SYNTHESIS AND REACTIONS OF HYDROXYDIAMANTANONES

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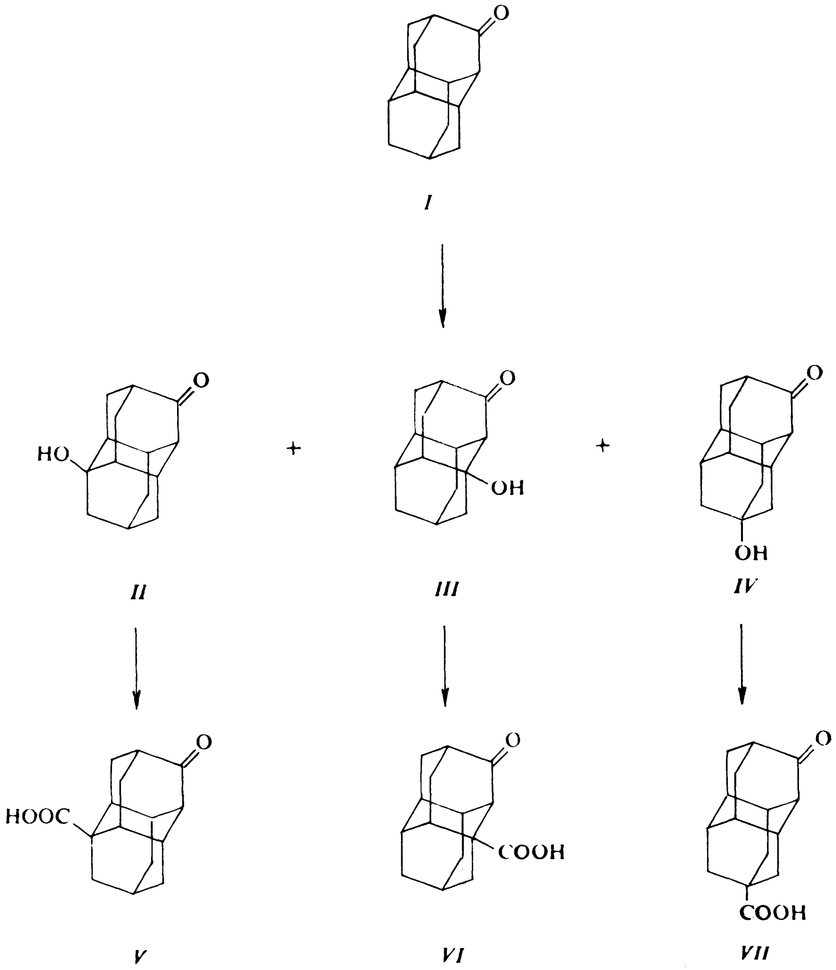
Diamantanone can be oxidized with chromium trioxide in acetic acid solutions to give 11-hydroxy-, 1-hydroxy-, and 9-hydroxy-3-diamantanone as the major products and two diamantanonediones of unelucidated structure as by-products. The Koch–Haaf carboxylation of hydroxydiamantanones results in the formation of the corresponding oxodiamantanecarboxylic acids. Reacted with 100% HNO_3, diamantanone transforms into 9-(3-diamantanonyl) nitrate. Reactions of the carbonyl groups of these compounds with H_2NOSO_2OH lead to hydrazidiamantane derivatives, which oxidized with CrO_3 provide the azidiamantane derivatives.

Hydroxydiamantanones can serve as intermediates for the synthesis of diamantane derivatives carrying a substituent at a secondary carbon atom and another at a tertiary carbon atom of the diamantane system. Up to now, these compounds were prepared by bromination of diamantanone and hydrolysis of the bromodiamantanones formed[1]. In the absence of catalyst the bromination takes 5 weeks, and 11-bromo-3-diamantanone is formed as the major product. In the presence of $AlBr_3$ (in an approximately fourfold molar excess), a roughly 1 : 1 mixture of 9-bromo- and 11-bromo-3-diamantanones emerges. 9-Hydroxy-3-diamantanone appears in a small amount (~ 6%) during the oxidation of diamantane with sulphuric acid[2].

