OXIDATION OF 1-ADAMANTYLMETHANOL AND ADAMANTAN-2-OL WITH LEAD TETRAACETATE*

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This study deals with the oxidation of 1-adamantylmethanol and adamantan-2-ol with lead tetraacetate in benzene, pyridine, and acetic acid, respectively. On oxidising 1-adamantylmethanol in pyridine 1-adamantane carbaldehyde is formed by a heterolytic mechanism. In benzene homolytic cleavage occurs and the intermediately formed 1-adamantyl radical furnishes both 1-acetoxy- and 1-phenyladamantane. In acetic acid, in addition to both above reaction types also acetoxylation of the starting alcohol and its conversion products takes place. With adamantan-2-ol oxidation proceeds in all reaction media by a ionic mechanism and adamantanone is produced as the main product. In benzene and acetic acid, besides this reaction proceeds also acetoxylation of the starting alcohol and of the other reaction products.

It is known that on oxidation of alcohols with lead tetraacetate the alkoxy derivative R—O—Pb.$(OCOCH_3)_3$ is produced first[1,2] which is then according to the reaction medium cleaved either by a homolytic or heterolytic mechanism. Polar media (except acids) suppress the homolytic reaction course and support the heterolytic one. Elimination of an α-hydrogen in the form of H^+ takes place and carbonyl compounds are formed as reaction products. By contrast, non-polar media suppress the heterolytic reaction course and support the homolytic one. Depending on the structure of the starting alcohol the alkoxy derivative R—O—$Pb(OCOCH_3)_3$ is either homolytically cleaved under formation of cyclic ethers (*via* a six- or seven-membered transition state), or a more profound decomposition takes place[3,4]. In the oxidation of ω-adamantylalkan--1-ols having a shorter alkyl chain than C_4 also the carbon atoms of the adamantane skeleton take part in the formation of the cyclic transition state. In the case of the so far published adamantylalkanols[5–8] the fixed conformation of the adamantane skeleton did not prevent the formation of this transition state. With 1-adamantylmethanol or adamantan-2-ol the formation of a six- or seven-membered transition state would require bridging the positions 1—3 and 1—4 respectively, which is not feasible without the adamantane skeleton being cleaved. Therefore, on oxidising these alcohols with lead tetraacetate cyclic ethers are not formed.

On oxidation of 1-adamantylmethanol (*I*) with lead tetraacetate in benzene, where the reaction proceeds predominantly by a radical mechanism, homolytic fragmentation of the alkoxy derivative *II* takes place (Scheme 1) under formation of $(CH_3.COO)_2Pb$, formaldehyde, the 1-adamantyl radical (*III*), and the acetoxy radical.

