

**REACTION OF HYDROXYDIAMANTANES WITH CHLOROETHYLENES
IN SULFURIC ACID**

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Reaction of hydroxydiamantanes with 1,1-dichloroethylene in concentrated sulfuric acid leads to complex reaction mixtures, containing predominantly diamantylacetic and diamantanebisacetic acids. The same reaction with trichloroethylene affords diamantylchloroacetic and diamantanebischloroacetic acids. In all these products the substituents are bonded to the apical and secondary carbon atoms of the diamantane skeleton. For steric reasons, acids with carboxyl in the medial position are not formed.

Derivatives of adamantane and its homologues react with chloroethylenes in concentrated sulfuric acid according to Scheme 1. The reaction with 1,1-dichloroethylene affords 1-adamantylacetic acid or 1-(alkyladamantyl)acetic acids (Ca)^{1,2}. Reaction with trichloroethylene at low temperature (0–20°C) leads predominantly to 1-adamantylchloroacetic acid (Cb)^{3,4} whereas at higher temperatures (80°C) it gives 1,3-adamantanebischloroacetic acid⁴. The present study of reaction of 1-hydroxy- (*I*), 4-hydroxy- (*II*), and 3-hydroxydiamantane (*III*) with 1,1-dichloroethylene, trichloroethylene, and tetrachloroethylene in concentrated sulfuric acid is aimed at its possible utilization in synthesis of the corresponding diamantylacetic and diamantylchloroacetic acids.

The reactions were carried out according to a general procedure. To simplify the analyses, the reaction products were divided into neutral and acidic portions. The results are given in Table I. According to gas-liquid chromatography and mass spectrometry, the neutral portions consisted of diamantane, 1-chlorodiamantane, 3-chlorodiamantane, hydroxydiamantanes *I–III*, and diamantanone (Table II).

The acidic portions were esterified with diazomethane and analyzed also by gas-liquid chromatography and mass spectrometry.

In the acidic portions obtained from reaction of hydroxydiamantanes *I–III* with 1,1-dichloroethylene (Table III) we found compounds of molecular weight 260, 276, 294, and 332 (Fig. 2). The mass 260 corresponds to methyl diamantylacetates. Mass spectra of these compounds (relative elution times 0.22 and 0.25) exhibit (in addition to the molecular ion) peaks at m/z 229 ($M-OCH_3$), 228 ($M-CH_3OH$), 201 ($M-COOCH_3$), and 186 ($M-CH_3COOCH_3$). The mass 276 corresponds to methyl

hydroxydiamantylacetates. Their mass spectra (relative elution times 1.06, 1.20, 1.30, and 1.41) exhibit peaks at m/z 259 (M-OH), 258 (M-H₂O), 245 (M-OCH₃), 244 (M-CH₃OH), 217 (M-COOCH₃), 216 (M-HCOOCH₃), 203 (M-

