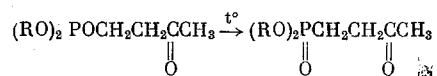


THERMAL REARRANGEMENT OF DIALKYL (3-KETOBUTYL)PHOSPHITES

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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).



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).