PYROLYSIS OF 2-ACETOXYCARBOXYLIC ACIDS

Ján GALOCI, Miloš PROCHÁZKA and Eva KLINOTOVÁ

Department of Organic Chemistry,
Charles University, 128 40 Prague 2

The pyrolysis of 2-acetoxycarboxylic acids may be described by the competing reactions R^1R^2C.$(OCOCH_3)COOH \rightarrow$ (a) $R^1R^2CO + CH_3COOH + CO$; (b) $R^1R^2CO + CH_3CHO + CO_2$; (c) $CH_3COOH +$ unsaturated acid. The formation of a carbonyl compound is the general character of the pyrolysis of this group of substances.

Pyrolytic cleavage of 2-acetoxypropionic acid at 500°C does not afford[1] the expected propenoic acid, but acetaldehyde, acetic acid and carbon monoxide and carbon dioxide instead (Scheme 1). For this thermal decomposition a cyclic mechanism has been proposed in paper[1], where acetaldehyde is formed only from the carbon chain of propionic acid, while in papers[2,3] quantitative pyrolysis of triterpenoid α-acetoxy acids is mentioned in which a ketone and acetaldehyde are formed at 270°C. The low temperature and the uniform course of the decomposition led us to check to what extent this reaction is general and how the products depend on the structure of the acetoxy acid. For this purpose we prepared various 2-acetoxycarboxylic acids and pyrolysed them in the 270–400°C temperature range, and then we analysed the products. On this basis we deduced the reaction mechanism of this pyrolysis.
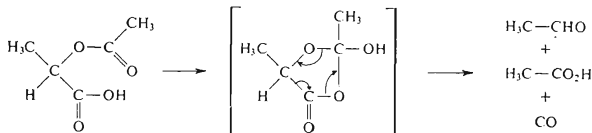
SCHEME 1

We pyrolysed the following acids: 2-acetoxy-2-methylpropionic acid (*I*), 2-acetoxy--2-phenylpropionic acid (*II*), 2-acetoxy-2-phenylacetic acid (*III*), 1-acetoxycyclo-pentanecarboxylic acid (*IV*) and 1-acetoxycyclohexanecarboxylic acid (*V*). The results are presented in Table I. The preparative pyrolysis of the substances investigated
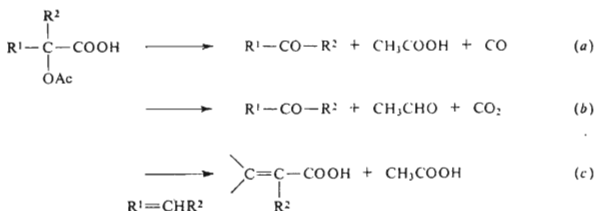
requires temperatures above 300°C; the unusually easy pyrolysis of triterpenic acetoxy acids[2,3] is probably due to the suitable orientation of the groups in the crystal lattice.

TABLE I

Products (yield in %) of the pyrolysis of 2-acetoxycarboxylic acids[a]

t, °C	R R >CO	CH_3COOH	CH_3CHO	CO_2	Starting compound, %
		2-Acetoxy-2-methylpropionic acid			
270	31[b]	11	23	27	83
330	63	42	17	17	58
400	76	65	2	11	26
450	70	69	—	8	4
		2-Acetoxy-2-phenylacetic acid			
270	66[c]	15	47	52	43
300	69	35	24	28	18
330	73	52	17	19	5
370	66	55	14	17	2
		2-Acetoxy-2-phenylpropionic acid			
270	53[d]	11	48	49	55
330	61	41	19	21	14
370	63	59	10	12	6
400	65	66	2	9	2
		1-Acetoxycyclopentanecarboxylic acid			
270[e]	29[f]	32	11	46	37
300[g]	33	39	9	49	11
330[h]	36	50	6	62	2
370[i]	37	57	5	66	0
		1-Acetoxycyclohexanecarboxylic acod			
270[j]	34[k]	30	15	29	25
300[l]	41	39	9	35	8
330[m]	41	54	5	49	—
370[n]	39	59	—	50	—

[a] Yield referred to the reacted compound in %; [b] CH_3COCH_3; [c] C_6H_5CHO; [d] $CH_3COC_6H_5$; [e] 11% of cyclopentene; [f] cyclopentanone; [g] 12% cyclopentene; [h] 22% cyclopentene; [i] 27% cyclopentene; [j] 15% cyclohexene; [k] cyclohexanone; [l] 19% cyclohexene; [m] 28% cyclohexene; [n] 30% cyclohexene.