TABLE I
Reaction of hydroxydiamantanes I-III with chloroethylenes

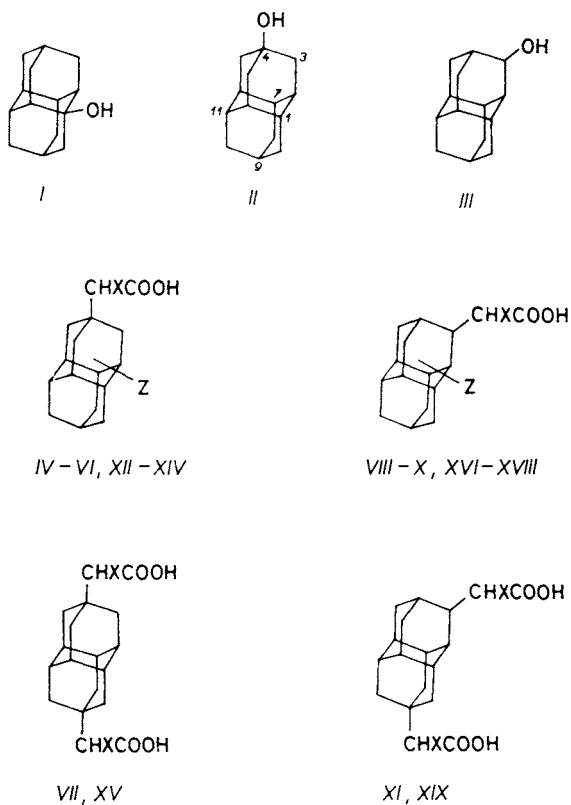
Reactants, g			Products, g	
Chloroethylene	Hydroxydiamantane	H ₂ SO ₄	neutral	acids
CCl ₂ =CH ₂ (25.5)	I (0.51)	100	0.52	0.21
CCl ₂ =CH ₂ (4.5)	II (0.10)	20	0.01	0.11
CCl ₂ =CH ₂ (12.8)	III (0.25)	50	0.25	0.20
CCl ₂ =CHCl (19.0)	I (0.51)	100	0.43	0.26
CCl ₂ =CHCl (3.8)	II (0.10)	20	0.04	0.10
CCl ₂ =CHCl (3.8)	III (0.25)	50	0.25	0.08
CCl ₂ =CCl ₂ (12.3)	I (0.51)	100	0.45	0
CCl ₂ =CCl ₂ (3.7)	II (0.10)	20	0.15	0
CCl ₂ =CCl ₂ (3.7)	III (0.10)	20	0.11	0

TABLE II
Reaction of hydroxydiamantanes I-III with chloroethylenes: composition of the neutral portion

Compound	<i>t</i> ^a	Content, %								
		CCl ₂ =CH ₂			CCl ₂ =CHCl			CCl ₂ =CCl ₂		
		I	II	III	I	II	III	I	II	III
Diamantane	0.03	9.7	61.1	8.8	38.1	25.7	32.8	50.3	45.4	54.3
1-Chlorodiamantane	0.09	61.6	35.3	5.6	52.3	63.0	52.5	24.3	8.8	25.6
1-Hydroxydiamantane (I) ^a										
3-Chlorodiamantane	0.11	17.3	<10 ⁻²	20.3	5.3	4.3	9.6	0	20.9	10.1
4-Hydroxydiamantane (II)	0.13	0	1.0	0	1.5	2.1	0	24.4	24.6	8.7
3-Hydroxydiamantane (III)	0.16	0	0	<10 ⁻²	0	0	0	0	0	1.3
Diamantanone	0.22	1.4	1.7	40.9	0.5	0	0.5	0	0	0
Unidentified	0.27	5.0	<10 ⁻²	24.4	1.3	2.6	2.2	1.0	0	0
Unidentified	0.31	5.0	0.9	0	3.1	2.3	1.6	0	0	0
Unidentified	0.35	0	0	0	0	0	0.8	0	0	0

^a Relative elution time.

