Chemistry

1963

SovietRxiv

Abstract

Full Text

Chemistry

A. N. Pudovik, I. V. Konovalova

Synthesis of Styrene and Its Homologs by Pyrolysis of Phosphates

(Presented by Academician B. A. Arbuzov, 27 XII 1962)

In earlier studies ([1–3]) we showed that the products of addition of dialkylphosphorous acids to acetophenone and to ethyl pyruvate—methyldiphosphoncarbinols and esters of oxymethyl-dialkylphosphonoacetic acid—undergo rearrangements on heating into the corresponding esters of phosphoric acid.

In further development of these investigations we obtained reactions of dialkylphosphorous acids with acetophenone and its alkyl derivatives: propiophenone, butyrophenone, and isovalerophenone, as well as with *p*-ethylacetophenone. Dimethyl-, diethyl-, diisopropyl-, di-*n*-propyl-, and di-*n*-butylphosphorous acids were used as the dialkylphosphorous acids. The reactions were carried out in the presence of saturated alcoholic solutions of sodium alcoholates. Upon addition of sodium alcoholate to an equimolar mixture of the ketone and dialkylphosphorous acid, an increase in the temperature of the mixture to 28–50° was observed. The reactivity of the ketones in the addition reaction decreased in the order from acetophenone to isovalerophenone. To complete the reaction, the reaction mixtures were heated for 1.5–2 hr at 100°; the reaction products were isolated by distillation in vacuo. Their examination showed that

Table 1

α-Phenylalkyldialkyl esters of phosphoric acid

$$C_6H_5 - \underset{\displaystyle R}{\underset{|}{C}}H - \underset{\displaystyle O}{\overset{\|}{O}}P(OR')_2$$

No.	R	R′	Yield, %	Empirical formula	Boiling point, °C/mm Hg	n_D^{20}	d_4^{20}	MR_D found	MR_D calculated	Phosphorus found, %	Phosphorus calculated, %
1	CH_3	C_2H_5	60	$C_{12}H_{19}O_4P$	150/3.5	1.4770	1.1051	65.95	66.00	11.61	12.01
2	C_2H_5	C_2H_5	77	$C_{13}H_{21}O_4P$	141.5/3	1.4769	1.0880	70.63	70.62	11.33	11.39
3	C_3H_7	C_2H_5	52	$C_{14}H_{23}O_4P$	148/3	1.4771	1.0692	75.58	75.23	10.82	10.84
4	iso-C_4H_9	C_2H_5	52	$C_{15}H_{25}O_4P$	155/3.5	1.4763	1.0543	80.26	79.85	10.29	10.33
5	CH_3	n-C_3H_7	40	$C_{14}H_{23}O_4P$	156.5–157/3.5	1.4779	1.0801	74.96	75.23	10.34	10.84
6	CH_3	iso-C_3H_7	45	$C_{14}H_{23}O_4P$	141.5/3	1.4732	1.0740	74.91	75.23	10.59	10.84
7	CH_3	n-C_4H_9	57	$C_{16}H_{27}O_4P$	163–164/4	1.4756	1.0531	84.09	84.47	9.6	9.8

they contain no hydroxyl group. In the infrared spectrum there is no absorption in the region 3200–3300 cm^{-1}. On this basis, the reaction products were assigned the structure of α-phenylalkyldialkyl esters of phosphoric acid (II). The formation of (II) proceeds in accordance with the following reaction scheme:

$$C_6H_5COR + (R'O)_2POH \xrightarrow{R'ONa} \underset{\text{(I)}}{\begin{matrix} OH \\ C_6H_5C{-}R \\ P(OR')_2 \\ \| \\ O \end{matrix}} \longrightarrow \underset{\text{(II)}}{C_6H_5CH{-}OP(OR')_2}$$

The esters of α-hydroxy-α-phenylalkylphosphinic acids (I) formed in the first stage undergo rearrangement into the corresponding esters of phosphoric acid (II). Phosphates (II) are liquids, readily soluble in organic solvents and sparingly soluble in water. Their characteristics are given in Table 1. The fluctuating, and in some cases low, yield of phosphates (40–77%) is explained by their partial pyrolysis during isolation by distillation, as is discussed in detail below.