The main product of pyrolysis is a carbonyl compound, formed by elimination of the acetyl and the carboxyl group. The unsaturated acids that are formed by elimination of acetic acid in acetoxy acids with a hydrogen atom in β-position (Scheme 2c) could not by detected in the pyrolysates. Only in the case of alicyclic acids *IV* and *V* their decarboxylation products could be detected, *i.e.* cyclopentene and cyclohexene, as well as a correspondingly increased content of carbon dioxide. From Table I it is evident that the relative content of the carbonyl compound does not increase much with increasing temperature, while the increasing content of acetic acid is accompanied by a decrease in the contents of acetaldehyde and carbon dioxide.

$$R^1-\underset{\underset{OAc}{|}}{\overset{\overset{R^2}{|}}{C}}-COOH \longrightarrow R^1-CO-R^2 + CH_3COOH + CO \qquad (a)$$

$$\longrightarrow R^1-CO-R^2 + CH_3CHO + CO_2 \qquad (b)$$

$$\longrightarrow \underset{R^1=CHR^2}{\overset{\diagdown}{\diagup}}C=\underset{\overset{|}{R^2}}{C}-COOH + CH_3COOH \qquad (c)$$

SCHEME 2

The formation of a carbonyl compound by thermal decomposition of 2-acetoxy acids (Scheme 2(a,b)) is thus a general reaction which is exclusive in the case of 2-acetoxy acids that do not contain any hydrogen atom in the β-position to the carboxyl group; in the case of acetoxy acids which do have this hydrogen atom the carbonyl compound formation represents an important reaction competing with the formation of 2-unsaturated acid (Scheme 2(c)). The decomposition of the acetoxy acid under formation of acetic acid and carbon monoxide (Scheme 2(a)) mainly takes place in consequence of a higher activation energy. Therefore, the course of the pyrolyses mentioned cannot be formulated generally as in ref.[1] by Scheme 1, because in all these substances *I — V* acetaldehyde is an important component of the pyrolysate,

$$\underset{R^2}{\overset{R^1}{>}}\underset{\overset{||}{O}}{\overset{O\cdots C\overset{\diagup CH_3}{\diagdown}_{O}}{\underset{C-OH}{C}}}$$
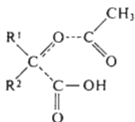
VI

formed from the acetyl group by attachment of the hydrogen atom from the carboxyl group. The transition state of the reaction pathway (*b*) may be formulated by formula *VI*, while the composition of the split off fragments corresponds to pyruvic acid.

EXPERIMENTAL

The purity of the substances was checked by measuring physical constants. The melting points were measured on a Kofler block, the densities were determined gravimetrically. Gas chromatographic analyses were carried out on a Chrom 4 apparatus, using the following columns: 120/0·6 cm with 2% silicone elastomer SE-30 on Chromosorb G-AW-DMCS 80/100; 190/0·3 cm with 10% diethylene glycol succinate; 120/0·6 cm with 20% Apiezon L and with 20% Carbowax 20M on the same support.

The pyrolyses were carried out in a continuous (through-flow) pyrolyser (a quartz tube, 60/1 cm, heated electrically) fixed at a 45° angle. The temperature was measured with Ni-NiCr thermocell. A spiral air condenser with a receiver were attached to the pyrolyser, and a condenser filled with dry ice in acetone. The uncondensed material was introduced into a 2,4-dinitrophenyl-hydrazine solution and then *via* a drying tube into an absorber with ground sodium hydroxide, behind which another absorber with palladium chloride was connected, serving to absorb the carbon monoxide. The whole apparatus was rinsed and kept under argon (5 ml min^{-1} flow). The substances were introduced at a rate of 100 mg of acetoxy acid in 5 ml of solvent (benzene or chlorobenzene) per 60 s. Acetyldehyde was determined as 2,4-dinitrophenylhydrazone after pyrolysis by distilling at 40°C in a stream of argon. The purity was checked by TLC (Silufol, benzene-acetone 5 : 1) and m.p. determination. The carbonyl compounds, acetic acid and the unreacted acetoxy acid were determined in the pyrolysate by gas chromatography, while the evaluation was made on the basis of calibration curves. The acids were converted to methyl esters with diazomethane. Carbon dioxide was detected as $BaCO_3$ and determined as sodium carbonate. Quantitative determination of carbon monoxide was not sufficiently accurate and therefore it is not shown in Table I.

2-Acetoxy-2-methylpropionic acid[4,5], 2-acetoxy-2-phenylacetic acid[6], 2-acetoxydiphenyl-acetic acid[7], 2-acetoxy-2-phenylpropionic acid[8], 1-acetoxycyclopentanecarboxylic acid[9] and 1-acetoxacyclohexynecarboxylic acid[9] were prepared according to literature. As standard for gas chromatography their methyl esters were prepared using ethereal diazomethane solution (b.p. °C/kPa; d_4^{20} g cm^{-3}):

Methyl 2-acetoxy-2-methylpropionate	(77/2·4; 1·058);
methyl 2-acetoxy-2-phenylacetate	(100/0·13; 1·116);
methyl 2-acetoxy-2-phenylpropionate	(108/2·26; 1·128);
1-acetoxy-1-methoxycarbonylcyclopentane	(87/2·26; 1·147);
1-acetoxy-1-methoxycarbonylcyclohexane	(79/2; 1·207).

All the esters had good elemental analyses.

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