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Pyrolysis of Dialkyl 2-Acyloxyalkylphosphonates

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Synopsis. The pyrolysis of dialkyl 2-acyloxyalkylphosphonates at 220—240 °C gave the corresponding alkyl carboxylates and olefins by the elimination of metaphosphoric acid $(HPO_3)_n$.

Tsurugi and his co-workers[1] reported that the pyrolysis of dimethyl 2-acetoxyethyl- or dimethyl 3-acetoxypropylphosphonate at 550—600 °C gave dimethyl vinyl- or dimethyl 3-propenylphosphonate in 51—58% yields respectively, but in the case of diethyl and dipropyl 2-acetoxyethylphosphonates, the corresponding unsaturated phosphonates could not be obtained.

We have found that dialkyl 2-acetoxyethylphosphonates (I), except in the case of the dimethyl derivative, gave alkyl carboxylates and olefins at 220—240 °C, along with the formation of metaphosphoric acids, $(HPO_3)_n$.

The I compounds were prepared by the reaction of acyl chlorides with the corresponding hydroxy derivatives, derived from dialkyl 2-oxoethylphosphonates by treating them with sodium borohydride.[2]

$RCOOR'CHCR''HPO(OR''')_2$ (I)

	R	R′	R″	R‴
I-a	CH_3	C_6H_5	H	C_2H_5
I-b	CH_3	C_6H_5	H	C_3H_7
I-c	CH_3	C_6H_5	H	CH_3
I-d	CH_3	C_6H_5	H	*iso*-C_3H_7
I-e	CH_3	CH_3	H	C_2H_5
I-f	CH_3	H	C_6H_5	C_2H_5
I-g	CH_3	C_6H_5	CH_3	C_2H_5
I-h	C_2H_5	C_6H_5	H	C_2H_5

Diethyl styrylphosphonate (II-a) was prepared from styrene and phosphorus pentachloride by the method of Anisimov.[2] Ethyl hydrogen styrylphosphonate (II-b) was prepared by the hydrolysis of II-a, using sodium hydroxide in ethanol. Styrylphosphonic acid (II-c) was prepared by the hydrolysis of II-a with 6-M hydrochloric acid. Acetyl diethyl phosphate was prepared by the phosphorylation of acetic acid with tetraethyl phosphorous-phosphoric anhydride.[3]

In each run of the pyrolysis of the phosphonate, 0.1 mol of the phosphonate was decomposed in a 10 ml distilling flask heated at the rate of 5 °C/min in a metal bath. The decomposition of the phosphonate began in the range from 220—240 °C and was finished in a few minutes. The pyrolysis products were trapped in a tube cooled with ice water. They were analyzed by means of glc on a 3 m×3 mmϕ column, packed with NDP (20%) on Celite (60—80 mesh), at the column temperature of 90 or 120 °C, using nitrogen gas as the carrier. The glc peaks were identified by comparing their retention times with those of authentic samples. The distillable products from I are given in Table 1.

TABLE 1. THE PRODUCTS OBTAINED BY THE PYROLYSIS OF I

Phosphonate	Beginning temp. of decomp. °C	Product (Yield %)
I-a	198—100	$C_6H_5CH=CH_2$ (90.7), CH_3COOEt (80.0)
I-b	195—200	$C_6H_5CH=CH_2$ (92.3), CH_3COOPr (84.3)
I-c	340[a]	
I-d	168—170	$C_6H_5CH=CH_2$ (80.9), CH_3COO–IsoPr(68.7)
I-e	195—198	$CH_3CH=CH_2$[b], CH_3COOEt (80.1)
I-f	195—197	$C_6H_5CH=CH_2$ (31.4), CH_3COOEt (46.3)
I-g	198—200	*t*-$C_6H_5CH=CHCH_3$ (42.5), CH_3COOEt (59.0)
I-h	195—197	$C_6H_5CH=CH_2$ (90.0), C_2H_5COOEt (80.9)

a) boiling point. b) undetermined.

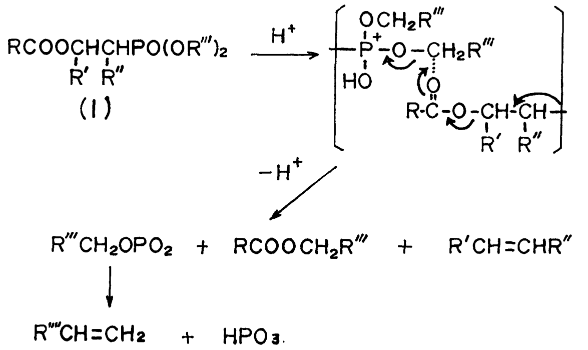
The temperature of the beginning of the decomposition were determined from the TGA curves. In the pyrolysis of those compounds, acetic acid or diethyl α,β-unsaturated phosphonate could not be detected. Ethylene was detected in all cases except I-b, -c, and -d. The analytical values of the pyrolyzed residues of I-a, -b, and -h were approximately in agreement with the $(HPO_3)_n$ formula. The decomposition temperature was affected by the structure of the alkoxy group (R‴O). I-c did not decompose even at 340 °C, its boiling point. I-d began to decompose at 168 °C. When small amounts of phosphoric acid were added, the temperature of the decomposition of I-a fell to 162 °C. The acid effectively catalyzed the initiation of the decomposition. The activation energy of the thermal decomposition of I-a was 33.1±3 kcal/mol, estimated from a TGA curve, on the assumption that the reaction obeyed first-order kinetics;[4] its value hardly changed upon the addition of the acid. The results of the thermal decompositions of II-a, -b, and -c are given in Table 2.

