

**OXIDATION OF ω -(2-ADAMANTYL)ALKAN-1-OLS
WITH LEAD TETRAACETATE***

J. BURKHARD, J. JANKŮ and S. LANDA

*Laboratory of Synthetic Fuels,
Institute of Chemical Technology, 166 28 Prague 6*

Received October 20th, 1972

This paper deals with the oxidation of the first four members of the homologous series of the ω -(2-adamantyl)alkan-1-ols with lead tetraacetate in pyridine and benzene, resp., and the authors discuss the formation of the individual products. In pyridine the corresponding aldehydes are formed as main products, in benzene the cyclic ethers. The identification of the compounds formed was carried out by a combination of gas chromatography and mass and NMR spectrometry. Also some results published in an earlier communication of this series are now given with greater accuracy.

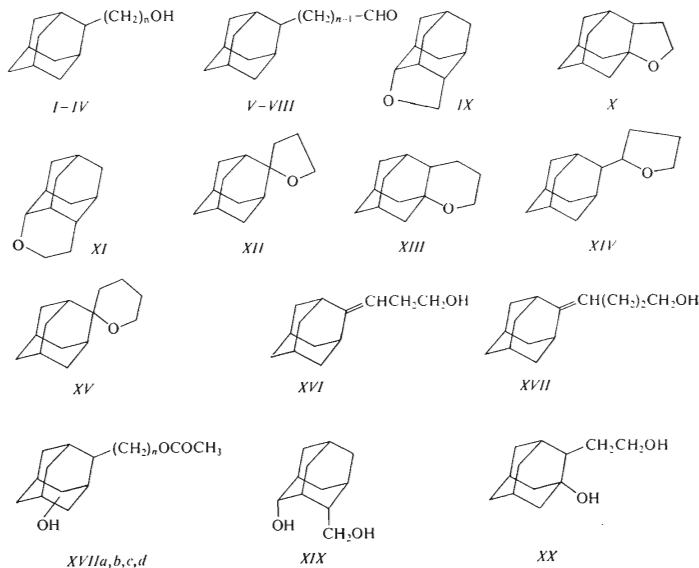
In oxidising alcohols with lead tetraacetate the first intermediate is the alkoxy derivative $R-CH_2-O-Pb(OCOCH_3)_3$ (*A*) (ref.^{1,2}) which undergoes further reactions according to the nature of the reaction medium^{3,4}. In polar medium (*e.g.* in pyridine) the reaction proceeds by a ionic mechanism. Splitting off of an α -proton (with respect to the oxygen atom) takes place and carbonyl compounds are formed. In a non-polar medium (*e.g.* in benzene) the reaction proceeds predominantly by a radical mechanism (Scheme 1). When the chain is sufficiently long, the reaction products are cyclic ethers with a five- or six-membered ring⁵. In the formation of five-membered cyclic ethers, the cyclic transition state *B* (Scheme 1) is six-membered, and therefore compounds of this type are usually the main reaction products. The isomeric six-membered cyclic ethers require a seven-membered less favourable transition state and are usually present in the reaction mixture in concentrations of smaller order of magnitude. Ethers with larger or smaller rings are generally not formed. Fragmentation⁵ is a radical side reaction (Scheme 1). The alkoxy derivative *A* breaks down to formaldehyde (with primary alcohols) and the radical *D*, which is either stabilised by formation of a saturated hydrocarbon having one carbon atom less than the starting alcohol, or is oxidised by the Pb(IV) salts present in the reaction mixture to the cation *E*. This cation is the intermediate product in formation of unsaturated hydrocarbons, acetates, and eventually further compounds. Besides these reaction products, the reaction mixtures contain also acetates and formates of the starting alcohols³.