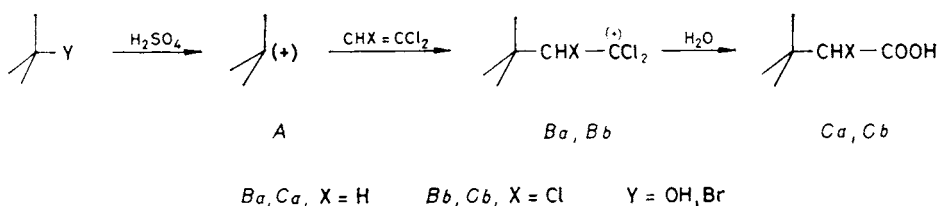
$\text{CH}_2\text{COOCH}_3$). The mass 294 corresponds to methyl chlorodiamantylacetates (relative elution times 0.66, 0.76, and 0.88). Their mass spectra display further peaks at m/z 262 ($\text{M}-\text{OCH}_3$), 261 ($\text{M}-\text{CH}_3\text{OH}$), 258 ($\text{M}-\text{HCl}$), 235 ($\text{M}-\text{COOCH}_3$), 234 ($\text{M}-\text{HCOOCH}_3$), 221 ($\text{M}-\text{CH}_2\text{COOCH}_3$). Finally, the mass 332 corresponds to dimethyl diamantanebisacetates (relative retention times 1.79 and 1.99). Their spectra contain peaks at m/z 301 ($\text{M}-\text{OCH}_3$), 300 ($\text{M}-\text{CH}_3\text{OH}$), 273 ($\text{M}-\text{COOCH}_3$), 259 ($\text{M}-\text{CH}_2\text{COOCH}_3$), 227 ($\text{M}-\text{CH}_2\text{COOCH}_3-\text{CH}_3\text{OH}$) and 199 ($\text{M}-\text{CH}_2\text{COOCH}_3-\text{HCOOCH}_3$). Crystallization of the acidic portion from the reaction of *II* with 1,1-dichloroethylene afforded a compound, melting at 338 to 339.5°C. On the basis of ^{13}C NMR spectrum of its dimethyl ester, it was assigned



IV, VIII, X = H; Z = H
 V, IX, X = H; Z = Cl
 VI, X, X = H; Z = OH
 VII, XI, X = H

XII, XVI, X = Cl; Z = H
 XIII, XVII, X = Cl; Z = Cl
 XIV, XVIII, X = Cl; Z = OH
 XV, XIX, X = Cl

the structure *VII* (4,9-diamantanebisacetic acid), in which both substituents occupy the apical positions. Compound *III* reacts with 1,1-dichloroethylene to give 3-diamantylacetic acid (*VIII*) as the main product (relative retention time of its methyl ester 0.25). The acid *VIII* was identified by comparison of the elution time and mass spectrum of an authentic sample⁵. The suggested structure of the remaining components of the acidic portions is based on the proved structures of compounds *VII* and *VIII*, isomerization results, Koch–Haaf carboxylation of hydroxydiamantanes⁶, dihydroxydiamantanes⁷ and hydroxydiamantanecarboxylic acids^{8–10}, and on the assumed reaction mechanism. As depicted in Scheme 1, the initial reaction step is



SCHEME 1

TABLE III

Reaction of hydroxydiamantanes *I–III* with 1,1-dichloroethylene: composition of the acidic portion (after esterification with diazomethane)

Compound	<i>t</i> ^a	Composition, %		
		<i>I</i>	<i>II</i>	<i>III</i>
4-Diamantylacetic acid (<i>IV</i>)	0.22	15.8	50.7	7.2
3-Diamantylacetic acid (<i>VIII</i>)	0.25	0.5	0	48.9
Unidentified	0.44	1.3	0	0
Chlorodiamantylacetic acids <i>V</i> and <i>IX</i>	0.66	9.3	0.3	<10 ⁻²
	0.76	39.7	11.0	<10 ⁻²
	0.88	24.3	8.7	10.3
Hydroxydiamantylacetic acids <i>VI</i> and <i>X</i>	1.06	0.8	0	4.4
	1.20	1.7	0.5	<10 ⁻¹
	1.30	0	0	6.2
	1.41	1.0	2.3	0
4,9-Diamantanebisacetic acid (<i>VII</i>)	1.79	5.7	25.0	10 ⁻²
3,9-Diamantanebisacetic acid (<i>XI</i>)	1.99	0.8	1.5	23.0

^a Relative elution time of methyl ester.