Since these procedures are little effective, the possibility of oxidation of diamantanone with chromium trioxide has been examined in this work in view of the fact that adamantane subjected to this treatment affords 5-hydroxy-2-adamantanone[3,4]. The composition of the reaction mixture resulting from the oxidation of diamantanone is given in Table I. The major products are 11-hydroxy, 1-hydroxy-, and 9-hydroxy-3-diamantanone (*II, III, IV*, Scheme 1). In addition to two unidentified minor components the mixture also contains two diamantanediones, the mass spectra of which only provided their molecular formula; the position of the two keto groups was not established. The hydroxy ketones *II*–*IV* can be separated by elution chromatography on silica gel using a hexane–isopropyl alcohol mixture for the elution. If a hexane–acetone mixture is used, the elution order is reversed and no sharp separation is achieved.

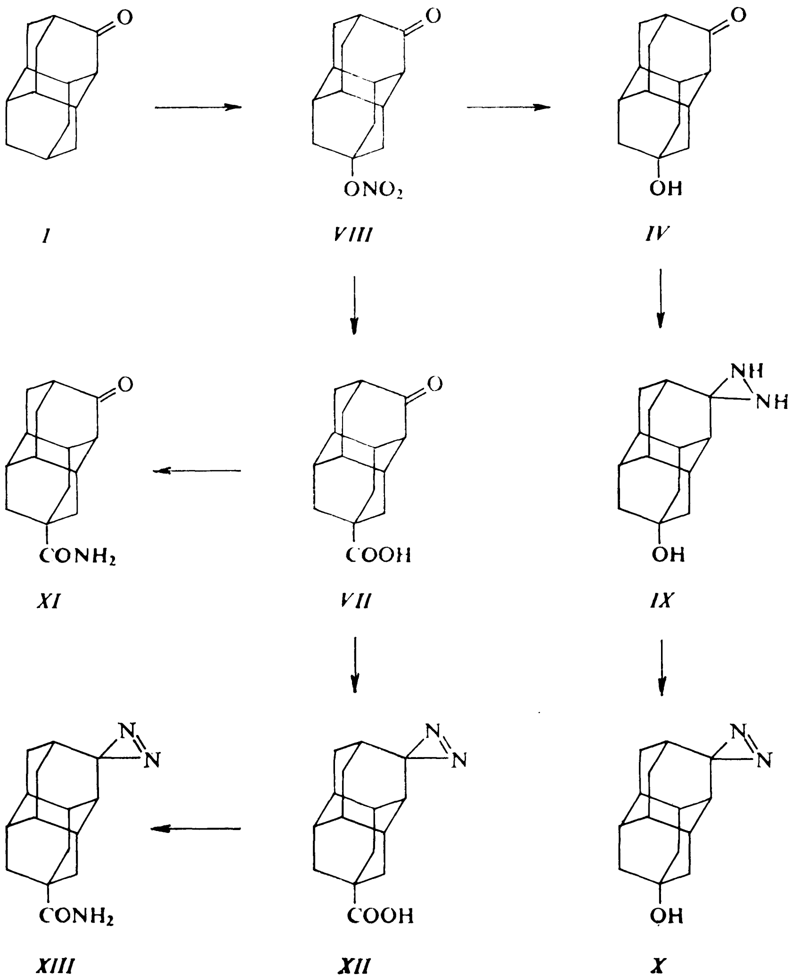
Reacted with 100% HNO_3 at 0°C diamantanone gives 9-(3-diamantanonyl) nitrate

(*VIII*, Scheme 2), which can be transformed into the hydroxy ketone *IV* by reaction with H_2SO_4.