TABLE 2. THE PRODUCTS OBTAINED BY THE PYROLYSIS OF II

Phosphonate	Beginning temp. of decomp. °C	Products (%)
II-a	260—265	$C_6H_5CH=CH_2$ (65)
II-a[a]	235—240	$C_6H_5CH=CH_2$ (91)
II-b	200—205	$C_6H_5CH=CH_2$ (48)
II-c	265—270	$C_6H_5CH_2CH_3$(22.4), C_6H_5 (25.5)

a) H_3PO_4 (5%) was added.

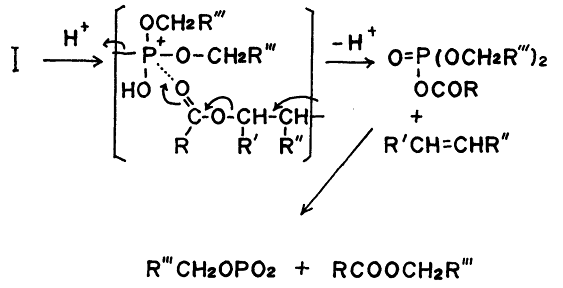
The pyrolysis behavior of II-a, which decomposed at a higher temperature than did I-a or -h, implied that the former is not involved as an intermediate in the thermal decomposition of the latter two. The temperature of the decomposition of II-c was the same as that of I-a, but the yield of styrene from the former was lower than that from the latter. This finding presumably eliminates the possibility of II-c being an intermediate in the pyrolysis of I-a. It was also supported experimentally by the DTA and TGA curves that the pyrolysis did not proceed step by step with the rise in the temperature. The pyrolysis of an equimolar mixture of I-b and -h began at 220 °C to give propyl acetate, ethyl acetate, ethyl propionate, and propyl propionate in the mole ratio of 1.1: 1.0: 1.3: 1.2. When the same mixture was pyrolyzed at 220—230 °C in a 10% solution of paraffinic hydrocarbon (mp 68—70 °C), the alkyl carboxylates mentioned above were given in the mole ratio of 0.9: 1.0: 1.3: 1.0. In the analysis of the phosphonate mixture immediately after the beginning of the decomposition, the ester-exchange between the phosphonates could not be observed. These facts implied that the formation of alkyl carboxylates might involve an intermolecular process. The pyrolysis of I may proceed by means of Scheme 1.



Scheme 1.

The nucleophilic attack of the carbonyl oxygen of the acetoxy group on the methylene carbon of the alkoxy group, followed by the migration of electrons as described in Scheme 1, resulted in the formation of alkyl carboxylate and olefin.

Another possible mechanism (Scheme 2) to account for the formation of those products can be proposed: At first, the nucleophilic attack of carbonyl oxygen occurred on the phosphorus atom and resulted in the formation of acyl dialkyl phosphate, followed by further decomposition in which alkyl carboxylate was given in the manner described above.



Scheme 2.

We found that acetyl diethyl phosphate decomposed to give ethyl acetate in a 70% yield at 170—190 °C.

It was reported that 2-hydroxyphosphonic acid bis(dimethylamide) underwent thermal decomposition to olefin and phosphoric acid bis-amide at reflux in a toluene solution.⁵⁾ In this reaction, it was assumed that the nucleophilic attack of the alkoxy anion on the phosphorus atom and the formation of a four-membered ring transition state were involved.

However, in our experiments, under the same conditions, the analogous transformation of diethyl 2-hydroxy-2-phenylethylphosphonate to olefin and the phosphoric acid diester did not occur, even though trace amounts of phosphoric acid were present, but diethyl α,β-unsaturated phosphonate was obtained in a 60% yield. The difference in behavior may arise from the difference in the electrophilicity of the phosphorus atom. The nucleophilic attack of the carbonyl oxygen of I may preferably occur at the methylene carbon (Scheme 1) rather than at phosphorus (Scheme 2). Scheme 1 resembles that of the pyrolysis of halogenated alkyl phosphates, in which the nucleophilic attack of halogen occurred preferentially at the methylene or methine carbon of an alkoxy group to give alkyl halide in an appreciable yield.⁷⁾

References

1) M. Yamagami, R. Nakao, T. Fukumoto, and J. Tsurugi, *Nippon Kagaku Kaishi*, **1972**, 1991.

2) K. Sasse, "Methoden der Organischen Chemie, XII/1, Organisch Phosphoverbindungen" ed. by E. Müller, Georg Thieme Verlag. Stuttgart (1963), p. 393.

3) J. Michalski and T. Modro, *Chem. Ber.*, **95**, 1629 (1962).

4) E. S. Freeman and B. Carrol, *J. Phys. Chem.*, **62**, 394 (1958).

5) E. J. Corey and G. T. Kwiathowski, *J. Amer. Chem. Soc.*, **90**, 6816 (1968).

6) Y. Okamoto, N. Kimura, and H. Sakurai, This Bulletin, **47**, 1294 (1974).