The present paper deals with the oxidation of the first four members of the homologous series of the ω -(2-adamantyl)alkan-1-ols with lead tetraacetate under such conditions that either the heterolytic reaction course (in pyridine) or the homolytic one (in benzene) will predominate. In the latter case to the reaction mixture was

* Part XXVIII in the series Adamantane and its Derivatives; Part XXVII: This Journal 38, 3302 (1973).

added benzoyl peroxide, in order to accelerate the reaction⁶, and dry calcium carbonate to neutralise the formed acetic acid and to suppress the formation of acetates. The composition of the reaction mixtures is presented in Tables I–IV. Oxidation in pyridine gives rise to the aldehydes *V–VIII* as main products. Their yields slightly decrease with increasing molecular weight of the starting alcohol. In addition to aldehydes and the unreacted starting alcohols, the reaction mixtures contain also the formates and acetates of the starting alcohols and products of the parallel proceeding radical reaction. The higher the molecular weight of the starting alcohol, the more these products are formed. The aldehydes can be isolated practically quantitatively by making use of their reaction with bisulphite. They are unstable and polymerise relatively quickly.

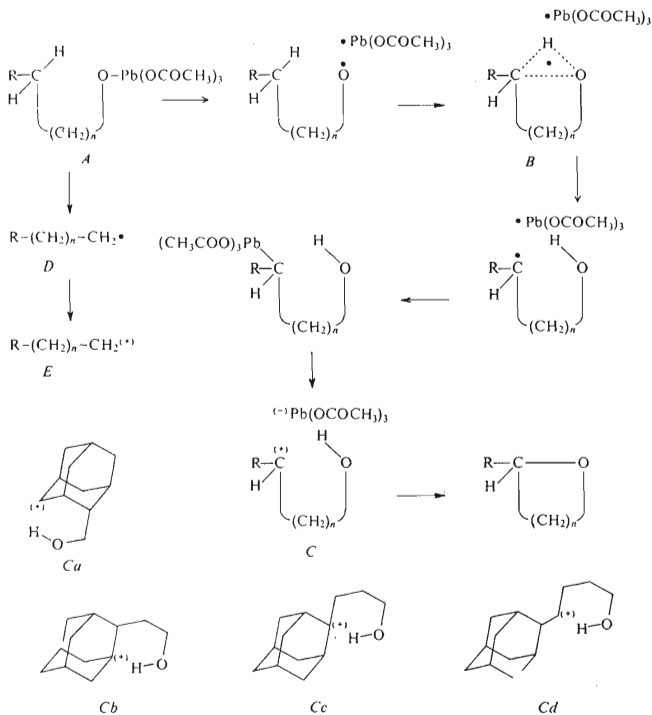
On oxidation in benzene the five-membered cyclic ethers *IX*, *X*, *XII*, and *XIV*, respectively are produced as main products by a mechanism indicated in Scheme 1. 2-Adamantylmethanol affords compound *IX* as the only one cyclisation product. Formation of the isomeric “six-membered” cyclic ether is prevented by the saddle