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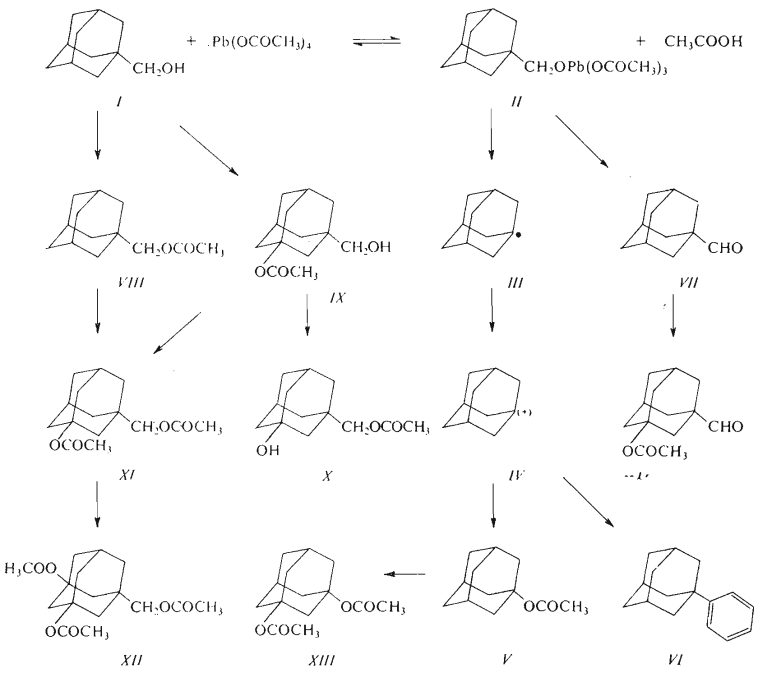
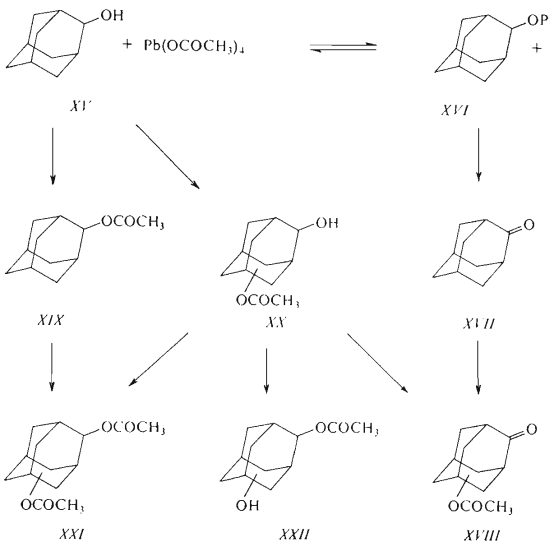
Radical *III* is partly converted into admantane (by splitting off of a hydrogen atom from the reaction medium), however the greater part undergoes further oxidation with Pb(IV) compounds to the adamantyl cation *IV* which by reaction with CH_3COO^- furnishes 1-acetoxyadamantane (*V*) and by reaction with benzene 1-phenyladamantane (*VI*). The adamantyl cation is also an intermediate in the formation of ada-



mantane-1-ol and adamantan-1-ol formate. Compounds *V* and *VI* are the main reaction products. The product of the competitive ionic reaction – the aldehyde *VII* – is present in the reaction mixture only in a very small amount. Also in a small amount are present the formate and acetate of the starting alcohol. These compounds result by esterification of *I* with acetic and formic acid, respectively. The source of formic acid is formaldehyde which is being formed on fragmentation.

As was to be expected, oxidation of *I* in pyridine gives rise to 1-adamantane carbaldehyde (*VII*) as the main product. The reaction mixture contains also the acetate of the starting alcohol (*VIII*) in a larger amount. The most likely explanation for the formation of this compound is the reaction of *I* with acetic anhydride derived from lead tetraacetate[9]. In pyridine the reaction takes place practically exclusively by the ionic mechanism. Products of the homolytic reaction are present in the reaction mixture only in a negligible quantity.

The reaction mixture from the oxidation in acetic acid is far more complicated. It contains very little 1-adamantanecarbaldehyde. An explanation of this fact is that acetic acid as a proton donor suppresses the splitting off of an α-H^+ and thus the formation of an aldehyde (in contrast to pyridine which is a proton acceptor). The homolytic reaction course is far less subjected to the influence of acetic acid and accordingly 1-acetoxyadamantane, the product of this reaction course, is one of the major reaction products. The oxidation mixture contains in largest amount the esteri-



SCHEME 2

fication product of the starting alcohol with acetic acid (*VIII*). The formation of further compounds, *i.e.* the acetoxy derivatives of the starting alcohol and of its oxidation, fragmentation, and esterification products (*IX*, *X*, *XI*, *XII*, *XIII*, *XIV*), cannot be explained merely by transformations of the alkoxy derivative *II*. They are probably formed by the following mechanism: At the reaction temperature (~120°C) decomposition of lead tetraacetate occurs, and the adamantane derivatives present in the reaction mixture react with the acetoxy radicals formed. The reaction takes place at the tertiary carbon atoms of the adamantane skeleton. The intermediary formed substituted adamantyl radical is oxidised to the cation which reacts with CH_3COO^- to give the acetoxy derivative. In the case of the acetoxy derivative of the starting alcohol *IX* reesterification from the tertiary hydroxy group to the primary one takes place[8] and in the reaction mixture appears mainly the reesterification product (*X*).

