

Reactions of *tert*-Butyl Phosphoramidites with Carbon Tetrachloride and Chloroform

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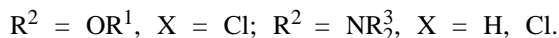
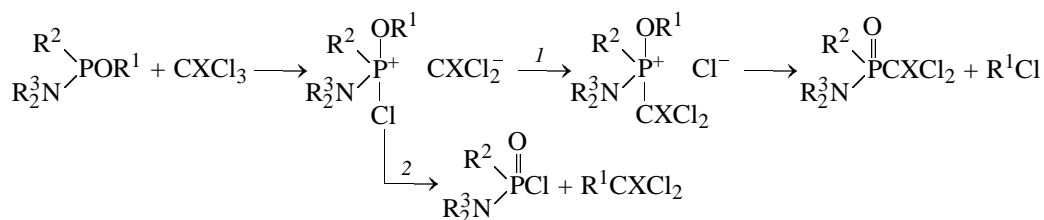
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Abstract—The reactions of 2-*tert*-butoxy-3-phenyl-1,3,2-oxazaphospholane and di-*tert*-butyl diethylphosphoramidite with carbon tetrachloride and chloroform were studied. These reactions proceed via formation of an intermediate quasiphosphonium compound. In the process, carbon tetrachloride acts as a source of positively charged halogen, and chloroform, as a C–H acid.

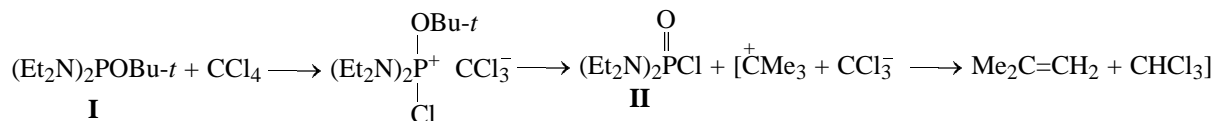
It is known that dialkyl dialkylphosphoramidites react with CCl_4 by two pathways: with the formation of alkyl *N,N*-dialkyltrichloromethylphosphonoamidate (major pathway, 1) and alkyl dialkylphosphoramidochloridate (pathway 2). Alkyl tetraalkylphosphorodi-

amidites react with carbon tetrachloride and chloroform to give tetraalkylphosphorodiamidic chloride [1]. In these reactions, carbon tetrachloride and chloroform presumably act as sources of positively charged chlorine [1, 2].



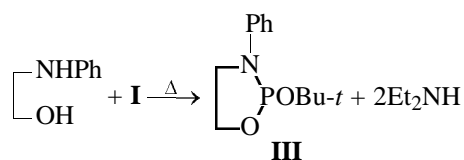
The reactions of *tert*-butyl phosphoramidites with carbon tetrachloride and chloroform were studied in detail in [3]. Because of the high rate of the second stage of the reaction (quasiphosphonium salts containing *tert*-butoxy group at phosphorus decompose very rapidly by the S_N1 mechanism [4, 5]), it could be expected that the process would yield compounds in

which the bonds formed in the initial stage would be preserved. Indeed, it was found that *tert*-butyl tetraethylphosphorodiamidite **I** reacts with carbon tetrachloride with the heat evolution to give tetraethylphosphorodiamidic chloride **II**, chloroform, and isobutylene. Carbon tetrachloride evidently acts as the source of positively charged chlorine [1, 2].