conformation of the cyclohexane ring in the rigid adamantane skeleton. In all other cases the main products are accompanied by a small amount of isomeric cyclic ethers with a six-membered ring (*XI*, *XIII*, *XV*). 3-(2-Adamantyl)propan-1-ol (*III*) and 4-(2-adamantyl)butan-1-ol (*IV*) afford as further products the unsaturated alcohols *XVI* and *XVII*, resp. They are produced by the same mechanism as the cyclic ethers with the difference, that in the last but one reaction step (C) elimination of a proton from the oxygen atom and cyclisation do not take place, but elimination of a proton from the carbon atom (α in respect to the position of the positive charge of the cation) and formation of a double bond. These intermediates possess the structure *Cc* and *Cd*, respectively (Scheme 1). In both cases elimination of the proton occurs in such a way, that a double bond between the carbon atom of the adamantane skeleton and the ω -carbon atom of ω -(2-adamantyl)alkan-1-ol is formed. As a side reaction fragmentation takes place and a radical having one carbon atom less is formed. In the case of 2-adamantylmethanol (*I*) this is the 2-adamantyl radical, which is stabilised to adamantane by splitting off a hydrogen atom from the reaction medium, or is oxidised by the present Pb(IV) salts to the 2-adamantyl cation. This cation provides by reaction with CH_3COO^- adamantan-2-ol acetate and with HCOO^- adamantan-2-ol formate. 2,4-Dehydroadamantane also found in the reaction mixture is probably formed directly from the 2-adamantyl radical. The preparation (or formation) of this hydrocarbon, in which the 2-adamantyl cation might be supposed as a reaction intermediate, has so far not been described in the literature. In the case of 2-(2-adamantyl)-ethan-1-ol, from the radical formation of 2-methyladamantane takes place and from the cation formation of both methyleneadamantane and 2-adamantylmethanol acetate. In the reaction mixtures from the higher alcohols (*III*, *IV*) fragmentation products have not been found. 2-Ethyladamantane, which was also identified in the oxidation mixture of 2-(2-adamantyl)ethan-1-ol, is probably formed from the dialkoxy derivative $(2 \text{ Ad}-\text{CH}_2-\text{CH}_2-\text{O})_2\text{Pb}(\text{OCOCH}_3)_2$ by decomposition to the hydrocarbon and a carbonyl compound³. Thus it is possible to explain partly also the presence of 2-(2-adamantyl)ethanal (*VI*) in the oxidation mixture. In a previous paper⁷ these compounds were not identified (because of their small content in the reaction mixture). All oxidation mixtures contain also acetates and formates of the starting alcohols. In the reaction mixtures of the alcohols *II*, *III*, and *IV* were found besides products of radical transformations also products of ionic reactions, viz. the aldehydes *VI*, *VII*, and *VIII*. In all oxidation mixtures occur acetoxy derivatives of the cyclic ethers having the acetoxy group bonded to one of the tertiary carbon atoms of the adamantane skeleton. The primary radical formed by reaction of the cyclic ethers with the acetoxy radical is probably further oxidised to the cation which by reaction with CH_3COO^- affords the acetoxy derivative. The reaction takes place at the reactive tertiary positions. Further reaction products are the hydroxy derivatives of the acetates of the starting alcohols (*XVIII*a,b,c, and *d*) in which the hydroxy group is attached to one of the tertiary carbon atoms of the

adamantane skeleton. They are formed in the same way as in the foregoing case by reaction of the starting alcohols with the acetoxy radical followed by reesterification from the adamantane skeleton to the side chain. Reesterifications of this type have already been observed⁸. In a previous paper⁷ was given a wrong structure for this derivative of alcohol *II*.

Cleavage of the ether bond of the cyclic ethers can be brought about with acetic anhydride in the presence of boron trifluoride etherate. In the first both cases (*IX*, *X*) alcohol diacetates are formed and from them, by hydrolysis, the diols *XIX* and *XX*.



SCHEME 1

Ether *IX* affords the diol *XIX* which on heating above 250°C is quantitatively converted back into the starting ether *IX*. On cleaving the cyclic ethers *XII* and *XIV* elimination and formation of a double bond occur, so that monoacetates of unsaturated alcohols are formed, giving after hydrolysis the unsaturated alcohols *XVI* and *XVII* which are accompanied by a small amount of isomeric alcohols having the double bond in a different position.

EXPERIMENTAL

Oxidation

The starting alcohols were prepared by reduction of the corresponding ω -(2-adamantyl) fatty acids with LiAlH_4 in abs. ether by the standard procedure. 2-Adamantylmethanol (*I*), yield 98%, 94.8–95.6°C (lit.⁹ gives m.p. 94.9–95.8°C). 2-(2-Adamantyl)ethan-1-ol (*II*), yield 97%, m.p. 68.8–70.3°C (lit.¹⁰ gives m.p. 68.8–70.3°C). 3-(2-Adamantyl)propan-1-ol (*III*), yield 97%, m.p. 33.0–34.0°C. For $\text{C}_{13}\text{H}_{22}\text{O}$ (194.3) calculated: 80.71% C, 11.41% H; found: 80.31% C, 11.37% H. 4-(2-Adamantyl)butan-1-ol (*IV*), yield 97%, colourless viscous liquid. For $\text{C}_{14}\text{H}_{24}\text{O}$ (208.3) calculated: 80.71% C, 11.61% H; found: 80.51% C, 11.72% H. The purity was checked by gas chromatography and the structure by means of mass spectrometry.

