Russian Journal of General Chemistry, Vol. 72, No. 8, 2002, pp. 1313–1314. Translated from Zhurnal Obshchei Khimii, Vol. 72, No. 8, 2002, pp. 1398–1399.

LETTERS TO THE EDITOR

New Syntheses of 1,1-Dichloro-2,2,2-trifluoroethyl Isocyanate and Its Reaction with Triethyl Phosphite

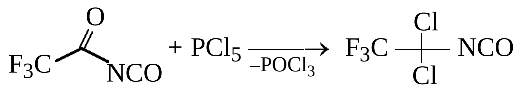
V. I. Boiko, L. N. Onikiichuk, A. V. Yakovenko, and V. I. Kal'chenko

Institute of Organic Chemistry, National Academy of Sciences of Ukraine, Kiev, Ukraine

Received July 22, 2001

1,1-Dichloro-2,2,2-trifluoroethyl isocyanate (**I**) and its derivatives are widely used for preparing of various trifluoro-substituted heterocycles [1–3]. The existing method of synthesis of isocyanate **I** by chlorination of *N*-trifluoroacetylcarbamate with phosphorus pentachloride at 170°C gives no more than 34% of the target product. Its purification is complicated [4].

We have developed a new method for preparing 1,1-dichloro-2,2,2-trifluoroethyl isocyanate (**I**) in 85% yield, based on the reaction of the available trifluoroacetyl isocyanate (**II**) with phosphorus pentachloride in toluene.

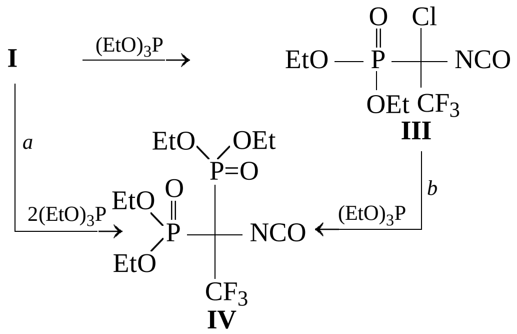


II **I**

Compound **I** contains labile chlorine atoms and is a convenient synthon for preparing α-phosphorylated alkyl isocyanates. One of the main methods of such phosphorylation is the Arbuzov reaction. The Arbuzov reactions with 1,1-dihaloalkyl isocyanates were previously used to prepare both mono- and diphosphorylated derivatives [8], but the yields, as a rule, were not high, and individual products could not always be isolated.

It occured that isocyanate **I** easily reacts with triethyl phosphite. Depending on the reagent ratio, 1-chloro-1-(diethoxyphosphinoyl)-2,2,2-trifluoroethyl isocyanate (**III**) or 1,1-bis(diethoxyphosphinoyl)-2,2,2-trifluoroethyl isocyanate are formed. Monophosphorylation takes place in boiling benzene, and diphosphorylation, in toluene.

Isocyanates **III** and **IV** are colorless liquids which can be distilled in a vacuum. The IR spectra of these substances contain strong N=C=O absorption bands at 2260 cm^{-1}. Note a strong effect of the phosphoryl group on the positions of signals in the ^{19}F NMR spectrum. Each group shifts the signal of the trifluoromethyl group by about 10 ppm downfield as compared to the starting isocyanate.



1,1-Dichloro-2,2,2-trifluoroethyl isocyanate (I). A mixture of 41.7 g of trifluoroacetyl isocyanate (**II**), 93.7 g of phosphorus pentachloride, and 75 ml of toluene were heated for 50 h. The temperature of the reaction mixture was gradually increased to keep the mixture boiling. Isocyanate **I** was isolates by fractional distillation. Repeated distillation gave 47.1 g (85%) of compound **I**, bp 65–66°C {published data [4]: bp 65°C). IR spectrum (CCl_4), ν, cm^{-1}: 2290 (N=C=O). ^{19}F NMR spectrum (acetone-d_6), δ_F, ppm: 83.0 s (CF_3).

