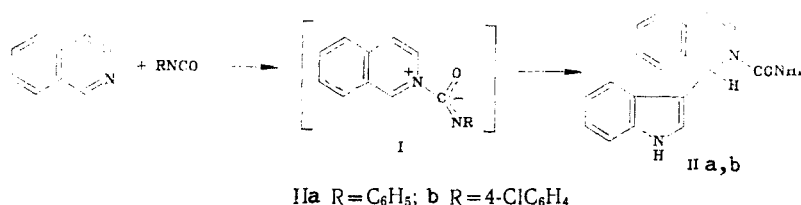


NOVEL REACTION OF AZINES WITH NUCLEOPHILES IN THE
PRESENCE OF ISOCYANATES

A. K. Sheinkman, T. S. Chmilenko, and
E. V. Fedash

UDC 547.833'753'241.04

The direct hetarylation of nucleophilic organic compounds with N-heteroaromatic bases in the presence of activating agents becomes possible if there are formed in the reaction sufficiently electrophilic N-substituted heteroaromatic cations. The degree of activation of the heteroaromatic nucleus therein is governed by the electronic nature of the attacking agent, and is in most instances sufficient in N-acylated compounds, which are formed when carrying out hetarylation in the presence of acylating agents [1]. We have found that in place of acylating agents, isocyanates may be used in these reactions, giving the intermediates (I), which are sufficiently active hetarylating agents in situ for such 'mild' organic nucleophiles as, for example, indole:



Reaction of 1.19 g (0.01 mole) of phenyl isocyanate and 1.23 g (0.01 mole) of isoquinoline with 1.17 g (0.01 mole) of indole in dry benzene at room temperature gave 2.6 g (55%) of 1-(3-indoyl)-2-(n-phenylcarbamoyl)-1,2-dihydroisoquinoline (IIa), mp 163-165°C. IR spectrum (KBr): 1610 (C=C), 1638 (C=O, amide I), 1590 (C=O, amide II), 3294 cm⁻¹ (N-H). PMR spectrum (DMSO-D₆): 6.11 (d, J = 7.6 Hz, 4-H); 7.12 (d, J = 7.6 Hz, 3-H); 7.22 (s, 1-H); 6.8-7.6 (m, 14H, aromatic protons); 8.95 (NH); 10.82 ppm (ind. NH).

Similarly reaction p-chlorophenyl isocyanate gave (IIb), mp 172-173°C.

Reaction of equimolar amounts of phenyl isocyanate, isoquinoline, and trinitrotoluene also resulted in hetarylation of the trinitrotoluene to give 1-(2,4,6-trinitrobenzyl)-2-phenylcarbamoyl-1,2-dihydroisoquinoline (IIc). Yield 49%, mp 120-130°C. IR spectrum (KBr): 1340, 1519 (NO₂), 1675 (CO), 3400 cm⁻¹ (NH). PMR spectrum (DMSO-D₆): 5.88 (d, 1-H, J = 8.2 Hz); 6.14 (d, 4-H, J = 8 Hz); 6.76 (d, 3-H, J = 8 Hz); 8.98 (s, C₆H₂(NO₂)₃); 9.28 ppm (s, NH). The elemental analyses (C, H, and N) for (IIa-c) were in agreement with the calculated values.

LITERATURE CITED

1. A. N. Kost, S. I. Suminov, and A. K. Sheinkman, *Iminium Salts in Organic Chemistry*, Part 2, Wiley, New York (1979), pp. 523-564.

Dnepropetrovsk Engineering and Constructional Institute, Dnepropetrovsk. Translated from *Khimiya Geterotsiklicheskikh Soedinenii*, No. 2, pp. 270-271, February, 1989. Original article submitted June 1, 1988.