TABLE I
Oxidation Products of 2-Adamantylmethanol (*I*)

Sequence in G.L.C.	Compound	Content (weight %)	
		pyridine	benzene
1	adamantane	<1	<1
2	2,4-dehydroadamantane	<1	<1
3	adamantan-2-ol	2	<1
4	2,4-(epoxymethano)adamantane (<i>IX</i>)	1	67
5	2-adamantane carbaldehyde	28	—
6	adamantan-2-ol formate	<1	<1
7	adamantan-2-ol acetate	5	5
8	2-adamantylmethanol (<i>I</i>)	48	19
9	2-adamantylmethanol formate	2	<1
10	2-adamantylmethanol acetate	13	5
11	?-acetoxy-2,4-(epoxymethano)adamantane	—	1
12	2-(?-hydroxyadamantyl)methanol (<i>XVIIIa</i>)	<1	1
Reaction time, min		20	330
Yield (g oxidation mixture per 1 g of <i>I</i>)		0.95	1.5

The acetates of the starting alcohols and of adamantan-2-ol were prepared by the following procedure: The alcohol (0.1 g) was treated with acetyl chloride (1 ml), the mixture heated under reflux for 30 min, then cooled and decomposed with water. The acids were neutralised with solid KHCO_3 and the products extracted with ether.

The formates of the starting alcohols and of adamantan-2-ol were prepared in the following way: The alcohol (0.1 g) was treated with 99% HCOOH (1 ml), the mixture heated for 60 min on a boiling water bath and then worked up in the same way as in the preceding experiments.

2,4-Dehydroadamantane was prepared by pyrolysis of the dry lithium salt of adamantanone tosylhydrazone in 74% yield; m.p. 201.8–203.1°C (lit.¹¹ gives 202.5–203.5).

Lead tetraacetate was prepared by reaction of Pb_3O_4 with a mixture of glacial acetic acid and acetic anhydride¹². The lead tetraacetate was filtered off with suction, dried and kept in a desiccator over P_2O_5 and anhydrous K_2CO_3 .

Oxidation in pyridine. The chemicals used in the oxidation were applied in the following ratio: 1 mol of the alcohol per 1 mol (+5–9%) of $(\text{CH}_3\text{COO})_4\text{Pb}$. For 1 g of lead tetraacetate were taken 3 ml of dry pyridine. To a mixture of dry pyridine and lead tetraacetate, previously stirred for 10 min at room temperature, 1 g of the alcohol was added. The flask containing the reaction

TABLE II
Oxidation Products of 2-(2-Adamantyl)ethan-1-ol (II)

Sequence in G.L.C.	Compound	Content (weight %)	
		pyridine	benzene
1	adamantane	<1	<1
2	methyleneadamantane	<1	—
3	2-methyladamantane	<1	<1
4	not identified	1	1
5	2-ethyladamantane	2	3
6	1,2-(epoxyethano)adamantane (X)	6	21
7	2-(2-adamantyl)ethanal (VI)	26	2
8	2,4-(epoxyethano)adamantane (XI)	—	1
9	2-(2-adamantyl)ethan-1-ol (II)	46	33
10	2-adamantylmethanol acetate	<1	—
11	2-(2-adamantyl)ethan-1-ol formate	<1	<1
12	2-(2-adamantyl)ethan-1-ol acetate	10	2
13	not identified	<1	<1
14	?-acetoxy-1,2-(epoxyethano)- adamantane	—	7
15	} isomers of 2-[2-(?-hydroxyadamantyl)]- ethan-1-ol acetate (XVIIIb)	1	1
16		6	25
Reaction time, min		20	90
Yield (g oxidation mixture per 1 g of II)		0.95	1.20