1-Chloro-2,2,2-trifluoro-1-(diethoxyphosphinoyl)ethyl isocyanate (III). *a.* A solution of 0.02 mol of triethyl phosphite in 5 ml of benzene was added to a solution of 0.02 mol of isocyanate **I** in 15 ml of benzene. After heat evolution had ceased, the reaction mixture was boiled for 2 h until ethyl chloride no longer evolved. The benzene was removed at reduced pressure, and the residue was distilled in a vacuum to obtain 79% of isocyanate **III**, bp 94–95°C (10 mm), n_D^{20} 1.4103. IR spectrum (CCl_4), ν, cm^{-1}: 2258 (N=C=O). ^1H NMR spectrum (acetone-d_6), δ, ppm: 1.34 t (6H, CH_3), 4.34 m (4H, CH_2). ^{19}F NMR spec-

1070-3632/02/7208-1313$27.00 ©2002 MAIK "Nauka/Interperiodica"

trum (acetone-d_6), δ_F, ppm: 75.5 s (CF_3). Found, %: P 10.46. $C_7H_{10}ClF_3NO_4P$. Calculated, %: P 10.48.

1,1-Bis(diethoxyphosphinoyl)-2,2,2-trifluoroethyl isocyanate. *a*. A solution of 0.04 mol of triethyl phosphite in 10 ml of toluene was added to a solution of 0.02 mol of isocyanate **I** in 15 ml of toluene. After heat evolution had ceased, the reaction mixture was heated under reflux for 2 h until ethyl chloride no longer evolved. The toluene was removed, and the residue was fractionated to obtain 53% of isocyanate **IV**, bp 111°C (0.03 mm), n_D^{20} 1.4232. IR spectrum (CCl_4), ν, cm^{-1}: 2261 (N=C=O). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.32 t, 1.33 t (12H, diastereotopic CH_3 groups), 4.27 m (8H, CH_3). ^{19}F NMR spectrum (acetone-d_6), δ_F, ppm: 66.1 s (CF_3). ^{31}P NMR spectrum ($CDCl_3$), δ_P, ppm: 9.34 s. Found, %: C 32.97, H 5.11, P 15.82. $C_{11}H_{29}F_3NO_7P_3$. Calculated, %: C 33.26, H 5.06, P 15.60. Together with target product **IV**, tetraethyl pyrophosphate was isolated in 25% yield, bp 39–40°C (0.03 mm), n_D^{20} 1.4071.

b. A solution of 0.02 mol of triethyl phosphite in 10 ml of toluene was added to a solution of 0.02 mol of isocyanate **I** in 15 ml of toluene. The resulting mixture was heated under reflux for 2 h until ethyl chloride no longer evolved. The toluene was removed at reduced pressure, and the residue was distilled in a vacuum to obtain 54% of isocyanate **IV**. The substance is identical to that prepared by procedure *a*. Yield of tetraethyl pyrophosphate 27%.

All the reactions were carried out in anhydrous solvents in moisture-proof conditions. The IR spectra were recorded on a UR-20 spectrometer. The ^1H (internal reference HMDS), ^{19}F (internal reference CCl_3F), and ^{31}P NMR spectra (external reference H_3PO_4) were obtained on a Varian VXR-300 spectrometer at 299.95, 282.20, and 121.42 MHz, respectively.

REFERENCES

1. Vovk, M.V., Dorokhov, V.I., Boiko, V.I., and Samaray, L.I., *Khim. Geterotsikl. Soedin.*, 1993, no. 11, pp. 1472–1475.
2. Uneyama, K., Yamashita, F., Sugimoto, K., and Morimoto, O., *Tetrahedron Lett.*, 1990, vol. 31, no. 19, pp. 2717–2718.
3. Vovk, M.V., Boiko, B.I., and Samaray, L.I., *Ukr. Khim. Zh.*, 1993, vol. 59, no. 10, pp. 1081–1082.
4. Boiko, V.I., Gertsyuk, M.N., and Samaray, L.I., *Zh. Org. Khim.*, 1988, vol. 24, no. 2, pp. 451–452.
5. Boiko, V.I. and Samaray, L.I., *Ukr. Khim. Zh.*, 1992, vol. 58, no. 9, pp. 797–798.
6. Boiko, V.I. and Samaray, L.I., *Ukr. Khim. Zh.*, 1995, vol. 61, no. 8, pp. 110–112.
7. Kiemstedt, W. and Sundermeyer, W., *Chem. Ber.*, 1982, vol. 115, no. 3, pp. 919–925.
8. Kozhushko, B.N., Lomakina, A.V., and Shokol, V.A., *Usp. Khim.*, 1989, vol. 58, no. 11, pp. 1869–1895.