Table 2

Dialkyl esters of α-hydroxy-α-phenylalkylphosphinic acids

$$R''C_6H_4C(R)(OH)-P(O)(OR')_2$$

No.	R	R′	R″	Yield, %	M.p., °C	Empirical formula	Phosphorus content, %, found	Phosphorus content, %, calculated
1	CH_3	C_2H_5	H	80	72–73	$C_{12}H_{19}O_4P$	12.10	12.01
2	C_2H_5	C_2H_5	H	84	65–67	$C_{13}H_{21}O_4P$	11.39	11.39
3	C_3H_7	C_2H_5	H	83	67–68	$C_{14}H_{23}O_4P$	11.09	10.84
4	C_2H_5	CH_3	H	92	139.5–140	$C_{11}H_{17}O_4P$	12.67	12.70
5	C_3H_7	CH_3	H	77	127.5–128	$C_{12}H_{19}O_4P$	12.03	12.01
6	iso-C_4H_9	CH_3	H	82	131–131.5	$C_{13}H_{21}O_4P$	11.46	11.39
7	CH_3	n-C_3H_7	H	80	59–59.5	$C_{14}H_{23}O_4P$	10.64	10.84
8	CH_3	iso-C_3H_7	H	79	58–58.5	$C_{14}H_{23}O_4P$	10.75	10.84
9	CH_3	CH_3	C_2H_5	81	139–140	$C_{12}H_{19}O_4P$	11.99	12.01
10	CH_3	C_2H_5	C_2H_5	83	65–66	$C_{14}H_{23}O_4P$	10.59	10.84

Esters of α-hydroxy-α-phenylalkylphosphinic acids (I) were obtained by carrying out the addition reaction under mild conditions, at a temperature not exceeding 50°. These are crystalline substances, poorly soluble in water and soluble in organic solvents. Their purification was carried out by recrystallization from benzene. Their characteristics are given in Table 2. The structure of (I) was confirmed by spectral data. In the IR spectrum of (I) there is a broad intense absorption band in the region of 3290 cm^{-1}. Thus, we have shown that esters of α-hydroxy-β-phenylalkylphosphinic acids, in the presence of sodium alcoholate at elevated temperature, rearrange into the corresponding phosphates. When these reactions are carried out carefully, the course of both phases can readily

be observed. Upon gradual addition of sodium alcoholate to a mixture of ketone and acid, the temperature of the reaction mixture rises to 40–50° in the case of the most active ketones; further addition of the alcoholate does not cause it to rise. From this mixture, on cooling, crystalline hydroxyphosphinic esters are readily isolated. If the mixture is not cooled, then after standing for 10–15 min a strongly exothermic reaction is observed; the temperature of the reaction mixture rises to 120–130°, and on distillation a phosphate is obtained.

The addition of dialkylphosphorous acids to acetophenone has been described previously ([4], [5]). In the case of dimethylphosphorous acid, the authors obtained a crystalline addition product, and in the case of diethyl- and dibutylphosphorous acids, liquid products. All of these, without any evidence, were assigned the structure of dialkyl esters of α-hydroxy-α-phenylethylphosphinic acids. In light of the investigations we have carried out, it is evident that the products described in ([4], [5]) from the reaction of diethyl- and dibutylphosphorous acids with acetophenone are not hydroxyphosphinic esters, but phosphates.

In addition to esters of phosphoric acid, low-boiling fractions were isolated in various experiments and in various amounts; these proved to be unsaturated hydrocarbons—styrene and its derivatives. The formation

these compounds is explained by pyrolysis of the phosphates, which already takes place during their distillation.

$$RC_6H_4CHCH_2R'' \longrightarrow RC_6H_4CH{=}CH{-}R'' + HOP(=O)(OR')_2$$

$$OP(=O)(OR')_2$$

With an increase in the distillation temperature to 150–160° and at a residual pressure of 10–15 mm Hg, styrene and its homologs are formed in high yields. After completion of the pyrolysis, viscous liquids remain, evidently dialkylphosphoric acids. The characteristics of the unsaturated hydrocarbons obtained are given in Table 3.

Table 3

Alkyl-substituted styrenes $R{-}C_6H_4{-}CH{=}CH{-}R'$

No.	R	R′	Empirical formula	B.p., °C/mm Hg	n_D^{20}	d_4^{20}	Yield, %
1*	H	H	C_8H_8	59/40	1.5465	0.9062	85
2**	H	CH_3	C_9H_{11}	70/14	1.5440	0.9141	88
3	H	C_2H_5	$C_{10}H_{13}$	89–90/23	1.5320	0.9096	77

Fig. 1. IR absorption spectra: I –diethyl ester of α-oxy-α-phenylethylphosphinic acid; II –α-phenylethyldiethyl ester of phosphoric acid

Figure 1: Fig. 1. IR absorption spectra: I –diethyl ester of α-oxy-α-phenylethylphosphinic acid; II –α-phenylethyldiethyl ester of phosphoric acid

No.	R	R′	Empirical formula	B.p., °C/mm Hg	n_D^{20}	d_4^{20}	Yield, %
4	H	iso-C_3H_7	$C_{11}H_{15}$	96-97/15	1.5158	0.9048	86
5	C_2H_5	H	$C_{10}H_{13}$	67-68/9	1.5340	0.8997	68

* B.p. 146°, n_D^{20} 1.5468, d_4^{20} 0.9060 (literature data ([9])).