mixture was then placed in a water bath at 80°C and the mixture stirred under exclusion of air moisture. Every five minutes a sample was withdrawn and tested for the presence of Pb(IV) (with starch-potassium iodide solution). When all lead tetraacetate had been consumed, the reaction was stopped by pouring the mixture into water and the products were extracted with three portions of ether. The combined extracts were washed with water, 5% HCl, again with water, and finally with 5% aqueous KHCO₃, dried over anhydrous Na₂SO₄ and the ether removed by distillation. A sample was then withdrawn which was immediately analysed by gas chromatography and mass spectrometry. Immediate analysis is necessary because the aldehydes present in the reaction mixtures relatively quickly undergo polymerisation. After two days standing at room temperature their content had decreased to about half. The ether was then distilled off, the residue dissolved in methanol (2 ml) and the solution treated with saturated aqueous KHSO₃ (10 ml). The mixture was allowed to stand overnight, whereupon the addition compound was filtered off with suction and washed with ether. After removing the ether, the residue was also immediately subjected to chromatographical analysis. After above reaction with KHSO₃, the oxidation mixture was already free from aldehydes. Form the bisulphite compound the aldehyde was set free by heating with 20% H₂SO₄. Reaction times, yields, and compositions of the reaction mixtures are given in Tables I—IV. Since the aldehydes isolated *via* the addition compounds are unstable, we employed for their characterisation the 2,4-dinitrophenylhydrazones which were prepared by the standard procedure¹³. 2,4-Dinitrophenylhydrazone of 2-adamantanecarbaldehyde m.p. 211.8—212.2°C,

TABLE III
Oxidation Products of 3-(2-Adamantyl)propan-1-ol (III)

Sequence in G.L.C.	Compound	Content (weight %)	
		pyridine	benzene
1	spiro[adamantane-2,2'-(1'-oxacyclopentane)] (XII)	8	29
2	1,2-(epoxypropano)adamantane (XIII)	<1	1
3	3-(2-adamantyl)propanal (VII)	16	3
4	3-adamantylidenepropan-1-ol (XVI)	8	20
5	3-(2-adamantyl)propan-1-ol (III)	52	40
6	3-(2-adamantyl)propan-1-ol formate	2	1
7	not identified	<1	<1
8	3-(2-adamantyl)propan-1-ol acetate	12	1
9	} isomers of ?-acetoxyspiro[adamantane- -2,2'-(1-oxacyclopentane)]	—	2
10			
11			
12	} isomers of 3-[2-(?-hydroxyadamantyl)]- -propan-1-ol acetate (XVIIIc)	<1	3
13			
14			
Reaction time, min		20	70
Yield (g oxidation mixture per 1 g of III)		0.95	1.10

of 2-(2-adamantyl)ethanal m.p. 167.0–168.5°C, of 3-(2-adamantyl)propanal m.p. 152.0–153.0°C, of 4-(2-adamantyl)butanal m.p. 157.0–158.0°C (all from methanol).

Oxidation in benzene. The substances used in the oxidation were applied in the following ratio: 1 mol of the alcohol per 1 mol (+5–9%) of lead tetraacetate, and 3 mol of dry CaCO_3 for 2500 ml of benzene. In a flask fitted with a reflux condenser and a stirrer lead tetraacetate, benzene, and CaCO_3 were stirred for 10 min at room temperature. Then the alcohol (1 g) and benzoyl peroxide (5 mg) were added, the flask put on a heated water bath the mixture refluxed under stirring. Every ten minutes a sample was withdrawn and tested for the presence of Pb(IV). After consumption of all lead tetraacetate, the benzene solution was decanted, the deposited salts were washed twice with benzene and the combined extracts with 5% KHCO_3 . The extract was dried and benzene removed by distillation. A sample was analysed by means of gas chromatography and mass spectrometry. Yields, reaction times, and compositions of the reaction mixtures are given in Tables I–IV. The crude reaction mixture was subjected to hydrolysis with methanolic potassium hydroxide and the cyclic ethers were isolated by elution chromatography on Al_2O_3 . 2,4-(Epoxyethano)adamantane (*IX*) m.p. 223.0–224.0°C (sealed off capillary). NMR spectrum: 3 H besides an ether bonded oxygen atom, asymmetric multiplet in the 350–400 p.p.m. region. For $\text{C}_{11}\text{H}_{16}\text{O}$ (164.3) calculated: 80.44% C, 9.78% H; found: 80.51% C, 9.78% H. 1,2-(Epoxyethano)adamantane (*X*): NMR spectrum: 2 H besides an ether bonded oxygen atom, symmetric multiplet in the 370–420 p.p.m. region. For $\text{C}_{12}\text{H}_{18}\text{O}$ (178.3) calculated: 80.85% C, 10.18% H; found: 80.61% C, 10.10% H. Spiro[adamantane-2,2'-(1-oxacyclopentane)] (*XII*)