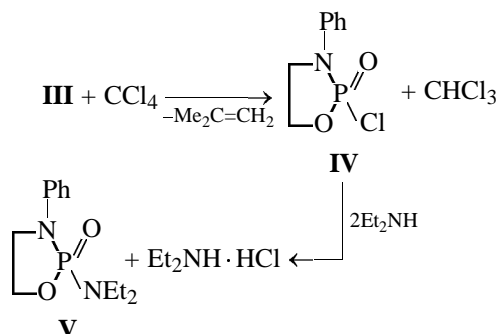


It was interesting to perform the reaction of CCl_4 with cyclic amido esters, which were not tested in this process previously. For this purpose, we prepared

2-*tert*-butoxy-3-phenyl-1,3,2-oxazaphospholane **III** by amide interchange of phosphite **I** according to the following scheme:



The released diethylamine was collected quantitatively. Phosphite **III** is a viscous liquid decomposing during attempted distillation with the evolution of isobutylene and formation of a phosphorus-containing viscous substance. Therefore, the purity of **III** was checked by TLC. Its structure was determined by IR and ^1H NMR spectroscopy. The IR spectrum contained the absorption bands (ν , cm^{-1}) characteristic of phenyl (1450, 1470, 1580), P–N (1350), C–N (1300), P–O–C (1010, 1030), and C–O (1080) groups. The protons of the *tert*-butoxy group give a strong singlet at 1.45 ppm (9H) in the ^1H NMR spectrum. The methylene protons of the ring are observed as two doublets at 2.95 [$\delta(\text{CH}_2\text{N})$] and 3.62 ppm [$\delta(\text{CH}_2\text{O})$]. Contrary to phosphite **I**, phosphite **III** reacts with CCl_4 only on heating, and the reaction is accompanied by evolution of isobutylene and chloroform.

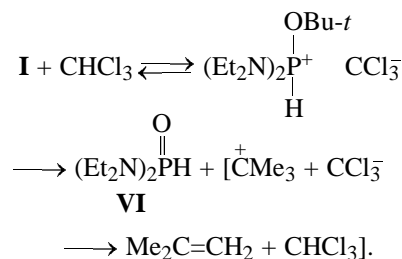


The IR spectrum of crude **IV** contains the absorption bands (ν , cm^{-1}) characteristic of P=O (1225), Ph (1475, 1510, 1600), P–O–C (990), P–Cl (540), and N–Ph (1325) groups. Treatment of the reaction mixture with 2 mol of diethylamine in petroleum ether gives 2-diethylamino-3-phenyl-1,3,2-oxazaphospholane 2-oxide **V**, mp 85–86°C. Diethylamine hydrochloride was also isolated quantitatively, mp 221°C.

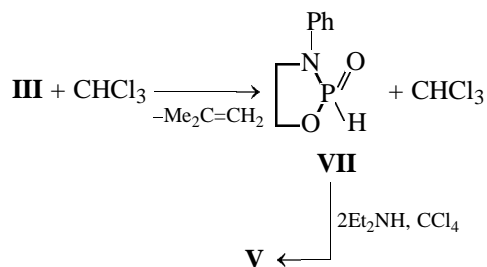
From the reaction of di-*tert*-butyl diethylphosphoramidite with carbon tetrachloride, we also isolated chloroform, isobutylene, and *tert*-butyl diethylphosphoramidochloridate (δ_p 9 ppm) as the reaction products. ^1H NMR spectrum of the latter compound contains the signal of CH_3 (1.4 ppm, t, 6H, $^3J_{\text{HH}}$ 7 Hz), CH_2 (3.2 ppm, m, 4H), and *tert*-butyl group (1.67 ppm, s, 9H) groups. It decomposes during attempted distillation.

It is known that phosphite **I** reacts with CHCl_3 on refluxing for 3 h to give hydrogen tetraethylphos-

phoramidite **VI** and isobutylene. Acid phosphite **VI** is evidently formed by fast decomposition of the P-protonated intermediate with the evolution of isobutylene and regeneration of chloroform.



Phosphite **III** reacts with CHCl_3 under more rigorous conditions (prolonged refluxing, TLC monitoring of the reaction progress). It evidently confirms the lower reactivity of phosphite **III** arising from the stability of phospholane ring due to the presence of the phenyl group, on the one hand, and steric hindrance to the formation of the intermediate quasiphosphonium compound, on the other. The reaction is also accompanied by evolution of isobutylene and regeneration of CHCl_3 .



