

PYROLYSES OF SUBSTITUTED ACETYLOXY COMPOUNDS

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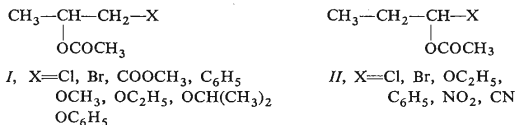
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Received August 2nd, 1973

Pyrolytic eliminations of the compounds $\text{CH}_3\text{CH}(\text{OAc})\text{CH}_2\text{X}$ and $\text{CH}_3\text{CH}_2\text{CH}(\text{OAc})\text{X}$, for $\text{X} = \text{Cl}, \text{Br}, \text{COOCH}_3, \text{OH}, \text{C}_6\text{H}_5$ and CN , were followed and the ratio of products in dependence on temperature determined.

The pyrolyses of esters represent an important method for the preparation of unsaturated compounds without isomerisation of the double bond¹. Although the preparation of olefins by pyrolysis of unsubstituted esters is extensively described in the literature¹⁻⁶, only scant data is available on the pyrolysis of substituted esters⁷⁻⁹. The electronic effects were studied in phenyl esters substituted in the nucleus¹⁰ but attention was also paid to the distribution of the products during the pyrolysis of more complex compounds. Literature data^{6-8,12,13} differs considerably and in some instances the products were not determined with certainty, while in the case of *cis-trans* isomers only the total amount of olefins was indicated¹¹.

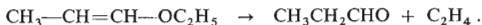
We now investigated the ratio of the pyrolysis products in dependence on the temperature in the series of acetates of type *I* and *II*. In addition to the orientation of the elimination and the ratio of the isomers it is also possible to follow the competitive elimination of hydrogen halides, alcohol, and other groups.



These compounds were prepared both from propylene oxide (*I*) and from propanal (*II*) as starting material. As standards for gas chromatography which was used for analysis of pyrolytic products unsaturated compounds were prepared which came into consideration as standards, or preparative gas chromatography was used for the isolation of products, and for quantitative application after their identification.

The results of the pyrolyses are presented in Table I. For the majority of substances the temperature 500–550°C was found suitable from the preparative point of view.

During the pyrolysis the ratio of the products is affected by subsequent reactions of which mainly polymerisation causes a decrease in the yields, and further by isomerisations which complicate the separation of the mixture. After the pyrolysis of 1-chloro-2-acetyloxypropane the yields are very low due to polymerisation, and the proportion of 1-chloro-1-propanes increases with the temperature. In addition to acetic acid elimination a splitting off of hydrogen chloride also takes place in spite of the fact that the elimination of hydrogen chloride requires much higher temperatures, in the case of 1-bromo-2-acetyloxypropane elimination of hydrogen bromide takes place already at 200°C but hydrogen bromide immediately undergoes an addition reaction, so that the primary product of the reaction is isomeric 2-bromo-2-acetyloxypropane. Because it was shown during the pyrolysis of simple halogen derivatives that the activation energies for chloro and bromo derivatives differ relatively little¹⁴⁻¹⁶, it is important to envisage the participation of the acetyloxy group and the halogen during elimination. Similarly, in the case of 1,3-dichloro-2-acetyloxypropane the elimination of the acetyloxy group and hydrogen chloride is commensurable. We were unable to demonstrate the formation of the isomerisation products for example in the case of 1-chloro-3-acetyloxy-2-propane or 1-acetyloxy-1-propane. In the case of 1-alkoxy-2-acetyloxypropanes the amount of allyl alkyl ethers decreases during pyrolysis, and that direction of the elimination prevails leading to propenyl alkyl ethers; however, the latter were not isolated because they react with acetic acid giving propanal and acetic acid esters. Only in the case of 1-phenyloxy-2-acetyloxypropane isopropenyl acetate was isolated, *i.e.* a splitting off of phenol takes place. The result of the reaction is complicated also by the possibility of a thermal cleavage of propenyl alkyl ethers¹