SCHEME 1

The hydroxy ketones *II*–*IV* and nitrate *VIII* subjected to the Koch–Haaf carboxylation at high dilution yield the correspondingly substituted oxodiamantanecarboxylic acids (*V*, *VI*, *VII*, Scheme 1). Other reactions accomplished in this work are shown in Scheme 2. The carbonyl groups in compounds *IV* and *VII* react with H_2NOSO_2OH to give diamatane hydrazi derivatives, which oxidized by chromium trioxide transform into the azi derivatives (*X*, *XII*).



SCHEME 2

EXPERIMENTAL

Analytical and Separation Techniques

Gas chromatography. The analyses were performed on a Chrom 5 gas chromatograph (Laboratorní přístroje, Prague) fitted with a glass column 1·2 m long, i.d. 3 mm, packed with Chromaton N-AW-DMCS of the grain size of 0·15—0·18 mm, wetted with 3% XF-1150. Flame ionizaton detection, carrier gas nitrogen, column temperature 180°C. The acids were analyzed in the form of their methyl esters obtained by esterification with CH_2N_2.

NMR *spectrometry.* The ^{13}C NMR spectra in $CDCl_3$ solutions at 35°C were measured on a Tesla BS 567 pulse spectrometer at 25·14 MHz. Again, the compounds were measured in the form of the methyl esters, which enabled the solutions to be obtained in sufficiently high concentrations.

Infrared spectroscopy. The spectra were scanned on a Perkin–Elmer 325 spectrophotometer using solutions in chloroform.

Elution chromatography. Glass columns 20 and 40 mm in diameter were packed with dry silica gel (grain size 0·10—0·15 mm) activated at 160°C for 4 h. The samples were dissolved in those solvents that subsequently served as the eluting agents, *viz.* hexane–acetone and hexane–isopropyl alcohol mixtures. The concentrations of acetone and isopropyl alcohol in hexane were initially 5% and 2% (*m*/*m*), respectively, and were increased gradually during the treatment. The fractions were analyzed by gas chromatography.

Diamantanone (*I*)

Diamantane (75 g, 399 mmol) was agitated with 96% H_2SO_4 (700 ml) at 70—75°C for 40 h, the mixture was cooled to 0°C, and 99% HCOOH (50 ml) was added dropwise. The unreacted diamantane (34 g) was filtered out on a glass filter, and the filtrate was poured onto ice. The product separated was extracted with ether, the extract was washed with 5% aqueous ammonia and water and dried, and the ether was distilled off. The residue was sublimed in vacuum. Yield 38·2 g (47%) of substance *I*, m.p. 249·0—250·8°C (ref.[5], 249—250°C).

Oxidation of Diamantanone with Chromium Trioxide

Substance *I* (10 g, 49 mmol) was dissolved in 98% CH_3COOH (141 ml), and CrO_3 (24·6 g, 246 mmol) was added portionwise. The mixture was stirred for 1 h at 50—55°C, diluted with water (100 ml), and extracted with chloroform (5 × 150 ml). The extract was washed with 10% aqueous $KHCO_3$ and dried, and the chloroform was removed by distillation. 7·65 g of a product was obtained; the composition as established by gas chromatography is given in Table I. 6·2 g of the oxidation product was separated into components by elution chromatography on silica gel using a hexane–acetone mixture for the elution. Fractions of 0·9 g of substances 1, 2, 3, 7, 8 (Table I), 2·6 g of substance *II* in a 95% purity, 0·7 g of substance *III* in a 70% purity, and 2·8 g

TABLE I

Composition of the product of oxidation of diamantanone by chromium trioxide

Order	Compound	Content % (*m*/*m*)
1	Diamantanone (*I*)	3·2
2	Unidentified	0·8
3	Unidentified	5·4
4	11-Hydroxy-3-diamantanone (*II*)	34·4
5	1-Hydroxy-3-diamantanone (*III*)	24·5
6	9-Hydroxy-3-diamantanone (*IV*)	20·6
7	Diamantanedione A	6·9
8	Diamantanonedione B	4·2

of substance *IV* in an 80% purity were obtained. 17·7 g of the oxidation product was separated by elution chromatography on silica gel using a hexane–isopropyl alcohol mixture. Fractions containing 2·6 g of compounds 1,2,3,7,8 (Table I), 2·35 g of substance *II*, 2·0 g of substance *III*, 2·7 g of substance *IV*, and 9·1 g of intermediate fractions containing hydroxyketones *II*–*IV* were obtained.