the formation of the diamantyl cation which is charged at the carbon atom bearing originally the hydroxy group. Thus, 4-hydroxydiamantane (*II*) affords 4-diamantyl cation which reacts with 1,1-dichloroethylene to give 4-diamantylacetic acid (*IV*, apical substitution). Although this compound has not been isolated (and its structure thus directly proved), this assumption is fully justified, since the diamantanebisacetic acid, arising from *IV* and isolated from the same reaction mixture, has been shown to have both the substituents in the apical positions (4, 9). 1-Hydroxydiamantane (*I*) gives first 1-diamantyl cation. This, however, is sterically hindered and cannot react with the relatively bulky molecule of 1,1-dichloroethylene (contrary to the reaction with CO in the Koch-Haaf carboxylation⁸). Its isomerization gives a mixture of diamantyl cations⁶ of which the 4-diamantyl cation reacts to give the acid *IV* (and minor amounts of acid *VIII*; *vide infra*). With 3-hydroxydiamantane (*III*), the first intermediate is the 3-diamantyl cation which is approximately as sterically hindered as the 4-diamantyl cation and gives 3-diamantylacetic acid (*VIII*). To a lesser extent, the 3-cation isomerizes to the 4-cation and this is transformed into the acid *IV*. The primarily formed acids *IV* and *VIII* react further with the diamantyl cations, present in the reaction mixture, under formation of diamantane (Table II) and carboxymethyldiamantyl cations in which the charge is localized at an apical or medial carbon atom. For steric reasons, only apical cations react further with 1,1-dichloroethylene. Thus, acid *IV* gives 4,9-diamantanebisacetic acid (*VII*) and acid *VIII* is transformed into 3,9-diamantanebisacetic acid (*XI*). Any carboxymethyldiamantyl cation can react with chloride or hydroxyl ions to give chlorodiamantylacetic and hydroxydiamantylacetic acids, respectively. On the basis of the results of isomerization of hydroxydiamantylcarboxylic acids⁹ we can assume that acid *IV* reacts with chloride or hydroxyl ions to give 4-(1-chlorodiamantyl)- and 4-(9-chlorodiamantyl)acetic acids (*V*) or 4-(1-hydroxydiamantyl)- and 4-(9-hydroxydiamantyl)acetic acids (*VI*). Analogously, acid *VIII* affords 3-(11-chlorodiamantyl)- and 3-(9-chlorodiamantyl)acetic acids (*IX*) or 3-(11-hydroxydiamantyl)- and 3-(9-hydroxydiamantyl)acetic acids (*X*). However, without isolation of the individual components and measurement of their ¹³C NMR spectra no structural assignment can be made. The diamantyl cations present in the reaction mixture react also with chloride ion to afford chlorodiamantanes (see Table II).

The outcome of reaction of hydroxydiamantanes *I-III* with trichloroethylene is seen from Table IV. Structural assignment has been done using the same reasoning as for the above-mentioned reaction with 1,1-dichloroethylene. In the mass spectra, the molecular ions of methyl esters of diamantylchloroacetic and diamantanebischloroacetic acids (*XII-XIX*) are of low intensity. Mass spectra of the methyl esters of *XII* and *XVI* show peaks at m/z 294 (M), 259 (M-Cl), 258 (M-HCl), 234 (M-HCOOCH₃), 228 (M-Cl-OCH₃), 226 (M-HCl-CH₃OH), 198 (M-HCl-HCOOCH₃), and 187 (M-CHClCOOCH₃). Methyl esters of *XIII* and *XVII* give rise to ions at m/z 328 (M), 293 (M-Cl), 292 (M-HCl), 269

(M-COOCH₃), 262 (M-Cl-OCH₃), 260 (M-HCl-CH₃OH), 221 (M-CHClCOOCH₃). Spectra of methyl esters of *XIV* and *XVIII* exhibit ions at m/z 310 (M), 293 (M-OH), 292 (M-H₂O), 275 (M-Cl), 274 (M-HCl), 251 (M-COOCH₃), 215 (M-HCl-COOCH₃), 203 (M-CHClCOOCH₃). Dimethyl esters of *XV* and *XIX* show the following ions: 400 (M), 399 (M-H), 341 (M-COOCH₃), 327 (M-H-2 HCl), 305 (M-COOCH₃-HCl), 293 (M-CHClCOOCH₃), 257 (M-CHClCOOCH₃-HCl), 225 (M-CHClCOOCH₃-HCl-CH₃OH). In the reaction of 3-hydroxydiamantane with trichloroethylene more isomerization occurs than with 1,1-dichloroethylene.