During all pyrolyses of alkoxy derivatives we observed the formation of gaseous olefins which we were, however, unable to determine quantitatively due to experimental difficulties. Propanal was one of the main products of pyrolysis of all 1-alkoxy-2-acetyloxypropanes. Only 2-phenyl-2-acetyloxypropane afforded 2-phenyl-1-propene in high yield without side reactions. In the case of 1-phenyl-2-acetyloxypropane and 1-phenyl-1-acetyloxypropane 2-phenyl-1-propene was detected in the reaction products in appreciable amount, *i.e.* during elimination isomerisation takes place under migration of the phenyl group. For the sake of comparison the equilibrium of *cis*- and *trans*-isomers of 1-phenyl-1-propene was determined by thermal isomerisation. At 300°C about 7.5% of *cis* and 88% of *trans* isomer was formed after 1.5 hours in addition to 2.5% of 3-phenyl-1-propene and 2% of 2-phenyl-1-propene. On further heating the ratio of the first three isomers remained unchanged, but the amount of 2-phenyl-1-propene increased. In the case of 1-chloro-1-propene 31% of *trans* and 69% of *cis* isomer were found at equilibrium at 250°C. During pyrolysis a mixture

TABLE I
Pyrolysis of Acetyloxy Compounds (yields in %)

<i>t</i> , °C	Regenerated			
	1-Chloro-2-acetyloxypropane	<i>trans</i>	<i>cis</i> -1-Chloro-1-propene	1-Chloro-2-propene
410	95	0.2	0.4	0.9
500	27	5.8	5.8	9.1
600	1.8	5.3	6.9	10.5
	1-Bromo-2-acetyloxypropane			2-bromo- -2-acetyloxypropane (%)
210	87.1			12.6
330	58.5			35.0
410	45.8			9.0
	Methyl 3-acetyloxybutanoate			
		3-methyl butenoate	methyl- <i>trans</i>	<i>cis</i> -2-butenoate
330	65.0	3.3	23.5	5.1
410	35	5.1	46.3	12.2
500	8.8	7.2	64.8	19.1
600	0	8.6	58.8	21.9
	1-Methoxy-2-acetyloxypropane			
		propanal	methyl acetate	methyl allyl ether
500	52	8.9	11.8	15.4
600	23.8	17.2	25.0	19.3
690 ^a	3.6	21.1	17.2	23.5
	1-Phenyl-2-acetyloxypropane			
		3-phenyl-1-propene	2-phenyl-1-propene	<i>trans</i> : <i>cis</i> -1-phenyl-1-propene
410°C	84	10.5	2.0	2.4 0
500	52	11.2	6.7	19.1 0
600	4.5	16.4	12.4	26.2 2.2
	1-Ethoxy-2-acetyloxypropane			
		propanal	ethyl acetate	ethyl allyl ether
500	40.2	9.2	27.2	5.3
600	13.5	13.2	24.1	7.7
690 ^a	0	14.1	5.5	8.4
	1-Isopropoxy-2-acetoxypropane			
		propanal	isopropyl acetate	isopropyl allyl ether
500	39.0	10.9	20.0	1.4
600	18.6	20.1	4.8	2.9
690 ^a	0	21.9	5.8	2.2

TABLE I
(Continued)
Pyrolysis of Acetyloxy Compounds (yields in %)

<i>t</i> , °C	Regenerated				
1-Phenyloxy-2-acetyloxypropane					
		propanal	isopropenyl acetate	phenyl- acetate	phenol
330	26	34.0	13.9	38.0	15.4
410	18.5	26.8	25.1	30.0	25.8
500	8.0	46.5	6.0	6.0	36.8
1,3-Dichloro-2-acetyloxypropane					
		<i>trans</i> -	<i>cis</i> -1,3-dichloropropene	1-chloro-2-acetyl- oxy-2-propene	
500	63	5.4	9.9	13.5	
600	37.5	8.0	17.2	17.8	
690	0	6.9	15.4	14.6	
1-Phenyl-1-acetyloxypropane					
		3-Phenyl-1-propene	2-phenyl-1-propene	<i>trans</i>	<i>cis</i> -1-phenyl-1-propene
330	75	0	8.9	14.0	0
410	26.4	0	10.8	61.5	0
500	0	0	14.4	69.0	3.8
600	0	4.1	20.8	52.5	8.4
2-Phenyl-2-acetyloxypropane					
		2-phenyl-1-propene	<i>trans</i>	<i>cis</i> -1-phenyl- -1-propene	
410	38.2	61.8	0	0	
500	19.0	72.2	0	0	
600	1.9	81.5	0	0	
1-Cyano-1-acetyloxypropane					
		<i>cis</i> -	<i>trans</i> -1-cyano-1-propene		
600	56.5	24.0	16.08		
690	15.2	49.8	29.6		

