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(*N*-Benzoyl)trichloroacetimidoylphosphonate

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A method for the synthesis of *O,O*-diethyl (*N*-benzoyl)trichloroacetimidoylphosphonate (**1**) by successive reaction of *N*-(1-diethoxyphosphoryl-2,2-dichlorovinyl)benzamide with Me_3SiCl and Cl_2 was proposed. The reaction of phosphonate **1** with R_3P follows the [4+1] cycloaddition mechanism to give phosphoranes, whose stability and further transformations are controlled by the nature of R.

Key words: acyl imines, imidoylphosphonates, cycloaddition, phosphoranes.

The first representatives of compounds containing the C-phosphorylated azomethine group were synthesized by M. I. Kabachnik *et al.* in 1945.[1] Important among those compounds are imidoylphosphonates, whose electron-withdrawing phosphoryl group predetermines their higher reactivity compared to ordinary azomethines.

Most of the known methods for the synthesis of imidoylphosphonates consist in nucleophilic replacement of the Cl atom of imidoyl chlorides under the action of trialkyl phosphites.[2] However, this method cannot be used for the synthesis of trichloroacetimidoylphosphonates because the reaction of phosphites with trichloroacetimidoyl chlorides involves the Cl atoms of the trichloromethyl group.[3]

Similarly to the earlier published procedure,[4] we attempted to obtain (*N*-benzoyl)trichloroacetimidoylphosphonate **1** from the known phosphonate **2** under the action of the complex of chlorine with pyridine. However, it turned out that the reaction was not completed under these conditions even with prolonged stirring (5 h) and a two-fold excess of chlorinating agent, which may be due to its instability and low rate of chlorination. The reaction is completed only when additional portions of freshly prepared complex are added from time to time, but its course is ambiguous and its reproducibility low.

We elaborated a more convenient method for the synthesis of imidoylphosphonate **1**, based on available[5] dichlorophosphonate **3**. Essentially, this method includes mild chlorination (Cl_2, benzene, 20—25 °C) of a silyl derivative of this compound, existing as a mixture of *N*- and *O*-isomers (δ^1P 8.0, δ^2P 8.7, $\delta^1 : \delta^2 = 6 : 1$), with subsequent elimination of Me_3SiCl. Unlike this, nonsilylated amide **3** cannot be chlorinated with chlorine even under more drastic conditions (heating, UV irradiation). Silyl derivative **4** is thermally unstable. When distilled (160—168 °C, 0.05 Torr), it is partially (up to 30%) converted into the known[6] oxazaphospholine **5** (δP = 19.96), which was isolated in the individual state (Scheme 1).

The thermal instability of compound **4** does not prevent the formation of phosphonate **1** because the

* Dedicated to the memory of Academician M. I. Kabachnik on his 90th birthday.

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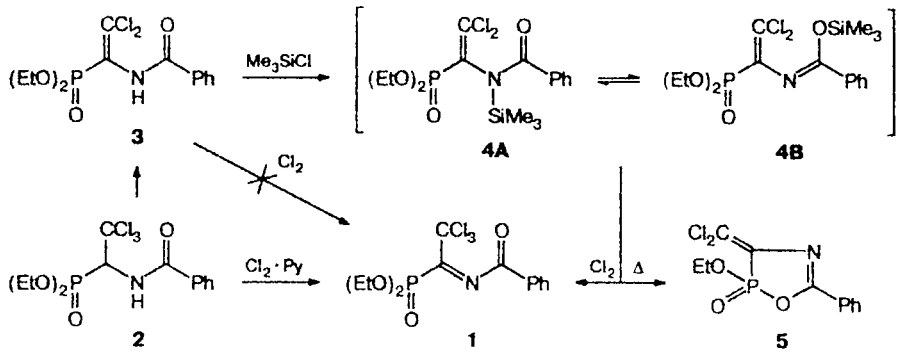
Scheme 1

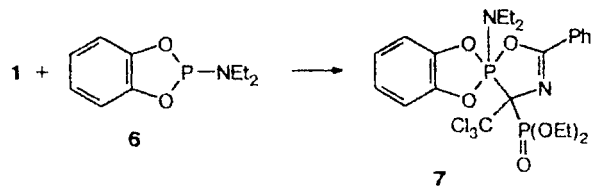


chlorination of a crude silylation product leads, according to ^{31}P NMR spectroscopy data, to its transformation into **1** in quantitative yield.

