

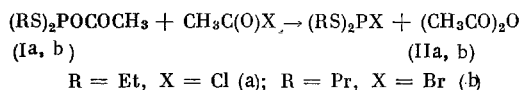
UNUSUAL ACTION OF CARBOXYLIC ACID HALIDES ON DIALKYLACETYLDITHIOPHOSPHITES

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UDC 542.91:547.1'118

It is known that O,O-dialkylacetylphosphites react with carboxylic acid halides according to the Arbuzov reaction scheme to give ketophosphonates [1, 2].

We found that, in contrast, S,S-dialkylacetyldithiophosphites (Ia, b) react with acyl halides with the substitution of the acetoxy group for the halogen atom, giving the corresponding dithiophosphorous acid halide and acetic anhydride.



In an Arbuzov flask, 2.9 g of (Ia) and 1.07 g of acetyl chloride were mixed. The mixture was left to stand for 30 min at $\sim 20^\circ\text{C}$. Distillation gave 1.87 g (72%) of (IIa), bp $52-53^\circ\text{C}$ (0.02 mm), n_D^{20} 1.5792, δP 188 ppm (cf. [3]). Distillation of the liquid condensed in a liquid nitrogen trap gave 1.26 g (89%) of acetic anhydride, bp 137°C , n_D^{20} 1.3903, which corresponds to the data in [4].

The reaction of (Ib) with acetyl bromide was carried out similarly. From 4.55 g of (Ib) and 2.33 g of acetyl bromide, 1.6 g (8.2%) of acetic anhydride, bp $138-139^\circ\text{C}$, n_D^{20} 1.4009, and 3.45 g (69%) of (IIb), bp $74-75^\circ\text{C}$ (0.02 mm), n_D^{20} 1.5836, δP 198 ppm, were obtained. Found: Br 30.37; P 11.62%. $\text{C}_6\text{H}_{14}\text{BrPS}_2$. Calculated: Br 30.65; P 11.88%.

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