^a At this temperature ketene appears in the product.

of *cis-trans* isomers is formed which approaches to equilibrium with increasing temperature¹⁷. When studying the pyrolyses of the compounds of series *II* the results of pyrolysis could be evaluated only in the case of $X = \text{CN}$ and C_6H_5 , because in the case of other substances where $X = \text{halogen}$, OR or NO_2 decomposition takes place already at a low temperature (in the case of the NO_2 group the reaction is explosive, while the analogous 2-acetyloxy-1-nitropropane affords 1-nitro-1-propene^{9,11} smoothly at 200°C). In the case of halogenoacetyloxypropanes *II* the propenyl acetates formed add hydrogen halides again on cooling, under formation of the original substance, but polymerisation also takes place to a large extent. Only a very low amount of propenyl chloride was detected.

EXPERIMENTAL

1-Chloro-2-acetyloxypropane, b.p. 151°C/750 Torr (90% (ref.¹⁸), *cis*-1-chloro-1-propene, *trans*-1-chloro-1-propene, 3-chloro-1-propene were prepared by pyrolysis of 1-chloro-2-acetyloxypropane at 500°C. After neutralisation of the pyrolysate with a sodium hydrogen carbonate solution the mixture was separated by preparative gas chromatography (column with 10% diethylene glycol succinate on porovina, linear temperature programme of the column 35–90°C; *cis*-isomer had b.p. 36°C, *trans*-isomer b.p. 23°C, 3-chloro-1-propene b.p. 44°C in agreement with lit.¹⁹.

1,3-Dichloro-2-acetyloxypropane b.p. 92°C/14 Torr (86%) (ref.²⁰). 1,3-Dichloropropene, *cis*-isomer b.p. 109°C, *trans*-isomer b.p. 102.5°C; lit.²¹ gives for the mixture of isomers b.p. 105–106°C. These substances were also prepared by pyrolysis of 1,3-dichloro-2-acetyloxypropane at 600°C, the pyrolysate was collected into a vessel containing a mixture of calcium chloride calcium carbonate and then rectified on a column of 15 TP, fraction of b.p. 101–115°C was further separated by gas chromatography (diethylene glycol succinate, column 3 m, 150°C). In the higher boiling fraction 3-chloro-2-acetyloxy-1-propene was present which was separated by preparative gas chromatography (10% of diethylene glycol adipate on porovina, column length 3 m, 150°C), and identified by IR spectra and analysis. Alkyl allyl ethers were prepared according to literature¹² in yields ranging from 50 to 60%.

1-Bromo-2-acetyloxypropane was prepared by esterification of 1-bromo-2-propanol¹¹ with boiling acetic anhydride, b.p. 81°C/20 Torr (83%). For $\text{C}_5\text{H}_9\text{BrO}_2$ (181.0) calculated: 33.2% C, 5.0% H; found: 32.9% C, 5.1% H.

2-Bromo-2-acetyloxypropane was prepared by pyrolysis of 1-bromo-2-acetyloxypropane at 260°C, the pyrolysate was washed with 5% NaHCO_3 and water and after drying over sodium sulfate it was distilled through a column of 15 TP. Yield 40%, b.p. 140–41°C/600 Torr. The substance was hydrolysed with a sodium hydroxide solution to acetone. For $\text{C}_5\text{H}_9\text{BrO}_2$ (181.0) calculated: 33.2% C, 5.0% H, 44.2% Br; found: 33.1% C, 5.05% H, 40.7% Br.

cis and *trans*-1-Bromo-1-propene were prepared by dropwise addition of 70 g of 1-bromo-2-propanol to 150 g of phosphorus pentoxide under continual distilling off of unsaturated bromo derivatives. The mixture was distilled on a 20 TP column; b.p. of the *trans*-isomer 57.5°C, a *cis* and *trans* mixture containing 93% of the *cis* isomer had b.p. 62–63°C and was used as a standard. In addition to this allyl bromide was also isolated, m.p. 71°C.