Imidoylphosphonate **1** was purified by distillation *in vacuo*. Its composition and structure were confirmed by analytical and spectral data. In particular, characteristic are the chemical shift of the phosphorus nuclei ($\delta P = -2.1$), typical of trihaloacetimidoylphosphonates, and the appearance of the stretching vibrations of the C=N and C=O bonds (1680 and 1710 cm^{-1}) in the IR spectra. Phosphonate **1** is highly reactive with respect to various nucleophiles. For example, when diluted in moist benzene or exposed to air, it is hydrolyzed with cleavage of the C—P bond.

$$1 + H_2O \longrightarrow (EtO)_2P(O)H + CCl_3CONHCOPh$$

The reaction of imidoylphosphonate **1** possessing a system of heterodiene bonds with phosphorus nucleophiles substantially depends on the nature of the phosphorus reagent. Thus, its reaction with cyclic amidophosphite **6** follows the mechanism of [4+1] cycloaddition to give stable spirophosphorane **7** containing tetra- and pentacoordinated P atoms at the same C atom. Compound **7** contains two chiral centers, *viz.*, the C and P atoms, that is why the diastereotopic OEt and NEt groups and the protons of one of the NCH_2 groups are not equivalent magnetically. In the ^1H NMR spectrum, a difference in the chemical shifts for the protons of the NCH_2 group reaches δ 0.42 (see Experimental). Such a large difference may be due to unequal positions of these protons in relation to the aromatic ring.



The reaction with acyclic P^{III} derivatives also yields [4+1] cycloaddition products, *viz.*, unstable monocyclic phosphoranes **8a—c**, which were detected only by NMR spectrometry. Even at room temperature, they undergo transformations resulting in the opening of the oxazaphospholine ring. The nature of the phosphorus reagent controls both the rate of formation of **8** and the direction of their decomposition. Thus, phosphorane **8a** (δP^V −33.1, δP^{IV} +13.0) is the main component (~90%) of the reaction mixture 1 h after the reaction starts (benzene, 20 °C). One day later, the signals of the phosphorane in the ^{31}P NMR spectra disappear. Instead, two equally intense signals corresponding to bisphosphorylated enamine **9** [δP −2.9 (NP) and +8.3 (CP)] and azadiene **10** [δP 0.05 (OP) and +6.2 (CP)] (**9** : **10** ≈ 0.7 : 1) are observed, both compounds resulting from dealkylation at the pentacoordinated P atom (Scheme 2).

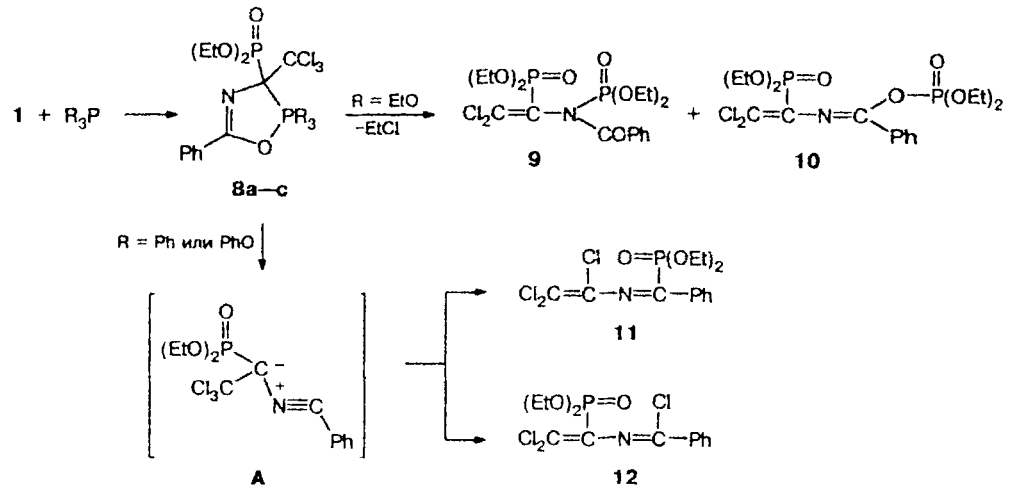
The dealkylation is impossible in the case of phosphoranes **8b,c**, and their decomposition occurs by elimination of R_3PO. Azadienes **11** (δP 5.1) and **12** (δP 8.9) are likely formed as a result of phosphorotropic or chlorotropic migration in the intermediate nitrilium ilide **A**. Phosphoranes **8b** (δP^V −41.7, δP^{IV} +14.8) and **8c** (δP^V −42.5, δP^{IV} +12.9) were detected in the reaction mixture only as minor components. Thus, 1.5 h after mixing of compound **1** with Ph_3P, the ratio **8b** : **11** : **12** was 1 : 2.6 : 2; 12 h after, the signals for **8b** disappear. Phosphonate **1** reacts with $(PhO)_3P$ similarly, but the formation and decomposition of phosphorane **8c** occurs at room temperature very slowly (over months). Compounds **9—12** were identified by reference of their spectra to the literature data.[4,7]

Thus, characteristic of imidoylphosphonate **1** are reactions at the 1,3-heterodiene system both involving and not the CCl_3 group. It is significant that the behavior of compound **1** in the reactions with phosphorus nucleophiles substantially differs from that of both (*N*-benzoyl)trifluoroacetimidoylphosphonate[8] and (*N*-formyl)- [4] or (*N*-phosphoryl)trichloroacetimidoylphosphonates,[9] all containing substituents at the C and N atoms of the C=N bond, close in electronic configuration.