11-*Hydroxy*-3-*diamantanone* (II). M.p. 328·2–331·5°C (ref.[1], 316–317°C). Mass spectrum: *m*/*z* 218 (60%, M), 201 (2%), 200 (9%, M–H_2O), 173 (17%), 172 (100%). ^{13}C NMR spectrum (ppm): 213·46 (C=O), 68·8 (C—OH), 30·48, 41·27, 42·99, 43·44, 54·37 (CH), 32·72, 36·12, 46·13 (CH_2).

1-*Hydroxy*-3-*diamantanone* (III). M.p. 336·2–338·7°C (sealed capillary). Mass spectrum: *m*/*z* 218 (100%, M), 201 (17%), 200 (97%, M–H_2O), 173 (16%). ^{13}C NMR spectrum (ppm): 209·98 (C=O), 74·64 (C—OH), 30·32, 33·24, 35·93, 36·08, 36·9, 38·7, 39·14, 42·73 (2 C), 43·78, 45·64, 62·6 (CH, CH_2).

9-*Hydroxy*-3-*diamantanone* (IV). M.p. 195·6–198·0°C (sealed capillary) (ref.[2], 191–193°C). Mass spectrum: *m*/*z* 218 (100%, M), 190 (22%), 175 (2%). ^{13}C NMR spectrum (ppm): 214·54 (C=O), 66·07 (C—OH), 35·86, 39·07, 42·43, 43·78, 54·76 (CH), 37·61, 44·63, 45·08 (CH_2).

Koch–Haaf Carboxylation of Hydroxydiamantanones

The hydroxy ketone-to-formic acid-to-sulphuric acid ratio was invariably 1 : 50 : 500. To 96% H_2SO_4 was added 99% HCOOH (0·3 ml), and within 3–4 h, solution of hydroxy ketone in the remaining HCOOH was added to the constantly stirred and cooled mixture. The stirring was continued for additional 5 h, and the mixture was poured onto ice and extracted with ether. The extract was washed with 5% aqueous ammonia and water and dried, and the ether was removed by distillation. The unreacted hydroxy ketone was reclaimed. The alkaline waters were acidified with 10% H_2SO_4 and extracted with ether. The extract was washed with water and dried, and the ether was distilled off to give oxodiamantanecarboxylic acids.

5-*Oxo*-1-*diamantanecarboxylic acid* (V). 0·6 g (2·7 mmol) of compound *II* was used, of which 0·1 g was reclaimed, and 0·5 g (75%) of acid *V* was obtained. M.p. 114–115°C (from methanol). For $C_{15}H_{18}O_3$ (246·3) calculated: 73·15% C, 7·37% H; found: 73·11% C, 7·12% H. Mass spectrum of methyl ester of acid *V*: *m*/*z* 260 (77%, M), 215 (16%), 202 (17%), 201 (100%, M–$COOCH_3$), 200 (42%), 173 (61%), 172 (63%). ^{13}C NMR spectrum of methyl ester of acid *V* (ppm): 215·78 (C=O), 176·48 (COO), 51·66 (OCH_3), 35·75 (2 C), 35·89 (2 C), 40·89 (CH_2), 26·03, 36·72 (2 C), 3914 (2 C), 42·92, 54·53 (CH), 46·35 (C_q).