Reaction of hydroxydiamantanes *I-III* with tetrachloroethylene does not afford any acids (Tables I and II).

TABLE IV

Reaction of hydroxydiamantanes *I-III* with trichloroethylene: composition of the acidic portion (after esterification with diazomethane)

Compound	t^a	Content, %		
		<i>I</i>	<i>II</i>	<i>III</i>
Unidentified	0.44	0.7	0	4.9
Unidentified	0.46	0.6	0	4.2
4-Diamantylchloroacetic acid (<i>XII</i>)	0.54	14.3	9.4	10.6
3-Diamantylchloroacetic acid (<i>XVI</i>)	0.59	0	0	1.2
Unidentified	0.71	0	0.8	0
Unidentified	1.13	0.6	0	0
Unidentified	1.53	0	1.7	1.1
Unidentified	1.60	3.4	0	1.1
	2.00	3.0	2.2	4.0
Chlorodiamantylchloroacetic acids <i>XIII</i> and <i>XVII</i>	2.21	0.3	0	2.8
	2.40	4.6	7.3	7.9
	2.63	0	0	3.3
Hydroxydiamantylchloroacetic acids <i>XIV</i> and <i>XVIII</i>	3.14	22.2	28.5	25.2
	3.99	0.9	0	1.7
	4.69	1.1	0	0.6
4,9-Diamantanebischloroacetic acid (<i>XV</i>)	12.65	48.3	50.1	25.7
3,9-Diamantanebischloroacetic acid (<i>XIX</i>)	14.15	0	0	3.8
Unidentified	15.18	0	0	1.9

^a Relative retention time of methyl ester.

EXPERIMENTAL

Analytical Methods

Gas-liquid chromatographic analyses were performed on a CHROM 5 instrument (Laboratorní přístroje, Prague), on a 1 200 mm column, internal diameter 3 mm, packed with 3% XF 1 150 on Chromaton N-AW-DMCS (0.15–0.18 mm); flame-ionization detector, carrier gas nitrogen, temperature 180°C. The acids were analyzed as methyl esters obtained by treatment with diazomethane. The relative elution times refer to dimethyl 4,9-diamantanedicarboxylate.

Mass spectra were taken on an LKB 9 000 spectrometer using the GC-MS technique (the spectra were taken at the peak maximum). ^{13}C NMR spectra were measured in the FT mode on a Tesla BS 567 instrument at 25.14 MHz in deuteriochloroform at 35°C with tetramethylsilane as standard. The spectra were interpreted using the additive rule, derived from the published results^{11,12}.

Reaction of Hydroxydiamantanes with Chloroethylenes

In all cases the molar ratio hydroxydiamantane : sulfuric acid was 1 : 400. A solution of the hydroxydiamantane in chloroethylene was added dropwise in the course of 1 h with cooling and stirring to sulfuric acid (96.6 wt.%, precooled to 0°C. After stirring for 30 min, the mixture was poured on ice and extracted three times with ether. The ethereal extract was washed with 5% aqueous potassium hydroxide, water and dried over sodium sulfate. The solvent was evaporated and the residue (neutral part) analyzed by gas-liquid chromatography and mass spectrometry. The components were identified by comparison of retention times and mass spectra with those of standards. For results see Table I and II.

The alkaline washings were acidified with hydrochloric acid and extracted three times with ether. The combined extracts were washed with water, dried and the solvent was evaporated. A sample of the residue (acidic portion) was dissolved in methanol, esterified with diazomethane and analyzed by gas-liquid chromatography and mass spectrometry. The results are given in Tables I, III, and IV.