1-Alkoxy-2-acetyloxypropanes were prepared by introducing 2 mol of propylene oxide into a solution of alcoholate (prepared from 170 ml of corresponding hydroxy derivative and 5 g

of sodium) at 60°C. The mixture was allowed to stand at room temperature for 2 days, then neutralised with acetic acid and after distilling off of the alcohol the residue was acetylated by two hours' boiling with acetic anhydride. 1-Methyloxy-2-acetyloxypropane, b.p. 145°C (40%)¹², 1-ethoxy-2-acetyloxypropane b.p. 58°C/12 Torr (34%), 1-isopropoxy-2-acetyloxypropane, b.p. 70°C/12 Torr (33%).

1-Bromo-1-acetyloxypropane: Propanal (58 g; 1 mol) was added dropwise and under stirring to 118 g (1.1 mol) of acetyl bromide and 0.1 g of zinc chloride at 0°C and when the reaction ceased the mixture was allowed to stand at room temperature for one hour. The excess acetyl bromide was distilled off and the fraction boiling at 76–80°C (140 g; 77%) was collected. For C₅H₉BrO₂ (181.0) calculated: 33.2% C, 5.0% H; found: 33.0% C, 5.1% H. 1-Chloro-1-acetyloxypropane, b.p. 42–45°C/14 Torr (84%) (ref.²²) was prepared in an analogous manner.

1-Phenyl-2-acetyloxypropane: 60 g of propylene oxide were added under stirring to a solution of 50 g of phenol in 20 ml of 10% KOH solution and the mixture heated at 100°C for 2 hours. After cooling and washing with water the mixture was dried over magnesium sulphate and the crude phenylpropanol was acetylated by heating with 78 mg of acetic anhydride and 0.1 g of zinc chloride. B.p. 112–114°C/12 Torr (54%). For C₁₁H₁₄O₃ (194.2) calculated: 68.0% C, 7.3% H; found: 67.6% C, 7.1% H.

1-Phenyl-1-acetyloxypropane was prepared on acetylation of the hydroxy derivative using an analogous procedure, b.p. 115–118°C/22 Torr (44%), lit.²³ gives b.p. 227°C (decomposition).

cis- and *trans*-1-Phenyl-1-acetyloxypropene and 3-phenyl-1-propene were prepared by pyrolysis of 1-phenyl-1-acetyloxypropane at 650°C and the pyrolysate was neutralised with sodium carbonate solution and after drying it was distilled on a 15 TP column under gas chromatographic control, *trans*-isomer b.p. 175°C and 3-phenyl-1-propene b.p. 154–156°C (boiling point coincides with the literature^{24,25}). The *cis*-isomer was obtained as a 86% mixture with the *trans*-isomer (concentration determined by gas chromatography). 1-Phenyl-2-acetyloxypropane, b.p. 116°C/20 Torr and 2-phenyl-2-acetyloxypropane were prepared on acetylation of the corresponding hydroxy derivatives with acetyl chloride and pyridine according to lit.²⁶; 1-cyano-1-acetyloxypropane²⁷ was prepared similarly.

2-Phenyl-1-propene was prepared by pyrolysis of 2-phenyl-2-acetyloxypropane, b.p. 161 to 162°C, lit.²⁸ gives 163–164°C/752 Torr.

Pyrolytic Procedure

The vapours of the pyrolysed substance were introduced into a quartz tube (50 cm long, 1.6 cm diameter) at a 0.2–0.25 mol/h rate and the tube was heated with a cantal spiral provided with an automatic temperature control ($\pm 5^\circ\text{C}$) in an insulating ceramic tube. The products were cooled to 0°C and the composition was followed by gas chromatography. Quantity was done on the basis of calibration. The following columns were employed: 15% tricresyl phosphate on porovina, 3 m, 0.1 kp/cm², N₂, for chloroacetyloxypropane, 8% diethylene glycol succinate on Chromosorb, 1 m, for dichloroacetyloxypropane and cyanoacetyloxypropane, 10% of tris-cyanoethoxypropane on Chromosorb for bromoacetyloxypropanes. For other separations elastomer SE-30 was found suitable.

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Translated by Ž. Procházka.