TABLE IV

Oxidation Products of 4-(2-Adamantyl)butan-1-ol (*IV*)

Sequence in G.L.C.	Compound	Content (weight %)	
		pyridine	benzene
1	2-(2-adamantyl)furan	—	<1
2	spiro[adamantane-2,2'-(1'-oxacyclohexane)] (<i>XV</i>)	<1	2
3	2-(2-adamantyl)tetrahydrofuran (<i>XIV</i>)	3	57
4	4-(2-adamantyl)butanal (<i>VIII</i>)	17	2
5	4-adamantylidenebutan-1-ol (<i>XVII</i>)	<1	6
6	4-(2-adamantyl)butan-1-ol (<i>IV</i>)	69	28
7	4-(2-adamantyl)butan-1-ol formate	1	—
8	not identified	<1	<1
9	4-(2-adamantyl)butan-1-ol acetate	10	1
10	} isomers of	—	3
11		2-[(2-(?-acetoxyadamantyl)]furan	—
12	} isomers of 4-[2-(?-hydroxyadamantyl)]-	<1	<1
13		-butan-1-ol acetate (<i>XVIII</i>)	<1
Reaction time, min		20	50
Yield (g oxidation mixture per 1 g of <i>IV</i>)		0.95	1.10

NMR spectrum : 2 H besides an ether bonded oxygen atom, symmetric multiplet in the 360 to 380 p.p.m. region. For $C_{13}H_{20}O$ (192.3) calculated: 81.20% C, 10.48% H; found: 81.13% C, 10.41% H. 2-(2-Adamantyl)tetrahydrofuran (XIV): NMR spectrum : 3 H besides an ether bonded oxygen atom, asymmetric multiplet in the 340–410 p.p.m. region. For $C_{14}H_{22}O$ (206.3) calculated: 81.50% C, 10.75% H; found: 81.44% C, 10.59% H.

Solvolysis of the cyclic ethers. The cyclic ether dissolved in a tenfold volume of acetic anhydride and cooled to $-20^{\circ}C$ was treated with boron trifluoride etherate (1.5 ml per 1 g of the cyclic ether) and allowed to stand at room temperature for 3 h. The reaction mixture was then decomposed by pouring it onto crushed ice, whereupon it was carefully neutralised with solid $KHCO_3$ and extracted three times with ether. After removing the ether by distillation, the residue was treated with a tenfold amount of 10% methanolic KOH and the mixture refluxed for 30 minutes. Most of the methanol was then removed by distillation. The residue was taken up in ether, the ethereal solution washed with water, dried and freed from solvent. The products were analysed by means of gas chromatography and mass spectrometry. 2,4-(Epoxyethano)adamantane afforded 2-hydroxy-4-hydroxymethyladamantane (XIX), m.p. $193.0-193.5^{\circ}C$ (sealed off capillary). For $C_{11}H_{18}O_2$ (182.3) calculated: 72.49% C, 9.55% H; found: 72.80% C, 9.68% H. 1,2-(Epoxyethano)adamantane afforded 2-[2-(1-Hydroxyadamantyl)]ethan-1-ol (XX), m.p. $97.6-98.0^{\circ}C$. For $C_{12}H_{20}O_2$ (196.3) calculated: 73.43% C, 10.27% H; found: 73.61% C, 10.17% H. Spiro[adamantane-2,2'-(1-oxacyclopentane)] afforded a mixture of 3-adamantylideneopropan-1-ol (XVI) with further two isomeric unsaturated alcohols, evidently *cis*- and *trans*-3-(2-adamantyl)-prop-2-en-1-ol. 2-(2-Adamantyl)tetrahydrofuran afforded a mixture of 4-adamantylidenebutan-1-ol (XVII) with further two isomeric unsaturated alcohols, but the position of their double bond was not determined.