It is known that 3-phenyl-1,3,2-oxazaphospholane 2-oxide **VII** is a light yellow oil usually decomposing during distillation [6]; therefore, compound **VII** was characterized in the form of 2-diethylamino-1,3,2-oxazaphospholane 2-oxide **V** obtained by treatment of **VII** with diethylamine and carbon tetrachloride under the conditions of the Todd–Atherton reaction. The IR spectrum of crude **VII** contains a strong band of phosphoryl group at 1270 cm^{-1} and a band at 2440 cm^{-1} characteristic of P–H stretching vibrations. Thus, 2-*tert*-butoxy-3-phenyl-1,2,3-oxazaphospholane **III** and di-*tert*-butyl diethylphosphoramidite react with carbon tetrachloride to form the corresponding phosphorochloridates, whereas chloroform in reaction with **III** plays the role of a C–H acid, converting the substrate to oxazaphospholane **VII**.

EXPERIMENTAL

The IR spectra were recorded on a Specord M-75 spectrometer in the range 400–4000 cm^{-1} (KBr pellets,

mulls in mineral oil). The ^1H NMR spectra were obtained on a Tesla BS-587 spectrometer (80 MHz) in C_6D_6 relative to internal HMDS. The ^{31}P NMR spectra were measured on a KGU-4 custom-made NMR spectrometer (10.2 MHz) against 85% H_3PO_4 . The melting points were measured on a Boetius heating stage.

Reaction of phosphite I with phenylaminoethanol. A mixture of 12.4 g of **I** and 6.9 g of phenylaminoethanol was heated in a distillation flask at a bath temperature of 80–90°C. Evolution of 3.4 g of diethylamine (93%) was observed. The purity of the resulting 2-*tert*-butoxy-3-phenyl-1,3,2-oxazaphospholane was checked by TLC. Found, %: C 60.88; H 7.18; N 5.23; P 12.68. $\text{C}_{12}\text{H}_{18}\text{NO}_2\text{P}$. Calculated, %: C 60.25; H 7.23; N 5.85; P 12.97.

Reaction of 2-*tert*-butoxy-3-phenyl-1,3,2-oxazaphospholane III with carbon tetrachloride. Phospholane **III**, 6.0 g, was placed in a flask equipped with a reflux condenser connected with a gasometer, and 3.9 g of carbon tetrachloride was added with stirring at 0–5°C. No heat evolution and no noticeable changes were observed. The reaction mixture was heated at 90–100°C (bath temperature), and active evolution of isobutylene was observed (490 ml, 87%). After the reaction completion, a solution of 3.7 ml of dry diethylamine in 50 ml of petroleum ether was added. A white precipitate of diethylamine hydrochloride formed. It was filtered off (2.2 g, 82%), the solvent was removed, and the residue was recrystallized from benzene to give 4.6 g (72.3%) of 2-diethylamino-3-phenyl-1,3,2-oxazaphospholane 2-oxide **V**,

mp 85–86°C. Published data [7]: mp 85–87°C. Found, %: C 56.45; H 7.97; N 10.78; P 12.51. $\text{C}_{12}\text{H}_{19}\text{N}_2\text{O}_2\text{P}$. Calculated, %: C 56.69; H 7.48; N 11.02; P 12.20.

Reaction of 2-*tert*-butoxy-3-phenyl-1,3,2-oxazaphospholane III with chloroform. A mixture of 6.0 g of **III** and 3.0 g of chloroform was refluxed for 5–6 h. The reaction was accompanied by evolution of isobutylene (400 ml, 71.4%). Distillation of the reaction mixture gave 2.4 g (82%) of chloroform. A solution of 3.6 g of diethylamine and 3.9 g of carbon tetrachloride in 50 ml of petroleum ether was added at room temperature with stirring. Diethylamine hydrochloride was filtered off, and the solvent was removed to give 4.0 g (63.2%) of 2-diethylamino-3-phenyl-1,3,2-oxazaphospholane 2-oxide **V**, mp 85–86°C.

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