 ml) was heated to 70°C until bromine evolution ceased (10 min), the bromine vapours being removed by a stream of air. The mixture was poured in water and extracted with ether. The ethereal extract was washed with 5% aqueous potassium hydrogen sulfite, dried and taken down, affording 1.05 g (88%) of a mixture of hydroxydiamantanedicarboxylic acids.

Koch-Haaf Carboxylation of Bromodiamantanedicarboxylic Acids

To 96% sulfuric acid (150 ml), pre-cooled to 0°C, were added with stirring 99% formic acid (3 ml), the product of bromination of *I* (1.7 g; 5.5 mmol) in tetrachloromethane (100 ml), and during 2.5 h further formic acid (30 ml). The mixture was stirred for 2 h, decomposed by pouring on ice and extracted three times with ether. The extract was washed with water, dried and taken down, leaving 1.35 g (80%) of a mixture of diamantanedicarboxylic acids of the following composition

(gas-liquid chromatography; relative elution volumes in parentheses): *VIIIa* (0.82) 18.6%, *VIIIb* (0.93) 14.9%, *IX* (1.00) 62.6%, *X* (1.29) 4.9%. Crystallization of the reaction product from hexane-benzene gave 0.05 g of the acid *IX*, m.p. 257.0—258.5°C. For $C_{16}H_{20}O_4$ (276.3) calculated: 69.54% C, 7.29% H; found: 69.45% C, 7.35% H.

Koch-Haaf Carboxylation of Hydroxydiamantanecarboxylic Acids

The reaction product from hydrolysis of bromodiamantanecarboxylic acids (0.75 g; 3.0 mmol) was added to 96% sulfuric acid (20 ml), pre-cooled to 0°C. Formic acid (99%; 7 ml) was added during 2 h and the mixture was stirred for another hour. After decomposition with ice, the product was extracted three times with ether. The extract was washed with water, dried and the solvent evaporated, affording 0.8 g (96%) of a mixture of diamantanedicarboxylic acids containing (according to gas-liquid chromatography) *VIIIa* (7.5%), *VIIIb* (5.5%), *IX* (22.6%) and *X* (64.4%). Crystallization of the product from hexane-benzene afforded 0.10 g of acid *X*, m.p. 279.2—280.6°C (decomposition). For $C_{16}H_{20}O_4$ (276.3) calculated: 69.54% C, 7.29% H; found: 69.50% C, 7.23% H.

The crystallization residues from both carboxylations (1.9 g; 6.9 mmol) were dissolved in methanol (50 ml) and refluxed with concentrated sulfuric acid (1 ml) for 7 h. After evaporation of methanol, the residue was dissolved in ether, the solution washed with 5% aqueous ammonia, dried and taken down, yielding 0.55 g of dimethyl ester of *X*, m.p. 46.8—47.6°C (hexane). For $C_{18}H_{24}O_4$ (304.4) calculated: 71.03% C, 7.95% H; found: 70.98% C, 7.91% H. Mass spectrum, m/z (%): 304 (21%, M), 272 (5%, M—CH₃OH), 246 (18%), 245 (100%, M—COOCH₃), 244 (44%), 216 (2%), 185 (32%). ¹³C NMR spectrum (ppm): 177.0 (2 C, COOCH₃), 51.4 (2 C, COOCH₃), 39.4 (C_q), 27.3, 33.5, 36.2, 37.9, 38.2, 38.6, 39.9, 50.4 (CH), 34.1, 37.2, 38.2, 39.6 (2 C, CH₂).

The aqueous ammonia washing was acidified with hydrochloric acid and extracted three times with ether. The ethereal extract was washed with water, dried and the solvent evaporated, affording 1.35 g of a mixture of monomethyl esters of *VIIIa, b* and *IX*. Crystallization from benzene-hexane gave 0.10 g of 5-monomethyl ester of *IX*, m.p. 165.2—167.3°C. For $C_{17}H_{22}O_4$ (290.4) calculated: 70.32% C, 7.64% H; found: 70.40% C, 7.69% H. The crystallization residue was dissolved in methanol and converted to the dimethyl esters by treatment with an ethereal solution of diazomethane. Chromatography of the mixture on silica gel (200 g) in hexane-ether (with gradient of ether) gave dimethyl ester of *IX* (0.60 g), m.p. 123.5—124.5°C, a mixture of dimethyl esters of *VIIIa, b* (0.50 g) and a middle fraction (0.15 g). Mass spectrum of dimethyl ester of *IX*, m/z (%): 304 (9%, M), 272 (2%, M—CH₃OH), 245 (100%, M—COOCH₃), 244 (24%), 216 (7%), 213 (7%), 187 (13%), 186 (9%), 185 (38%). ¹³C NMR spectrum, ppm: 178.1 (2 C, COOCH₃), 51.5 (2 C, COOCH₃), 47.1 (C_q), 26.1, 26.5, 28.0, 33.9, 36.8, 37.1, 38.0, 50.4 (CH), 31.2, 35.8, 36.8, 37.4, 41.7 (CH₂). For $C_{18}H_{24}O_4$ (304.4) calculated: 71.03% C, 7.95% H; found: 71.16% C, 8.02% H.

The mixture of dimethyl esters of *VIIIa, b* was separated by preparative gas-liquid chromatography, affording a colourless oil, containing dimethyl ester of *VIIIa* (0.15 g), and dimethyl ester of *VIIIb* (0.20 g), m.p. 109.8—111.5°C. For $C_{18}H_{24}O_4$ (304.4) calculated: 71.03% C, 7.95% H; found: 70.98% C, 7.84% H. Mass spectrum *VIIIb* (GC-MS), m/z (%): 304 (8%, M) 272 (5%, M—CH₃OH), 246 (21%), 245 (100%, M—COOCH₃), 244 (34%), 187 (13%), 186 (7%), 185 (39%). ¹³C NMR spectrum, ppm: 174.3, 177.4 (COOCH₃), 51.5 (2 C, OCH₃), 46.7 (C_q), 25.3, 27.6, 33.8, 37.1 (2 C), 37.3, 38.8, 50.1 (CH), 34.8, 35.0, 37.7 (2 C), 38.1 (CH₂). On the basis of these data, the most probable structure of the dimethyl ester of *VIIIb* is dimethyl 1,8^a-diamantane dicarboxylate (e and a denote the relative position of the substituent to the cyclohexane ring bearing both substituents). The oily concentrate of the dimethyl ester of

VIIIa was not pure enough to allow an unequivocal interpretation of its ^{13}C NMR spectrum. Mass spectrum (GC-MS), m/z (%): 273 (9%), 272 (28%, M— CH_3OH), 246 (24%), 245 (100%, M— COOCH_3), 187 (22%), 186 (18%), 184 (15%). The compound is probably dimethyl 1,8^e-diamantanedicarboxylate.

REFERENCES

1. Vodička L., Janků J., Burkhard J.: *This Journal* 48, 1162 (1983).
2. Janků J., Burkhard J., Vodička L.: *Sb. Vys. Šk. Chemicko-Technol. Praze D* 49, 25 (1984).
3. Janků J., Burkhard J., Vodička L.: *Z. Chem.* 21, 67 (1981).
4. Dheu M. L., Gagnaire D., Dudeck H., Hollowood F., McKervey M. A.: *J. Chem. Soc., Perkin Trans. 2*, 1979, 357.
5. Hájek M., Vodička L., Trška P., Sklenář V.: *Org. Magn. Reson.* 23, 57 (1985).

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