SHORT COMMUNICATIONS

The Deoxygenation of Isocyanates by 2-Phenyl-3-methyl-1, 3, 2-oxazaphospholidine. A Convenient Method for the Preparation of Isonitriles

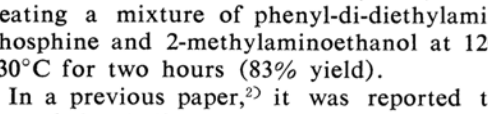
By Teruaki MUKAIYAMA and Yukio YOKOTA

(Received January 25, 1965)

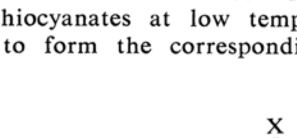
The preparation of 2-phenyl-3-methyl 1, 3, 2-oxazaphospholidine (I) and its application to a synthesis of isonitriles will be described.

The oxazaphospholidine, b. p. 72—75°C/0.3 mmHg (Found: C, 60.21; H, 6.64; N, 7.82. Calcd. for $C_9H_{12}ONP$: C, 59.66; H, 6.68; N, 7.72%), was prepared by treating phenylphosphonous dichloride¹⁾ with 2-methylaminoethanol in the presence of two molecular equivalents of triethylamine (41% yield), or by heating a mixture of phenyl-di-diethylaminophosphine and 2-methylaminoethanol at 120—130°C for two hours (83% yield).

In a previous paper,²⁾ it was reported that several isonitriles were obtained in 20—57% yields by treating isocyanates with triethyl phosphite above 150°C. In the present study, it was found that I reacted with isocyanates or isothiocyanates at low temperatures (5—36°C) to form the corresponding isonitriles (II) and 2-phenyl-3-methyl-1, 3, 2-oxyzaphospholidine-2-one (IIIa) or 2-phenyl-3-methyl-1,3,2-oxazaphospholidine-2-thione (IIIb) in high yields. IIIa or IIIb was always contaminated with a small amount of 3-substituted-per-2-phenyl-5-methyl-1, 3, 5, 2-oxadiazaphosphepine-4-one (IVa) or -4-thione (IVb). For example, when phenyl isocyanate was added drop-by-drop to a solution of I in petroleum ether (b. p. 34—36°C), the solution began to reflux. After the reaction mixture had been refluxed on a water bath for half an hour under nitrogen, the mixture was fractionated into two fractions. Fraction I was phenylisocyanide (b. p. 70—72°C/31 mmHg), and the yield was 57%. Fraction II consisted mainly of IIIa (b. p. 135—138°C/0.1 mmHg, m. p. 73—75°C) (Found: C, 54.94; H, 6.36; N, 7.26. Calcd. for $C_9H_{12}O_2NP$: C, 54.84; H, 6.11; N, 7.11%), plus a small amount of IVa.



IIIa (X=O)
IIIb (X=S)



IVa (X=O)
IVb (X=S)

Similarly, phenylisocyanide, *o*-tolylisocyanide, and *p*-chlorophenylisocyanide were obtained in 93, 70 and 51% yields respectively by a reaction of I with phenylisothiocyanate,* *o*-tolylisocyanate, and *p*-chlorophenylisocyanate in refluxing petroleum ether.

On the other hand, a solution of cyclohexylisocyanate and I in ligroin (b. p. 72—80°C) was refluxed on a water bath for two hours under nitrogen; a mixture of cyclohexylisocyanide and cyclohexylisocyanate, and IIIa (82%) were thus obtained, and 5% of I was recovered. The respective yields of cyclohexylisocyanide (74%) (b. p. 76—78°C/27 mmHg) (Found: C, 76.48; H, 10.64; N, 12.60. Calcd. for $C_7H_{11}N$: C, 77.01; H, 10.16; N, 12.83%) and cyclohexylisocyanate (8%) were determined by the addition of cyclohexylamine to the

---

1) B. Buchner and L. B. Lochhart, "Organic Syntheses," **31**, 88 (1951).

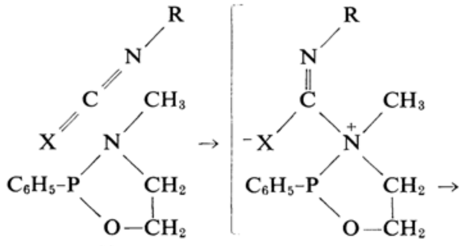
2) T. Mukaiyama, H. Nambu and M. Okamoto, *J. Org. Chem.*, **27**, 3651 (1962).

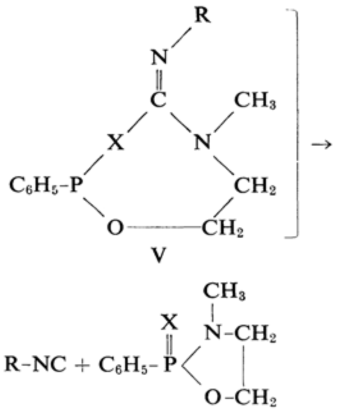
* IIIb (b. p. 148—152°C/0.09 mmHg, m. p. 65—67°C) (Found: C, 50.77; H, 5.82; N, 6.69. Calcd. for $C_9H_{12}ONSP$: C, 50.71; H, 5.63; N, 6.57%).

mixture in dry ether and by weighing the amount of *N, N'*-dicyclohexylurea produced.

When a mixture of I and ethylisocyanate or ethylisothiocyanate was allowed to stand one day at room temperature (5—10°C) under nitrogen, ethylisocyanide (b. p. 80—82°C) was obtained in a 65 or an 87% yield respectively. The ethylisocyanide was identified by gas chromatography.

The most probable pathway of the deoxygenation by means of this cyclic oxazaphospholidine (I) may be sketched in the following manner:


(I)


V

(II) (III)

Further study of analogous deoxygenations of the other compounds with a carbonyl group by means of I is now in progress.

Laboratory of Organic Chemistry
Tokyo Institute of Technology
Ookayama, Tokyo