With adamantan-2-ol (*XV*) besides cyclisation also fragmentation of the primarily formed alkoxy derivative *XVI* (Scheme 1) is precluded, as this would also require opening of the considerably stable adamantane skeleton. In all three reaction media decomposition of the alkoxy derivative *XVI* proceeds therefore by the heterolytic mechanism. The content of the product of this reaction, *i.e.* of adamantanone (*XVII*), in the reaction mixture is the highest on performing the oxidation in pyridine and the lowest in acetic acid on grounds stated above. In a reversed ratio the oxidation mixture contains the product of the esterification (*XIX*) which proceeds as a side reaction. As in the case of 1-adamantylmethanol and ω-(2-adamantyl)alkan-1-ols[8], both in benzene and acetic acid the acetoxy derivatives of the individual reaction products with the acetoxy and hydroxy group, resp. at tertiary carbon atoms of the adamantane skeleton (*XVIII*, *XXI*, *XXII*) are formed. In contrast to the previously studied alcohols[8], in the reaction mixture appear also isomers of the acetoxy derivative of the starting alcohol *XX* in which reesterification from the tertiary to the secondary hydroxyl group proceeds evidently more slowly then the reesterification of the cited alcohols from the tertiary to the primary hydroxyl group, so that it is possibly to seize them in the reaction mixture.

EXPERIMENTAL

Oxidation

1-Adamantylmethanol (*I*) was prepared by reduction of 1-adamantanecarboxylic acid with $LiAlH_4$ in 98% yield, m.p. 115·5—116·8°C (lit.[10] gives m.p. 115°C). Adamantan-2-ol (*XV*) was prepared by reduction of adamantanone with $LiAlH_4$ in 95% yield, m.p. 294·6—296·7°C (lit.[11] gives m.p. 296·2—297·2°C). The acetates and formates of the starting alcohols, adamantan-1-ol, and adamantan-1,3-diol were prepared by the same procedure as in the foregoing communication[8]. 1-Phenyladamantane was generously supplied by Dr S. Hála[12].

The oxidation in both benzene and pyridine was performed in the manner described in the foregoing communication[8].

Oxidation in acetic acid. Per 1 g of the alcohol 12 ml of glacial acetic acid and 2·9 g of lead tetraacetate were used. The mixture was stirred and heated under reflux as long as it still contained Pb(IV). Samples were withdrawn every five minutes. After the reaction was over, the mixture was poured into water and three times extracted with ether. The combined ethereal extracts were washed with water and 5% aqueous $KHCO_3$, then dried and the ether removed by distillation. For the isolation of adamantanone from the reaction mixtures the bisulphite method could not be applied, as this compound does not react neither with $KHSO_3$, nor with $NaHSO_3$. The reaction time, yield, and composition of the reaction mixtures are given in Tables I and II. The compounds are ranked according to their retention times on SE-30. Their content was calculated from the chromatograms and is expressed in weight per cent.

Analytical Section

The identification of the individual components of the reaction mixtures was accomplished by a combination of gas liquid chromatography, mass and NMR spectrometry on apparatuses and under conditions reported in the preceeding communication[8]. By comparing the number, concentration, and retention times of the components with the retention times of the standards

TABLE I

Oxidation Products of 1-Adamantylmethanol (*I*)