Analytical

Gas chromatography, mass and NMR spectrometry were the fundamental methods used for identification. First the oxidised mixture was analysed by gas chromatography both on a non-polar (SE-30) and a polar (FF AP) stationary phase. From the chromatograms the concentrations of the individual components were calculated. By comparing the number and concentration of the individual components and their retention times with the retention times of standard compounds some of the compounds were identified (the starting alcohols, the acetates and formates of the starting alcohols as well as the acetates and formates of alcohols having in their chain one carbon atom less). By gas chromatography (on SE-30) coupled to mass spectrometry the mass spectra of all components of the mixture were then measured. By comparing the spectra with those of standard compounds was not only confirmed the structure of the compounds which were determined by means of gas chromatography, but also suggested the structure of the remaining compounds. The aldehydes and cyclic ethers were isolated by the above described procedure, and the others, as far as their content was at least 5%, were isolated by means of preparative gas chromatography. The NMR spectra of all these compounds (except those of the aldehydes) were taken.

ω -(2-Adamantyl)alkan-1-ols. The mass spectra of this class of compounds show the characteristic ionic species M^+ , m/e 135 (Ad^+), and 148 ($AdCH^+$). m/e 135 is the base peak in the spectra of alcohols with an even number of carbon atoms in the alkane chain, and m/e 148 is the base peak in the spectra of alcohols with an odd number of carbon atoms in the alkane chain. Further ionic species are $[M-18]^+$ (H_2O), $[M-31]^+$ (CH_2OH), $[M-32]^+$ (CH_3OH), $[M-45]^+$ ($CH_2 \cdot CH_2OH$), and $[M-46]^+$ (CH_3CH_2OH).

Formates of ω -(2-adamantyl)alkan-1-ols and adamantan-2-ol. The molecular ion in the mass spectra of these compounds is of very small intensity or entirely lacking. All mass spectra of these compounds exhibit the distinct $[M-46]^+$ ion (HCOOH). Further fragmentation is analogous to that of the starting alcohols.

Acetates of ω -(2-adamantyl)alkan-1-ols and adamantan-2-ol. The molecular ion in the mass spectra is likewise of small intensity or lacking. The highest ion in the spectrum is $[M-60]^+$ (CH_3COOH). Further fragmentation is the same as in the case of the formiates.

ω -(2-Adamantyl)alkanals. The mass spectra of these compounds contain the ions M^+ , $[M-18]^+$, $[M-28]^+$ (CO), $[M-29]^+$ (CHO), and m/e 135. Very helpful in identifying these compounds was the formation of the 2,4-dinitrophenylhydrazones and bisulphite additional compounds.

Cyclic ethers with a five-membered ring. The mass spectra of these compounds differ markedly from each other. This is probably due to the different substitution of the adamantane skeleton in each compound. To the identification of these compounds contributed mostly the NMR spectra (see above), whereas the mass spectra served mainly for the identification of the cyclic ethers with a six-membered ring.

Cyclic ethers with a six-membered ring. The identification was performed essentially by comparing the mass spectra of these compounds with those of the cyclic ethers with a five-membered ring, the adamantane skeleton in both series of compounds being identically substituted. The mass spectra of compounds IX and XI (2,4 substitution of the adamantane skeleton) contain an intense molecular ion (rel. intensity, IX 100%, XI 74%). The spectra exhibit the ions m/e 134 (IX 14%, XI 59%) and 135 (IX 43%, XI 35%), which are practically lacking in the case of other cyclic ethers, and $[M-18]^+$. Compounds X and XIII (1,2-substitution of the adamantane skeleton) afford molecular ions of comparable intensity (X 20%, XIII 26%). Both spectra show the ions $[M-18]^+$, $[M-31]^+$, and $[M-30]^+$, but are devoid of the ions m/e 134 and 135. Base peak of X 121^+ and of XIII 161^+ . Compounds XII and XV (2,2 substitution of the adamantane skeleton) give very intense molecular ions (XII 70%, XV 80%) and the ion m/e 150 (XII 100%, XV 87%). In both spectra is present the ion $[M-18]^+$.

ω -Adamantylidenealkan-1-ols (XVI and XVII). The mass spectra of both compounds contain the ions M^+ and $[M-18]^+$. Ions at m/e 135 are practically absent (the double bond goes out from the adamantane skeleton). NMR spectrum of XVI. 2 H: triplet in the 330–360 p.p.m. region ($-\text{CH}_2\text{OH}$), 2 H: multiplet in the 200–230 p.p.m. region ($=\text{CHCH}_2\text{CH}_2\text{OH}$), 1 H: triplet in the 480–510 p.p.m. region (proton on the double bond), 2 H: two multiplets in the 220–240 and 270–290 p.p.m. regions (hydrogen atoms on carbon atoms 1 and 3 of the adamantane skeleton). The spectrum of XVII is similar to that of XVI with the difference that the multiplet in the 200–230 p.p.m. region is due to 4 H.

