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The Pyrolysis of Dialkyl α-Acyloxyphosphonates

Yoshiki Okamoto and Hiroshi Sakurai
The Institute of Scientific and Industrial Research, Osaka University, Yamada-kami, Suita-shi, Osaka

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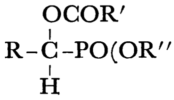
Several dialkyl α-acyloxyalkyl (aralkyl) phosphonates (I) were prepared,[1] and their behavior in pyrolysis was investigated.

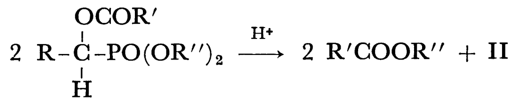


$$\text{R-}\underset{\text{H}}{\overset{\text{OCOR}'}{\text{C}}}\text{-PO(OR}'')_2 \qquad \text{I}$$

I-a,	R = C_6H_5,	R' = CH_3,	R'' = C_2H_5
I-b,	C_6H_5,	CH_3,	C_3H_7
I-c,	C_6H_5,	C_3H_7,	C_2H_5
I-d,	C_3H_7,	C_6H_5,	C_2H_5
I-e,	C_3H_7,	CH_3,	C_2H_5
I-f,	C_6H_5,	CH_3,	CH_3
I-g,	C_2H_5,	CH_3,	CH_3
I-h,	C_6H_5,	CH_3,	$CH(CH_3)_2$

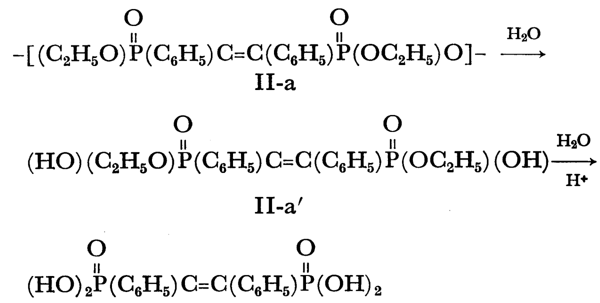
In every run, 0.1 mol of I was pyrolyzed in a distillation flask heated by means of a metal bath. I-a, I-b, I-c, I-d, and I-e decomposed rapidly in the range from about 260 to 280°C, and alkyl carboxylates (R'COOR'') were quantitatively obtained as the sole distillable product (>97% pure by glc).

The pyrolysis was over in a few minutes. However, I-f and I-g were stable at this temperature. I-f and I-g began to decompose at 320°C and gave a mixture of methyl acetate, acetic acid, methyl alcohol, and benzaldehyde or propionaldehyde. In the presence of a catalytic amount of phosphoric acid, the temperature of the beginning of decomposition of I-f fell to 260°C and only methyl acetate was obtained. I-h decomposed at 190°C, and propylene, benzaldehyde, and acetic acid were obtained. When the pyrolysis of an equimolar mixture of I-b and I-c was performed, propyl acetate, ethyl acetate, ethyl butyrate, and propyl butyrate were obtained in the mole ratio 1.1: 1.0: 1.2: 1.1, as was determined by glc analysis. When a mixture of propyl acetate and ethyl butyrate was refluxed for 10 min in the presence of a small amount of phosphoric acid, interesterification did not occur. These results indicate that the formation of alkyl carboxylate from I is catalyzed by acid and proceeds by means of an intermolecular mechanism:



$$2\ \text{R-}\underset{\text{H}}{\overset{\text{OCOR}'}{\text{C}}}\text{-PO(OR}'')_2 \xrightarrow{\text{H}^+} 2\ \text{R}'\text{COOR}'' + \text{II}$$

The structure of the undistillable product (II-a) obtained by the pyrolysis of I-a was identified from the following findings. II-a was a resin-like and hygroscopic solid, softening at 140—150°C. It was dissolved in water, and a small amount of an insoluble, oily matter was removed. When the solution was acidified with hydrochloric acid, a viscous matter was precipitated; this matter was separated and dried in a vacuum (yield, 98%), (II-a') mp 135—140°C. Found: C, 54.21; H, 5.54; P, 15.52%. Calcd for $C_{18}H_{22}O_6P_2$: C, 53.92; H, 5.59; P, 15.63%. UV λ_{max} 260 mμ, 11400 (in water). II-a' was refluxed with 6N hydrochloric acid for 24 hr. The hydrolyzed product: mp 142—145°C. Found: C, 47.06; H, 5.18; P, 18.08%. Calcd for $C_{14}H_{14}O_6P_2$: C, 49.42; H, 4.18; P, 18.20%. Acid value, 549 (Calcd for $C_{14}H_{14}O_6P_2$, tetrabasic acid 564). When treated with bromine water, II-a' gave a quantitative yield of the bromide, which was then recrystallized from ether; mp 159—160°C. Found: C, 39.75; H, 4.33; Br, 30.82%. Calcd for $C_{18}H_{22}O_6Br_2P_2$: C, 38.87; H, 4.28; Br, 29.93%. The methyl ester of II-a', esterified with diazomethane, MW: 435.5 (Cryscopic in benzene). Calcd for $C_{20}H_{26}O_6P_2$: 424.4. NMR τ(CCl_4) 8.8 (6H, t), 6.2—6.6 (10H, m), 2.72 (10H, s).



$$\underset{\text{II-a}}{\text{-[}(C_2H_5O)\overset{\text{O}}{\overset{\|}{\text{P}}}(C_6H_5)C{=}C(C_6H_5)\overset{\text{O}}{\overset{\|}{\text{P}}}(OC_2H_5)O\text{]-}} \xrightarrow{H_2O}$$

$$\underset{\text{II-a}'}{(HO)(C_2H_5O)\overset{\text{O}}{\overset{\|}{\text{P}}}(C_6H_5)C{=}C(C_6H_5)\overset{\text{O}}{\overset{\|}{\text{P}}}(OC_2H_5)(OH)} \xrightarrow[H^+]{H_2O}$$

$$(HO)_2\overset{\text{O}}{\overset{\|}{\text{P}}}(C_6H_5)C{=}C(C_6H_5)\overset{\text{O}}{\overset{\|}{\text{P}}}(OH)_2$$

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[1] M. S. Kharasch, R. A. Mosher, and I. S. Bengelsdorf, *J. Org. Chem.*, **25**, 1000 (1960).