3-*Oxo*-1-*diamantanecarboxylic acid* (VI). 0·1 g (0·46 mmol) of substance *III* was taken, and 0·1 g (88%) of acid *VI* was obtained, m.p. 279·0–280·5°C (from benzene, with decomposition). For $C_{15}H_{18}O_3$ (246·3) calculated: 73·15% C, 7·37% H; found: 73·21% C, 7·40% H. Mass spectrum of methyl ester of acid *VI*: *m*/*z* 260 (73%, M), 202 (15%), 201 (86% M–$COOCH_3$), 200 (100%, M–$HCOOCH_3$), 173 (44%), 172 (40%). ^{13}C NMR spectrum of the methyl ester (ppm): 214·66 (C=O), 175·74 (COO), 51·81 (OCH_3), 34·81, 35·86, 36·68, 39·48, 39·59 (CH_2), 26·03, 36·27, 36·83, 37·54, 41·05, 43·40, 55·80 (CH), 50·20 (C_q).

8-*Oxo*-4-*diamantanecarboxylic acid* (VII). Of the 1·0 g of substance *IV* taken for the reaction, 0·3 g was reclaimed, and 0·8 g (71%) of acid *VII* was obtained, m.p. 243·2–244·2°C (from benzene). For $C_{15}H_{18}O_3$ (246·3) calculated: 73·15% C, 7·37% H; found: 73·04% C, 7·21% H. Mass spectrum of methyl ester of acid *VII*: *m*/*z* 260 (77%, M), 201 (100%, M–$COOCH_3$), 173 (21%). ^{13}C NMR spectrum of the methyl ester (ppm): 216·34 (C=O), 177·27 (COO), 51·69 (OCH_3), 38·02 (2 C), 38·10 (2 C), 38·96 (CH_2), 35·82 (2 C), 36·31, 39·44 (2 C), 43·47, 54·76 (CH), 38·96 (C_q).

9-(3-Diamantanoyl) Nitrate (*VIII*)

Diamantanone (8·5 g, 42 mmol) was dissolved in 100% HNO_3 (106 g) and the solution was allowed to stand for 150 h at 0°C, poured onto ice, and the product separated was collected, washed with water, and dried. Yield 9·15 g (82%) of substance *VIII*, m.p. 157—158°C (from benzene). For $C_{14}H_{17}NO_4$ (263·3) calculated: 63·86% C, 6·51% H, 5·32% N; found: 63·76% C, 6·58% H, 5·38% N. The infrared spectrum exhibits bands at 1 615 and 1 705 cm^{-1}.

Hydrolysis of 9-(3-Diamantanoyl) Nitrate

9-(3-Diamantanoyl) nitrate (0·11 g, 0·42 mmol) was dissolved in 96% H_2SO_4 (1 ml), the solution was heated at 50°C for 10 min and poured onto ice. H_2SO_4 was neutralized with K_2CO_3 and the product was extracted with ether. Yield 0·08 g (88%) of substance *IV*.

8-Oxo-4-diamantanecarboxylic Acid (*VII*)

Substance *VIII* (3·0 g, 11·4 mmol) and 99% HCOOH (10 ml) were added portionwise within 30 min to 96% H_2SO_4 (100 ml) cooled to 0°C. The reaction mixture was poured onto ice and extracted with chloroform. The extract was washed with 10% K_2CO_3 and water, dried, and the chloroform was distilled off. Substance *IV* was obtained in a yield of 0·65 g. The alkaline waters were acidified and extracted with chloroform. Acid *VII* was obtained in a yield of 1·95 g (69%)

8-Oxo-4-diamantanecarboxylic Amide (*XI*)

To substance *VII* (3·0 g, 12·2 mmol) was added $SOCl_2$ (10 ml), and the mixture was boiled under reflux for 45 min. The excess $SOCl_2$ was removed by distillation, the residue was dissolved in CCl_4, To the stirred solution was added 25% aqueous ammonia (10 ml). The product was extracted with chloroform to give 1·1 g (35%) of substance *XI*, m.p. 227—229°C (from chlorobenzene). For $C_{15}H_{19}NO_2$ (245·3) calculated: 73·44% C, 7·81% H, 5·71% N; found: 73·38% C, 7·66% H, 5·21% N.