Hydroxy derivatives of the acetates of the starting alcohols. The mass spectra are devoid of the molecular ion. The highest ions in the spectra are $[M-18]^+$, $[M-60]^+$ (CH_3COOH), and $[M-78]^+$. The ions m/e 135 are practically absent. NMR spectrum: 2 H besides $\text{CH}_3\text{COO}-$ (in the region of 400–420 p.p.m.), no proton besides OH (substitution of OH on a tertiary carbon atom of the adamantane skeleton).

Acetoxy derivatives of the cyclic ethers. The mass spectra contain M^+ of low intensity and $[M-42]^+$ (CH_2CO). Further are present the ions $[M-60]^+$ which are the base peaks. The NMR spectrum does not contain protons adjacent to $\text{CH}_3\text{COO}-$ (bound to a tertiary carbon atom of the adamantane skeleton).

Gas chromatographical analyses were performed on a Chrom III apparatus equipped with flame ionisation detector in 10 m long stainless capillary columns of 0.25 mm I.D. As stationary

phases were used SE-30 (temperature of the column 110–160°C according to the nature of the analysed compounds) and FF-AP (150–200°C). Carrier gas N₂. Mass spectra were taken on a mass spectrometer LKB 9000. Chromatographic separations were carried out on SE-30 (3 m long glass column, I.D. 3 mm, 3% Se-30 on Chromosorb W, carrier gas He). NMR spectra were taken on a Varian XL-100. Preparative gas chromatography was performed on a Chrom III apparatus in 2 m long columns of 6 mm I.D. packed with SE-30 (20% on Chromosorb P), PEGA (20% on Chromosorb P), and Carbowax 20M (20% on Chromosorb P). Carrier gas H₂. The composition of the reaction mixtures calculated from the chromatograms is given in weight per cent. Within the limit of experimental error there is very a good agreement between the results obtained by this method and the actual quantity of substance gained *e.g.* by elution chromatography or preparative gas chromatography. The compounds listed in the Tables are ranked according to their retention times on SE-30.

REFERENCES

1. Criegee R.: *Angew. Chem.* 70, 173 (1958).
2. Moriconi E. J., Wallenberger F. T., O'Connor W. F.: *J. Am. Chem. Soc.* 80, 656 (1958); 82, 3122 (1960).
3. Mihailović M. L., Maksimović Z., Jeremić D., Čeković Ž., Milovanović A., Lorenc L.: *Tetrahedron* 21, 1395 (1965).
4. Mihailović M. L., Bošnjak J., Maksimović Z., Čeković Ž., Lorenc L.: *Tetrahedron* 22, 955 (1966).
5. Mihailović M. L., Čeković Ž., Maksimović Z., Jeremić D., Lorenc L., Mamuzić R. I.: *Tetrahedron* 21, 2799 (1965).
6. Mihailović M. L., Čeković Ž., Jeremić D.: *Tetrahedron* 21, 2813 (1965).
7. Burkhard J., Janků J., Landa S.: *This Journal* 37, 3342 (1972).
8. Stepanov F. N., Krasutskij P. A., Jurčenko A. G.: *Ž. Org. Chim.* 8, 1179 (1972).
9. Burkhard J., Vais J., Landa S.: *Z. Chem.* 9, 29 (1969).
10. Landa S., Vais J., Burkhard J.: *This Journal* 38, 1445 (1973).
11. Udding A. C., Strating J., Wynberg H., Schlatmann J. L. M. A.: *Chem. Commun.* 1966, 657.
12. *Inorg. Syn.* 1, 47 (1938).
13. Ernest I., Heřmánek S.: *Preparativní reakce v organické chemii*, Vol. IV, p. 478. Published by Nakladatelství ČSAV, Prague 1957.

Translated by R. Wicks.