

LETTERS
TO THE EDITOR

Unusual Alcoholysis of *tert*-Butyl tetraethylphosphorodiamidite with *N*-Acetylcolamine

L. K. Sal'keeva, M. T. Nurmaganbetova, E. V. Minaeva, and B. Z. Kokzhalova

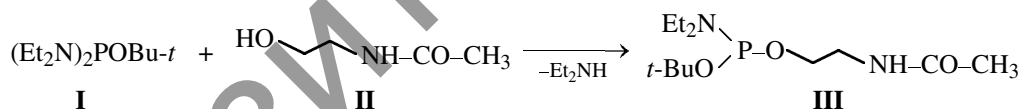
Buketov Karaganda State University,
Universitetskaya ul. 28, Karaganda, 100026 Kazakhstan
e-mail: L.Salkeeva@kargu.krg.kz

Received May 31, 2006

DOI: 10.1134/S1070363206110296

Amidoesters of phosphorous acids fairly readily exchange the amido group under the action of alcohols, amines, or phenols. This method is convenient for preparing phosphoramidites hardly available by the direct synthesis. With this purpose we have studied the reaction of *tert*-butyl tetraethylphosphorodiamidite (**I**) with *N*-acetylcolamine (**II**). As known, *N*-acetylated 4,5-benzo-1,3,2-oxazaphospholanes were prepared in high yield by the reaction of *N*-acetyl-*o*-aminophenol with alkyl phosphorodiamidites [1]. The reaction under study gave, instead of the expected

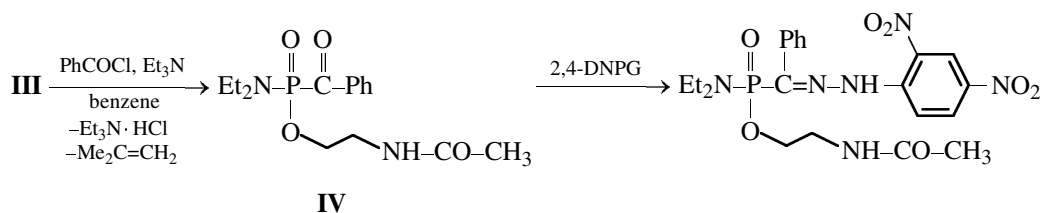
3-acetyl-2-*tert*-butoxy-1,3,2-oxazaphospholane, the product of alcoholysis involving the OH group of *N*-acetylcolamine. Therewith, instead of two, only one mol of diethylamine was isolated. This reaction product was identified by physical constants and as diethylamine hydrochloride. Obviously, the alcoholysis involves exclusively the OH group of *N*-acetylcolamine, because the basicity of the amino group is decreased by conjugation with carbonyl. The reaction progress was monitored by TLC.



The model reaction of phosphoramidite **I** with acetamide failed, and the reaction with colamine gave ambiguous results. The synthesized 2-(acetylamino)-ethyl *tert*-butyl diethylphosphoramidite (**III**) is a colorless mobile liquid. It was identified crude. Compound **III** decomposes with vigorous liberation of isobutylene even under high-vacuum distillation. The instability of the product is evidently connected with the presence of the *tert*-butyl group and also with

the possibility of quarternization of the diethylamino nitrogen atom under the action of the carbonyl carbon atom.

Treatment of phosphoramidite **III** with benzoyl chloride in presence of triethylamine caused vigorous liberation of isobutylene and formation of equimolar amount of triethylamine hydrochloride. The resulting ketophosphonate **IV** was identified as 2,4-dinitrophenylhydrazone.



2-(Acetylamino)ethyl *tert*-butyl diethylphosphoramidite (III). IR spectrum, ν , cm^{-1} : 1657.7 (NH-C=O), 3289.4 (NH), 1063.3 (P-O-C). ^1H NMR spectrum, δ , ppm: 1.21 s [9H, $(\text{CH}_3)_3\text{C}$], 1.00 t (6H, CH_3 , $^3J_{\text{HH}}$ 7 Hz), 2.57 m (4H, CH_2), 2.02 s [3H, $\text{C}(\text{O})\text{CH}_3$], 8.0 s (1H, NH).

The IR spectra were obtained on a Specord IR-75 spectrometer in thin layer in the range $3700\text{--}400\text{ cm}^{-1}$

and on a Nicolet Avator-360 spectrometer. The ^1H NMR spectra were measured on a Bruker DRX-500 spectrometer (500 MHz) against internal TMS.

REFERENCES

1. Pudovik, M.A., Terent'eva, S.A., and Pudovik, A.N., *Zh. Obshch. Khim.*, 1974, vol. 44, no. 5, p. 1020.

Репозиторий КарГУ