8-Hydrazi-4-hydroxydiamantane (*IX*)

Substance *IV* (1·75 g, 6·7 mmol) was dissolved in 16% NH_3 in methanol (25 ml), and $NH_2.OSO_2OH$ (3 g) was added at −10°C. The reaction mixture was allowed to stand for 15 h at 0°C, methanol was distilled off in vacuum, and the residue was dissolved in chloroform. The solution was washed with 10% H_2SO_4 and water, and the chloroform was distilled off. Substance *IV* was obtained in a yield of 0·33 g. The acid washing waters were alkalized with 25% aqueous ammonia and extracted with chloroform to give 0·92 g (59%) of substance *IX*, m.p. 200—202°C. For $C_{14}H_{20}N_2O$ (232·3) calculated: 72·38% C, 8·68% H, 12·06% N; found: 72·21% C, 8·63% H, 12·00% N.

8-Azi-4-hydroxydiamantane (*X*)

CrO_3 (0·2 g) in 0·1M-H_2SO_4 (15 ml) was added within 30 min to substance *IX* (0·6 g, 2·6 mmol) dissolved in 0·1M-H_2SO_4 and cooled at 0°C. Extracted with chloroform, substance *X* was obtained in a yield of 0·5 g (85%); m.p. 140°C (from benzene, decomposition). For $C_{14}H_{18}N_2O$ (230·3) calculated: 73·01% C, 7·88% H, 12·16% N; found: 72·90% C, 7·86% H, 12·20% N.

8-Azi-4-diamantanecarboxylic Acid (*XII*)

Acid *VII* (1·5 g, 6·1 mmol) was dissolved in 16% ammonia in methanol (25 ml), the solution was cooled to 0°C, NH_2OSO_2OH (3·0 g) was added, and the mixture was allowed to stand at that temperature for 3 h. Methanol was distilled off under vacuum, the residue was dissolved in 0·1M-H_2SO_4 (25 ml) and held at 0°C, and solution of CrO_2 (1·0 g) in 0·1M-H_2SO_4 (50 ml) was added within 1 h. The mixture was extracted with chloroform, and the crude product (1·0 g) was crystallized from a methanol–water mixture to give 0·73 (52%) of acid *XII*, 200°C (decomposition). For $C_{15}H_{18}N_2O_2$ (258·6) calculated: 69·74% C, 7·02% H, 10·84% N; found: 69·80% C, 7·17% H, 10·71% N.

8-Azi-4-diamantanecarboxylic Amide (*XIII*)

Acid *XII* (0·5 g, 1·9 mmol) was dissolved in $SOCl_2$ (6 ml), a drop of dimethylformamide was added, and the mixture was heated for 1 h and allowed to stand at 20°C for 48 h. The excess $SOCl_2$ was distilled off under vacuum, and the residue was dissolved in absolute ether (10 ml) and added dropwise to stirred 25% aqueous ammonia (30 ml). The product was extracted with chloroform, the solvent was removed by evaporation, the residue was dissolved in methanol, and the product was precipitated with a portion of water to give 0·37 g (74%) of amide *XIII*, m.p. 140°C (from a benzene–hexane mixture, with decomposition). For $C_{15}H_{19}N_3O$ (257·3) calculated: 70·01% C, 7·44% H, 16·33% N; found: 69·90% C, 7·53% H, 16·19% N.

REFERENCES

1. Courtney T.: *Thesis*. The Queen's University of Belfast, Belfast 1972.
2. Courtney T., Jonston D. E., McKervey M. A., Rooney J. J.: J. Chem. Soc., Perkin I *1972*, 2691.
3. Vodička L., Hlavatý J., Sevostyanova V. V.: Sb. Vys. Šk. Chem.-Technol. Praze D *39*, 357 (1978).
4. Morat C., Rassat A.: Tetrahedron Lett. *1979*, 4409.
5. Gund T. M., Nomura M., Williams V. Z. jr, Schleyer P. v. R., Hoogzand C.: Tetrahedron Lett. *1970*, 4875.

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