4,9-Diamantanebisacetic Acid (VII) and Its Dimethyl Ester

Crystallization of the combined acidic portions (2.4 g) from the reaction of *II* with 1,1-dichloroethylene afforded 0.45 g of acid *VII* (purity 96%), m.p. 338–339.5°C after two crystallizations from benzene. For $\text{C}_{18}\text{H}_{24}\text{O}_4$ (304.4) calculated: 71.03% C, 7.95% H; found: 70.94% C, 7.97% H. The acid *VII* (0.31 g) was dissolved in methanol and a solution of diazomethane was added dropwise under stirring at –10°C until nitrogen no longer evolved. Evaporation afforded 0.32 g (94%) of dimethyl ester of *VII*, m.p. 108.6–110.2°C (hexane). For $\text{C}_{20}\text{H}_{28}\text{O}_4$ (332.4) calculated: 72.26% C, 8.49% H; found: 72.30% C, 8.53% H. ^{13}C NMR spectrum (ppm): 172.4 (COO), 51.1 (OCH₃), 47.7 (C_q), 42.5 (CH₂), 37.1 (CH), 30.7 (CH₂COO).

4,9-Diamantanebischloroacetic Acid (XV) and Its Dimethyl Ester

Combined acidic portions (3.2 g) from reactions of *I* and *II* with trichloroethylene were boiled with chloroform (50 ml), cooled and the insoluble material was crystallized from methanol. Yield 1.05 g of acid *XV*, m.p. above 360°C. For $\text{C}_{18}\text{H}_{22}\text{Cl}_2\text{O}_4$ (373.3) calculated: 57.92% C, 5.94% H, 19.00% Cl; found: 57.80% C, 6.17% H, 18.57% Cl.

A mixture of acid *XV* (0.54 g; 1.45 mmol), thionyl chloride (8 ml) and dimethylformamide (2 drops) was set aside overnight. Excess thionyl chloride was removed *in vacuo* and the residue

was refluxed with methanol (15 ml) for 3 h. The mixture was poured into water, extracted three times with ether, the combined ethereal extracts were washed with water and dried. Evaporation of the solvent afforded 0.55 g (95%) of dimethyl esters of *XV*; m.p. 153.2–154.7°C (benzene). For $C_{20}H_{26}Cl_2O_4$ (401.3) calculated: 59.86% C, 6.53% H, 17.67% Cl; found: 59.78% C, 6.60% H, 17.23% Cl. ^{13}C NMR spectrum (ppm): 169.2 (COO), 57.0 (OCH₃), 52.4 (CHCl), 38.5 (CH₂), 36.5 (CH), 24.7 (C_q).

REFERENCES

1. Bott K., Hellmann H.: *Angew. Chem.* 78, 932 (1966).
2. Bott K.: *Chem. Ber.* 101, 564 (1968).
3. Bott K.: *Angew. Chem.* 79, 943 (1967).
4. Janků J., Burkhard J., Landa S.: *Sb. Vys. Šk. Chemicko-Technol. Praze D* 29, 135 (1973).
5. Vodička L., Burkhard J., Zachář P., Isaev S. D., Saichenko S. I., Yurchenko A. G., Janků J.: *Zh. Org. Khim.* 21, 2569 (1985).
6. Johnston D. E., McKervey M. A., Rooney J. J.: *J. Chem. Soc., Chem. Commun.* 1972, 29.
7. Burkhard J., Janků J., Vodička L.: *Sb. Vys. Šk. Chemicko-Technol. Praze D* 50, 231 (1984).
8. Vodička L., Janků J., Burkhardt J.: *This Journal* 48, 1162 (1983).
9. Janků J., Burkhard J., Vodička L.: *Sb. Vys. Šk. Chemicko-Technol. Praze D* 49, 25 (1984).
10. Vodička L., Burkhard J., Janků J.: *This Journal* 51, 867 (1986).
11. Dheu M. L., Gagnaire D., Duddeck H., Hollowood F., McKervey M. A.: *J. Chem. Soc., Perkin Trans. 2*, 1979, 357.
12. Hájek M., Vodička L., Trška P., Sklenář V.: *Magn. Reson. Chem.* 23, 57 (1985).

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