** B.p. 176°, n_D^{20} 1.5490, d_4^{20} 0.9141.

The literature contains data on the pyrolysis of phosphates having aliphatic radicals. It proceeds at 300° with the formation of olefins ([6]).

Fig. 1. IR absorption spectra: *I* –diethyl ester of α-oxy-α-phenylethylphosphinic acid; *II* –α-phenylethyldiethyl ester of phosphoric acid.

The preparation of acrylonitrile has also been described: in this case pyrolysis was carried out at 820° and a residual pressure of 3-4 mm Hg ([7,8]). The preparation of styrene and its derivatives in our case can readily be carried out in one phase, at considerably lower temperatures, which makes this method very simple and convenient from the preparative standpoint. By analogy

with the pyrolysis of acetones and sulfites, the pyrolysis of α-phenylalkyldialkyl esters of phosphoric acid may be represented as proceeding through a six-membered cyclic electronic complex.

$$\begin{array}{c} C_6H_5{-}CH \\ | \\ R{-}CH \end{array} \left(\begin{array}{c} O \\ P(OR')_2 \\ O \end{array} \right) \longrightarrow \begin{array}{c} C_6H_5{-}CH \\ \| \\ R{-}CH \end{array} + (R'O)_2POH$$

Experimental Part

1. Preparation of α-phenylalkyldialkyl phosphates. To an equimolecular mixture of dialkylphosphorous acid and acetophenone or its homolog, a saturated alcoholic solution of sodium alcoholate was added. The reaction mixtures were heated for 2 hr at 110°, after which they were distilled under vacuum at a residual pressure not exceeding 5 mm Hg (Table 1).

2. Preparation of esters of α-phenyl-α-oxyalkylphosphonic acids. To an equimolecular mixture of phenyl alkyl ketone and dialkylphosphorous acid, a saturated alcoholic solution of sodium alcoholate was gradually added. The temperature of the reaction mixtures rose in different experiments to 28–50°, after which they were cooled to room temperature. The precipitated crystals of the α-phenyl-α-oxyalkylphosphonic esters were recrystallized from benzene (Table 2).

3. Pyrolysis of α-phenylalkyldialkyl phosphates. The phosphates were heated at 150–160° for 1–1.5 hr at a residual pressure of 15 mm. Styrene or its homologs were thereby slowly distilled into the receiver.

4. Preparation of styrene and its homologs in one stage. To an equimolecular mixture of diethylphosphorous acid and acetophenone or its derivative, a saturated solution of sodium ethylate was added, after which the reaction mixture was heated at 100° for two hours. Distillation of the reaction mixtures was carried out at a residual pressure of not less than 15 mm Hg. The yield of styrene and its homologs was 85–90%, calculated on the fatty-aromatic ketone taken into the reaction. The characteristics of styrene and its homologs obtained by this method are given in Table 3.

Kazan State University
named after V. I. Ulyanov-Lenin

Received
18 XII 1962

References

1. A. N. Pudovik, I. V. Konovalova, ZhOKh, **32**, 467 (1962).
2. A. N. Pudovik, I. V. Konovalov, DAN, **143**, 875 (1962).
3. A. N. Pudovik, I. V. Konovalova, L. V. Dedova, ZhOKh, **33**, No. 2 (1963).
4. V. S. Abramov, ZhOKh, **22**, 647 (1952).
5. V. S. Abramov, R. V. Dmitrieva, A. S. Kapustina, ZhOKh, **23**, 257 (1953).
6. H. E. Baumgarten, R. A. Setterquist, J. Am. Chem. Soc., **79**, 2605 (1957).
7. L. A. R. Hall, C. W. Stephens, J. Am. Chem. Soc., **78**, 2565 (1956).
8. L. A. R. Hall, C. W. Stephens, J. J. Drysdall, J. Am. Chem. Soc., **79**, 1768 (1957).
9. A. E. Chichibabin, *Fundamental Principles of Organic Chemistry*, 2, Moscow, 1957, p. 401.

Note: Figure translations are in progress. See original paper for figures.

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.