THERMAL REARRANGEMENT OF DIALKYL (3-KETOBUTYL)PHOSPHITES

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We have reported the synthesis and certain properties of dialkyl (3-ketobutyl)phosphites obtained by reaction of dialkyl chlorophosphites with β-ketoalcohols in the presence of base [1]. Continuing the study of the properties of these phosphites, we found that upon heating to 160-200°C for 5-10 h, they rearrange to esters of γ-ketophosphonic acids (by an Arbuzov-type rearrangement).

$$(RO)_2POCH_2CH_2\underset{\underset{O}{\|}}{C}CH_3 \xrightarrow{t^\circ} (RO)_2\underset{\underset{O}{\|}}{P}CH_2CH_2\underset{\underset{O}{\|}}{C}CH_3$$

Absorption bands of P=O at 1250 cm^{-1} and of C=O at 1720 cm^{-1} are observed in the IR spectrum of the rearrangement products. We heated 7.6 g of diethyl (3-ketobutyl)phosphite for 9 h in a sealed ampule in an atmosphere of nitrogen at 160°C. No pressure was observed upon opening the ampule. Fractionation of the contents of the ampule yielded 5.2 g (68%) of diethyl (γ-ketobutyl)phosphonate having bp 75-78° (0.02 mm); n_D^{20} 1.4388; d_4^{20} 1.0901. Found %: C 46.30; H 8.15; P 14.70. MR 50.21. $C_8H_{17}O_4P$. Calculated %: C 46.15; H 8.23; P 14.87. MR 50.02. Literature data [2]: 105-107° (0.3 mm); n_D^{25} 1.4353.

Analogously, 5 g of dibutyl (3-ketobutyl)phosphite was heated for 7.5 h at 190°. We isolated 3.1 g (62%) of dibutyl (γ-ketobutyl)phosphonate having bp 110-112° (0.05 mm); n_D^{20} 1.4420; d_4^{20} 1.0168. Found %: C 54.42; H 9.61; P 11.56. MR 68.75. $C_{12}H_{25}O_4P$. Calculated %: C 54.54; H 9.46; P 11.74. MR 68.49.

LITERATURE CITED

1. N. I. Rizpolozhenskii and F. S. Mukhametov, Izv. AN SSSR, Ser. Khim., No. 12 (1968).
2. T. C. Myers, R. G. Harvey, and E. V. Jensen, J. Am. Chem. Soc., 77, 3101 (1955).

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