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INTERACTION OF DIALKYL TRIMETHYLSILYL PHOSPHITES WITH CARBON TETRACHLORIDE

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Trialkyl phosphites interact with CCl_4 to form the corresponding dialkyl trichloromethyl phosphonates [1]. These reactions begin with nucleophilic attack by the phosphorus atom on a chlorine atom of the CCl_4 [2, 3] and proceed through the formation of a quasiphosphonium compound containing the trichloromethyl anion as the counterion. It is also known that in reactions of dialkyl trimethylsilyl phosphites with electrophilic reagents, the stage of desilation of the intermediate product proceeds very rapidly [4]. We have investigated reactions of dialkyl trimethylsilyl phosphites with CCl_4 , emphasizing particularly the properties of the quasiphosphonium compounds, which carry alkoxyl and trimethylsiloxyl groups simultaneously on the phosphorus atom, and which contain the trichloromethyl anion as the counterion.

In these studies we found that diethyl trimethylsilyl phosphite (I) interacts with CCl_4 to form diethyl chlorophosphate (II), diethyl trichloromethyl phosphonate (III), trimethyl chlorosilane (IV), trimethyltrichloromethyl silane (V), dimethylmethylenesilane (VI) in the form of the dimer, and chloroform (VII)

In the reaction of the phosphite (I) with CCl_4 , the intermediate quasiphosphonium compound, in which the phosphorus atom carries simultaneously the ethoxysilyl and trimethylsiloxyl groups and the trichloromethyl anion, is desilylated to form the phosphate (II), the silane (V) (direction 1, i.e., S_N2 -desilylation), or to form the phosphate (II), chloroform, and the silane (VI) (direction 2, apparently an E2 reaction); the intermediate may also enter into an anion exchange reaction to form a new quasiphosphonium compound containing the chlorine anion as the counterion (direction 3). The new intermediate decomposed to form the phosphonate (III) and the silane (IV).



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The reactions of the dimethyl (VIII) and dipropyl trimethylsilyl phosphite (IX) with CCl_4 proceed analogously. As the size of the alkyl group is reduced in the series Pr > Et > Me, the decrease in steric shielding apparently results in a greater tendency for the reaction to go in the direction of higher yields of products formed through anion exchange in the intermediate product. The ratio of yields of dialkyl chlorophosphates to dialkyl trichloromethylphosphonates in this series changes as follows: 1:4.80, 1:3.03, 1:1.63.

EXPERIMENTAL

The GLC was carried out in a Khrom-41 chromatograph with a flame ionization detector and a heatresistant glass column (2 m) packed with 10% polyethylene glycol adipate on Tsvetokhrom 1K DMDKhS (0.250-0.315 mm), column temperature 140°, vaporizer 160°C.

Reaction of Diethyl Trimethylsilyl Phosphite with CCl_4 . To 59.6 g (0.28 mole) of the phosphite (I), 43.7 g (0.28 mole) of CCl_4 was added, and the mixture was stirred for 3 h at 45-55°. The low-boiling product was distilled off in the interval 50-70°. Upon heating the reaction mixture to 100° for 10-15 min with a reflux condenser 7.2 g (13.2%) of crystals of the silane (V), mp 47°, precipitated in the condenser. Found: C 25.48; H 4.89; Cl 55.82; Si 14.60%. C₄H₉Cl₃Si. Calculated: C 25.06; H 4.70; Cl 55.61; Si 14.62%.

GLC of the low-boiling products gave the silane (IV) (30.86%), chloroform (3.71%), and the dimer of the silane (VI). In the IR spectrum of the mixture there were absorption bands at 693, 870, and 935 cm⁻¹, characteristic for 1,1,3,3-tetramethyl-1,3-disilacyclobutane, i.e., the dimer of the silane (VI) [5]. According to the reaction scheme, the yield of the dimer of the silane (VI) should be half the yield of chloroform.

Distillation of the still residue gave 9.7 g (19.7%) of the phosphate (II), bp 80.5-82° (9 mm), n_D^{20} 1.4170, d_4^{20} 1.1919 [6]; and 38.3 g (59.7%) of the phosphonate (III), bp 121-123° (10 mm), n_D^{20} 1.4601, d_4^{20} 1.3658 [7].

In the reaction of the phosphites (VIII) and (IX) with CCl_4 under analogous conditions, the products recovered in the first case were dimethyl chlorophosphate (10.2%) and dimethyl trichloromethyl phosphonate (49.1%), and in the second case, dipropyl chlorophosphate (30.8%) and dipropyl trichloromethylphosphonate (50.5%).

CONCLUSIONS

In the interaction of dialkyl trimethylsilyl phosphites with carbon tetrachloride, the products that are formed are a dialkyl chlorophosphate, a dialkyl trichloromethylphosphonate, trimethylchlorosilane, trimethyltrichloromethylsilane, dimethylmethylenesilane, and chloroform.

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