Sequence in G.L.C.	Compound	Content (weight %) benzene	pyridine	acetic acid
1	adamantane	<1	1	<1
2	adamatan-1-ol	<1	<1	<1
3	1-adamantane carbaldehyde (*VII*)	<1	39	1
4	adamatan-1-ol formiate	<1	<1	—
5	1-adamantylmethanol (*I*)	12	48	13
6	adamantan-1-ol acetate (*V*)	63	1	21
7	1-adamantylmethanol formiate	<1	1	—
8	1-adamantylmethanol acetate (*VIII*)	1	10	45
9	1-(3-acetoxyadamantane)carbaldehyde (*XIV*)	—	—	<1
10	1,3-diacetoxyadamantane (*XIII*) + 1-(3-hydroxyadamantyl)methanol acetate (*X*)	—	—	4
11	1-(3-acetoxyadamantyl)methanol (*IX*)	—	—	<1
12	1-phenyladamantane (*VI*)	21	—	—
13	1-(3-acetoxyadamantyl)methanol acetate (*XI*)	—	—	13
14	not identified	—	—	<1
15	not identified	—	—	1
16	1-(3,5-diacetoxyadamantyl)methanol acetate (*XII*)	—	—	<1
Reaction time, min		350	20	40
Yield (g oxidation mixture per 1 g of *I*)		1·20	0·97	1·35

prepared and also by comparing the mass spectra of the components with those of the standards, the starting alcohols as well as their acetates and formates, adamantane, adamantan-1-ol, adamantan-1-ol acetate and formiate, adamantanone, and 1-phenyladamantane were identified. The other compounds were identified by their mass spectra and compounds *XVIII* and *XX—XXIII*, which we succeded in isolating by means of preparative gas chromatography[8], also by their NMR spectra.

1-*Adamantanecarbaldehyde* (VII) was isolated from the reaction mixture *via* the aldehyde bisulphite. The mass spectrum contains the ions M^+ (8%), $[M-28]^+$ (CO, 17%), and $[M-29]^+$ (CHO, 100%). M.p. of the 2,4-dinitrophenylhydrazone 230·4—231·6°C (literature[13] gives m.p. 221—222°C).

1-(3-*Acetoxyadamantane)carbaldehyde* (XIV). Its mass spectrum contains the ions M^+ (8%), $[M-28]^+$ (10%), $[M-29]^+$ (33%), $[M-59]^+$ (CH_3COO, 33%), $[M-60]^+$ (CH_3COOH, 33%), $[M-71]^+$ ($CHO + CH_2CO$, 100%), and further *m/e* 135 (33%), 134 (50%), and 133 (22%).

1,3-*Diacetoxyadamantane* (XIII) *and* 1-(3-*hydroxyadamantyl)methanol acetate* (X). These compounds are eluted on both stationary phases in the same chromatographic wave. The mass spectrum of the mixture does not show molecular ions of either compound. For *XIII* are characteristic especially the ions *m/e* 139, *i.e.* $[M-CH_3COOH]^+$, and 150, *i.e.* $[M-CH_3COOH—CH_2.CO]^+$, whose intensities in the spectrum of the pure compound are 100% and 97%, respectively. This ratio is retained also in the spectrum of the mixture of *XIII* and *X*. For compound *X* are especially characteristic the ions *m/e* 164, $[M-CH_3COOH]^+$, and 151, *i.e.* $[M-CH_2OCOCH_3]^+$ (intensity ratio 100/44).

TABLE II

Oxidation Products of Adamantan-2-ol (*XV*)

Sequence in G.L.C.	Compound	Content (weight %) benzene	pyridine	acetic acid
1	adamantanone (*XVII*)	38	66	26
2	adamantan-2-ol (*XV*)	40	34	12
3	adamantan-2-ol acetate (*XIX*)	2	$\sim 10^{-2}$	25
4	isomers of 2-acetoxyadamantan-?-ol (*XXII*)	7	—	4
5		3	—	6
6	isomer of ?-acetoxyadamantan-2-one (*XVIII*)	1	—	1
7	not identified	4	—	—
8	isomer of ?-acetoxyadamantan-2-one (*XVIII*)	3	—	2
9	isomers of ?-acetoxyadamantan-2-ol (*XX*)	1	—	5
10		1	—	4
11	isomers of 2,?-diacetoxyadamantane (*XXI*)	—	—	4
12		—	—	6
13		—	—	4
Reaction time, min		350	20	40
Yield (g oxidation mixture per 1 g of *XV*)		1·15	0·95	1·15

1-(3-*Acetoxyadamantyl)methanol* (IX). The mass spectra contains M^+ (6%), $[M-18]^+$ (H_2O, 20%), $[M-31]^+$ (CH_2OH, 5%), $[M-42]$ (CH_2CO, 4%), and $[M-60]^+$ (100%).

