REACTION OF ETHYL THIODICHLOROPHOSPHITE WITH BENZALDEHYDE AND ACETONE

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UDC 542.91:547.1'118

The reactions of acid chlorides derived from P(III) acids with carbonyl compounds, as a rule, proceed with the involvement of the P—Cl bond and lead to the formation of α-chlorophosphonic derivatives or the products of their dehydrochlorination [1]. In contrast to this behavior, ethyl thiodichlorophosphite (I) reacts with benzaldehyde (IIa) and acetone (IIb) to form α-ethylthioalkyl dichlorophosphonates (III), i.e., with the participation of the P—S bond and retention of the P—Cl bonds:

$$\underset{(I)}{Cl_2PSEt} + \underset{(II)}{RR'C(O)} \rightarrow \underset{(III)}{Cl_2P(O)C(SEt)RR'}$$

R = H, R′ = Ph (a); R = R′ = Me (b).

The IR spectra of (III) have bands at 532-500, 550-570 (P—Cl), 659 (S—Et), and 1263-1275 cm^{-1} (P=O). Hydrogen chloride accelerates the formation of (III).

Equimolar mixtures of (I) with (IIa) or (IIb) were maintained in sealed ampuls at about 20°C for 2 or 5 days, respectively. In the case of (IIa), the reaction mixture was subjected to molecular distillation (130-140°C (0.008 mm) spiral temperature) with subsequent purification of (IIIa) by vacuum distillation.

α-Ethylthiobenzyl dichlorophosphonate was obtained in 29.7% yield, bp 123-124°C (0.007 mm), d_4^{20} 1.2721, n_D^{20} 1.5794. PMR spectrum (60 MHz, CCl_4 from TMS, δ, ppm, J, Hz) 1.25 t (CH_3CS, $^3J_{HH}$ = 7.5), 2.14 d.q (CH_2S, $^3J_{HH}$ = 7.5, $^4J_{HP}$ = 3.0), 4.55 d (PCH, $^2J_{HH}$ = 13.0), 7.15-7.56 m (C_6H_5). ^{31}P NMR spectrum (10.2 MHz, from 85% H_3PO_4, δ, ppm) Found: C, 39.93; H, 4.18; Cl, 26.24; P, 11.62; S, 12.15%. $C_9H_{11}Cl_2OPS$. Calculated: C, 40.17; H, 4.12; Cl, 26.35; P, 11.51; S, 11.91%.

α-Ethylthio-α-methylethyl dichlorophosphonate (IIIb) was obtained in 22.6% yield, bp 118-119°C (10 mm), d_4^{20} 1.2318, n_D^{20} 1.5244. PMR spectrum (CCl_4, δ, ppm, J, Hz) 1.25 t (CH_3CS, $^3J_{HH}$ = 7.5), 1.64 d (CH_3CP, $^3J_{HP}$ = 24.0), 2.22 d.q (CH_2S, $^3J_{HH}$ = 7.5, $^4J_{HP}$ = 3.0). δP 56 ppm. Found: C, 27.24; H, 5.06; Cl, 32.30; P, 14.24; S, 14.62%. $C_5H_{11}Cl_2OPS$: Calculated: C, 27.15; H, 4.98; Cl, 32.13; P, 14.03; S, 14.48%.

The fractionation of (III) is accompanied by considerable tar formation, resulting in relatively low yields of these products.

LITERATURE CITED

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A. E. Arbuzov Institute of Organic and Physical Chemistry, Kazan Branch, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 10, pp. 2413-2414, October, 1985. Original article submitted June 13, 1985.

0568-5230/85/3410-2237$09.50