Experimental

^1H and ^{31}P NMR spectra were recorded on a Varian VXR-300 spectrometer (299.95 and 121.42 MHz, respectively). Chemical shifts are given with respect to tetramethylsilane as

Scheme 2



R = EtO (**a**), Ph (**b**), PhO (**c**)

the internal standard (^{1}H) and 85% H_3PO_4 as the external standard (^{31}P). IR spectra were recorded on a UR-20 instrument (KBr pellets or in thin film).

O,O*-Diethyl (*N*-benzoyl)trichloroacetimidoylphosphonate (1).** ***A. A solution of Me_3SiCl (12 mmol) in 15 mL of benzene was added dropwise with stirring to a solution of phosphonate **3** (10 mmol) in 45 mL of benzene and triethylamine (12 mmol). Stirring was continued at 25 °C for 5 h, whereupon the triethylammonium chloride was filtered off. A solution of chlorine (12 mmol) in benzene was added dropwise with stirring to the filtrate. The reaction mixture was kept at 25 °C for 12 h, the solvent evaporated, and the residue distilled *in vacuo*. Yield 84%, b.p. 95—100 °C (0.05 Torr). IR, ν/cm^{-1}: 1710 (C=O), 1680 (C=N), 1280 (P=O). ^{1}H NMR ($CDCl_3$), δ: 1.23 (t, 6 H, CH_3, J = 7.0 Hz); 4.19 (m, 4 H, CH_2); 7.49 and 7.82 (both m, 3 + 2 H, Ph). ^{31}P NMR (CCl_4), δP: −2.17. Found (%): P, 7.90; Cl, 27.73. $C_{13}H_{15}Cl_3NO_4P$. Calculated (%): P, 8.02; Cl, 27.51.

B. Anhydrous pyridine (24 mmol) was added with stirring and cooling with ice water to a solution of chlorine (12 mmol) in 35 mL of CCl_4. The reaction mixture was stirred for 30 min. Then amidophosphonate **2** (10 mmol) was added, and stirring was continued for extra 5 h. The course of the reaction was monitored by ^{31}P NMR spectroscopy. If the signal for the initial compound **2** (δP = 14.7) still persisted in the spectrum of the reaction mixture, another portion of the freshly prepared chlorinating agent was added, and stirring was continued for extra 3 h. The precipitate was filtered off, the filtrate evaporated, and the residue distilled *in vacuo*. Yield 68%, b.p. 95—100 °C (0.05 Torr).

7,8-Benzo-4-diethoxyphosphoryl-5-diethylamino-2-phenyl-4-trichloromethyl-1,6,9-trioxa-3-aza-5-phosphaspiro[4.4]non-2-ene (7). A solution of amidophosphite **6** (5 mmol) in 10 mL of benzene was added dropwise with stirring to a solution of phosphonate **1** (5 mmol) in 10 mL of benzene. The reaction mixture was kept at 25 °C for 12 h. Removal of the solvent gave an oily liquid (yield 93%). A sample for analysis was purified by column chromatography on silica gel (benzene and then THF as the eluents) with subsequent crystallization from petroleum ether. M.p. 138—140 °C. IR, ν/cm^{-1}: 1630 (C=N), 1250 (P=O). ^{1}H NMR ($CDCl_3$), δ: 0.90 (t, 3 H, CH_3, J = 7.2 Hz); 1.19 (t, 3 H, CH_3, J = 7.2 Hz); 1.26 (t, 3 H, CH_3, J = 7.2 Hz); 1.33 (t, 3 H, CH_3, J = 7.2 Hz); 2.89 (m, 2 H, NCH_2); 3.39 (m, 1 H, NCH); 3.81 (m, 1 H, NCH); 4.13 (m, 4 H, 2 OCH_2); 6.9 (m, 3 H, Ar); 7.03 (d, 1 H, Ar, J = 6.9 Hz); 7.4—7.6 (m, 3 H, Ar); 8.14 (d, 2 H, Ar, J = 6.9 Hz). ^{31}P NMR ($CDCl_3$), δP: −16.3 (d, $P_{endocycle}$, J_{PP} = 20 Hz); 11.73 (d, $P_{exocycle}$, J_{PP} = 20 Hz). Found (%): P, 10.26; Cl, 17.83. $C_{23}H_{29}Cl_3N_2O_6P_2$. Calculated (%): P, 10.36; Cl, 17.79.

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