Tetrahedron Letters No.8, pp. 935-936, 1968. Pergamon Press. Printed in Great Britain.

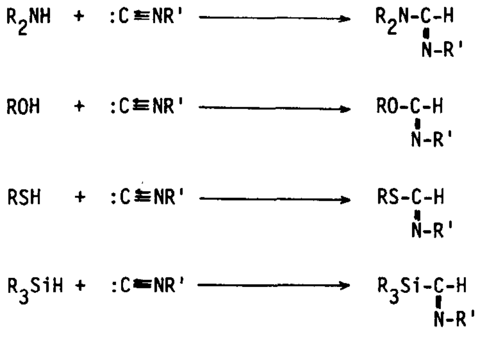
SYNTHETIC REACTIONS BY COMPLEX CATALYSTS VII

A NEW INSERTION REACTION OF ISOCYANIDE INTO PHOSPHORUS-HYDROGEN BOND

Takeo Saegusa, Yoshihiko Ito and Shiro Kobayashi
Department of Synthetic Chemistry, Faculty of Engineering,
Kyoto University, Kyoto, Japan

(Received in Japan 6 October 1967)

We have reported a series of insertion reactions of isocyanides into nitrogen-hydrogen of amine,[1] oxygen-hydrogen of alcohol,[2] sulfur-hydrogen of thiol,[3] and silicone-hydrogen of silane[4] to produce the corresponding derivatives of N-alkylformimidic acid in high yields.



$$R_2NH + :C\equiv NR' \longrightarrow R_2N-\underset{\underset{N-R'}{\|}}{C}-H$$

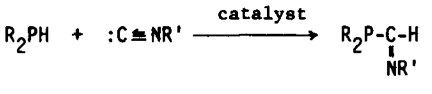
$$ROH + :C\equiv NR' \longrightarrow RO-\underset{\underset{N-R'}{\|}}{C}-H$$

$$RSH + :C\equiv NR' \longrightarrow RS-\underset{\underset{N-R'}{\|}}{C}-H$$

$$R_3SiH + :C\equiv NR' \longrightarrow R_3Si-\underset{\underset{N-R'}{\|}}{C}-H$$

All of these reactions are catalyzed by copper compounds.

This communication describes the reaction of dialkylphosphine with isocyanide in which the isocyanide carbon atom is inserted between phosphorus and hydrogen of dialkylphosphine.



$$R_2PH + :C\equiv NR' \xrightarrow{\text{catalyst}} R_2P-\underset{\underset{NR'}{\|}}{C}-H \qquad (1)$$

A

This is a new reaction to form the phosphorus-carbon bond by the α,α addition of phosphine to the carbon atom of isocyanide, which is interestingly compared with the α,β addition of phosphine to olefin through radical mechanism.[5] The product, N-substituted formimidoylphosphine (A) may be regarded as the Schiff base of formylphosphine, which has not been known until now. The new phosphine compound is stable under dry nitrogen at room temperature, but decomposes gradually in air. The present reaction (eq.(1)) provides a new preparative method of such Schiff base.

Under nitrogen atmosphere a mixture of 4.4 g (40 mmoles) of cyclohexyl isocyanide, 2.7 g (30 mmoles) of diethylphosphine and 0.021 g (1.5 mmoles) of copper(I) oxide was heated in a sealed test tube at 110°C for 6 hrs. Nearly complete conversion of diethylphosphine was indicated by the disappearance of ν_{P-H} band at 2280 cm^{-1} in the infrared spectrum of the reaction mixture. Then the mixture was distilled to isolate N-cyclohexylformimidoyldiethylphosphine (B), bp 110-112° (6 mm), n_D^{20}1.5059. Anal. Calcd for $C_{11}H_{22}NP$: C, 66.30; H, 11.13; N, 7.03; P, 15.54. Found: C, 65.94; H, 11.14; N, 7.07; P, 14.79. Mol. wt. Calcd for B: 199. Found (cryoscopy in benzene): 202. The yield of B based on diethylphosphine was 81 %. The structure of B was confirmed by infrared and nmr spectra. The infrared spectrum of B (neat) showed an absorption at 1605 cm^{-1} (>C=N-). The nmr spectrum in $CDCl_3$ showed a doublet centered at τ 1.65 (1H, >P-CH=, J_{P-H} 32.9 cps), a broad signal centered at τ 7.1 (1H, =N-CH<), and a multiplet (10H, $-P(C_2H_5)_2$) and a broad signal (10H, $-(CH_2)_5-$ of cyclohexane ring) in the region of τ 8.0-9.2.

The reaction (1) requires catalysts of the Group IB and IIB metal compounds. In the absence of catalyst, cyclohexyl isocyanide and diethylphosphine were recovered unchanged from the heat-treated reaction mixture. So far as we have examined, copper(I) oxide was excellent and copper(II) acetylacetonate, zinc chloride, cadmium chloride and murcury(II) acetate were fairly good. Typical Friedel—Crafts catalysts such as aluminum chloride were inactive. The Group VIII metal compounds such as nickel(II) and cobalt(II) chlorides caused exclusively the polymerization of isocyanide to form insoluble, light-brown solid.

REFERENCES

1) T. Saegusa, Y. Ito, S. Kobayashi, K. Hirota and H. Yoshioka, *Tetrahedron Letters*, 6121 (1966).

2) (a) T. Saegusa, Y. Ito, S. Kobayashi and K. Hirota, *Tetrahedron Letters*, 521 (1967);
(b) T. Saegusa, Y. Ito, S. Kobayashi, N. Takeda and K. Hirota, *ibid*., 1273 (1967).

3) T. Saegusa, Y. Ito, S. Kobayashi, K. Hirota and Y. Okumura, Presented at 20th Annal Meeting of Chemical Society of Japan, Tokyo, April, 1967.

4) T. Saegusa, Y. Ito, S. Kobayashi and K. Hirota, *J. Am. Chem. Soc*., **89**, 2240 (1967).

5) F. W. Stacey and J. F. Harris, Jr., "*Organic Reactions*" Vol. 13, John Wiley and Sons, Inc., New York, N. Y., 1963, P.150.