1-(3-*Acetoxyadamantyl)methanol acetate* (XI). The mass spectrum is devoid of M^+. The highest ion in the spectrum is $[M-60]^+$ (100%). Further ions in the mass spectrum are $[M-73]^+$ (CH_2. .$OCOCH_3$), 19%), $[M-102]^+$ ($CH_3COOH + CH_2CO$, 85%), $[M-115]^+$ ($CH_2OCOCH_3 +$ $+ CH_2CO$, 40%) and $[M-120]^+$ (2 CH_3COOH, 76%).

1-(3,5-*Diacetoxyadamantyl)methanol acetate* (XII). In the mass spectrum M^+ is lacking. The highest ion in the spectrum is $[M-60]^+$ (69%). The mass spectrum contains further the ions $[M-102]^+$ (42%), $[M-120]^+$ (85%), $[M-133]^+$ ($CH_3COOH + CH_2OCOCH_3$, 5%), $[M-161]^+$ (31%), $[M-162]^+$ (2 $CH_3COOH + CH_2CO$, 100%), $[M-163]^+$ (53%).

In the foregoing cases all substituents were attached to tertiary carbon atoms of the adamantane skeleton, and thus only one isomer occured (1,3- and 1,3,5-substitution, respectively). Compounds *XVIII* and *XX—XXII* contain two substituents of which one is attached to a secondary and the other to a tertiary carbon atom of the adamantane skeleton. Such compounds can occur in two or three isomeric forms (*XVIII* 1,2- and 1,4-substitution; *XX—XXII* 1.2-, $1,4^{eq}$-, and $1,4^{ax}$-substitution). The mass spectra of the individual isomers practically do not differ from each other, and other methods for the exact determination of the position of the substituents could not be used, as at best we succeeded only in obtaining a mixture of at least two isomers.

Isomers of ?-*acetoxyadamantanone* (XVIII). The mass spectra contain the ions M^+ (20%), $[M-42]^+$ (CH_2CO, 31%), $[M-43]^+$ (CH_3CO, 25%), $[M-58]^+$ (CH_2COO, 39%), and $[M-60]^+$ (CH_3COOH, 32%). The NMR spectrum displays 3 protons of the acetoxy group (singlet, 204 p.p.m.) and does not contain any proton besides the acetoxy group.

Isomers of ?-*acetoxyadamantan-2-ol* (XX). The mass spectrum is devoid of M^+. The highest ion in the spectrum is M-18 (71%). Further ions are $[M-42)^+$ (4%) and $[M-60]^+$ (100%). The NMR spectrum contains 3 protons of the acetoxy group (singlet at 204 p.p.m.) and 1 proton besides the OH group (multiplet in the 400—415 p.p.m. region).

Isomers of 2-*Acetoxyadamantan-*?-*ol* (XXII). The mass spectrum contains the little intense ions M^+ (1%) and $[M-42]^+$ (2%) and the intense ion $[M-60]^+$. The base peak appears at *m/e* 58. The NMR spectrum exhibits 3 protons of the acetoxy group (singlet at 212 p.p.m.) and 1 proton besides the acetoxy group (multiplet in the 475—490 p.p.m. region).

Isomers of 2,?-*diacetoxyadamantane* (XXI). The mass spectrum contains the little intense ions M^+ (1%) and $[M-42]^+$ (0·5%) and the intense ions $[M-60]^+$ (100%) and $[M-102]^+$ (48%). The NMR spectrum exhibits two separated signals for 2 times 3 protons of the acetoxy groups (singlets at 204 and 212 p.p.m.) and one proton besides the acetoxy group (multiplet in the region of 470—495 p.p.m.).

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