ISSN 1070-3632, Russian Journal of General Chemistry, 2010, Vol. 80, No. 5, pp. 1039–1040. © Pleiades Publishing, Ltd., 2010.
Original Russian Text © T.V. Baulina, P.V. Petrovskii, E.I. Goryunov, E.E. Nifant'ev, 2010, published in Zhurnal Obshchei Khimii, 2010, Vol. 80, No. 5, pp. 868–870.

LETTERS
TO THE EDITOR

Reactions of Phosphonic and Phosphoric Dichlorides with Sodium Cyanate as a General Synthesis Method of Phosphoryldiisocyanates

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Received April 14, 2009

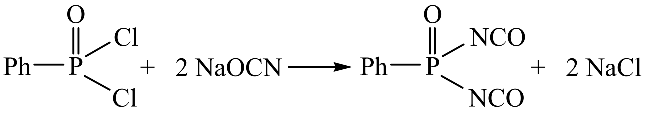
DOI: 10.1134/S1070363210050324

Phosphoryldiisocyanates XP(O)$(NCO)_2$ are promising precursors for synthesis of various classes of organophosphorus compounds: phosphorylated ureas, urethans, carbodiimides, heterocycles, etc, which are in turn of great interest as organophosphorus extractants, complexing agents, sorbates, polymers, biologically active compounds and other practically useful substances.

Although various approaches to phosphoryldiisocyanates: thermal decomposition of phosphoryldicarbamates [1], oxidation of the corresponding trivalent phosphorus diisocyanates [2–4], etc. are proposed to date, reaction of the easily available phosphoryldichlorides RP(O)Cl_2 with cyanates is the most simple and rational method to their obtaining [4–7].

At the same time the literary data on the synthesis of phosphoric diisocyanates given by the different authors with the use of a last method often do not correlate. And the end-products were not reliably characterized.

In this connection we investigated the reactions of some typical phosphonic and phosphoric dichlorides with accesible sodium cyanate. It was established that reaction of phenyldichlorophosphonate with sodium cyanate proceeds at room temperature in anhydrous acetonitrile medium for 4 h, the content of diisocyanate in the mixture formed 93% according to the ^{31}P NMR data. After distilling the product yield comprises 61% (Tables 1, 2).



Under the similar conditions the reactions of methyldichlorophosphonate and phenyldichlorophosphate with sodium cyanate either do not go at all or go very slowly.

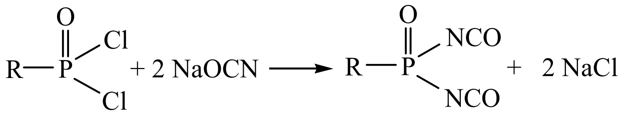
Earlier we proposed an effective catalytic method to obtain the phosphorus monoisocyanates on the basis of the corresponding monochlorides and sodium cyanate [8]. We used this approach to the synthesis of methyldichlorophosphonate and phenyldichlorophosphate. The Lewis acid, anhydrous magnesium chloride, was used as catalyst in these reactions (Table 1).

Table 1. Reaction of phosphoryldichlorides with sodium cyanate

R	Catalyst	Temperature, °C	Reaction time, h	Content of diisocyanate in the reaction mixture by the ^{31}P NMR spectral data, %	Yield, %
Ph	–	20	4	93	61
Me	$MgCl_2$	50	1	97	60
PhO	$MgCl_2$	~80	1	95	42

Table 2. Boiling points, $^{31}P\{^1H\}$ NMR spectra and elemental analysis data for phosphoryldiisocyanates $RP(O)(NCO)_2$

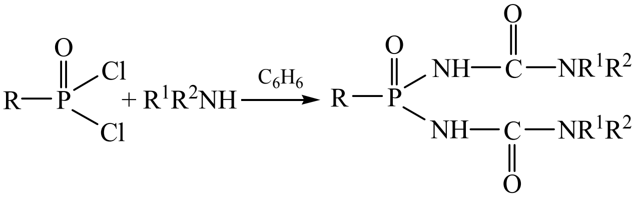
R	bp, °C (*p*, Torr)	Found/Calculated, %				$^{31}P\{^1H\}$ NMR spectrum, δ, ppm, s
		C	H	N	P	
Ph	133.5–134 (5)	46.19	2.49	13.40	14.80	–7.1
		46.17	2.42	13.46	14.88	
Me	77–78 (2)	24.50	2.13	19.20	21.14	–3.4
		24.67	2.07	19.19	21.21	
PhO	93–94 (1)	43.00	2.49	12.33	13.85	–30.1
		42.87	2.25	12.50	13.82	



R = PhO, Me.

The mixture of dichlorides with sodium cyanate excess was heated at 50ºC (R = Me) or refluxed (R = OPh) in absolute acetonitrile medium for 1 h in the presence of 2.5 mol % of $MgCl_2$. The target diisocyanates were isolated by vacuum distillation in 42–61% yields. They are colorless, labile liquids, sensitive to the air moisture. Their structure was confirmed by elemental analysis data and also by IR and ^{31}P NMR spectroscopy (Table 2).

For the chemical identification of these diisocyanates we used reaction with dialkylamines resulting in the corresponding phosphorylated bisureas in high yields.



R = Ph, Me, PhO; $R^1 = R^2 = C_2H_5, C_3H_7$-*n*.

Bisureas isolated are colorless crystalline substances, which are melted without the decomposition. Their structure was confirmed by elemental analysis data and also by NMR (^{31}P, ^1H) and IR spectroscopy.

Hence we pioneered in discovering the effect of electrophilic catalysis in the reaction of phosphoryldichlorides with sodium cyanate. Using this effect, we developed the simple and effective synthesis method of the both phosponic and phosphoric diisocyanates.

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