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2- AND 4-ISOCYANATOPYRIDINES : TRANSIENT INTERMEDIATES

John Chambers and Colin B. Reese

Department of Chemistry, King's College,
Strand, London, WC2R 2LS, England.

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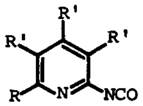
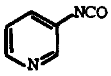
Of the three possible mono-isocyanatopyridines, only the 3-isomer (2) has been described in the literature[1]. Attempts to generate the 2-isomer (1a) have led to the formation of its dimer (4a). Thus Gizycki and Oertel[2] obtained (4a) in good yield by pyrolysis of the phenylurethane (5a). However, 2,6-di-isocyanatopyridine[1] (1; R = NCO, R' = H) and 2-isocyanato-3,4,5,6-tetrachloropyridine[3] (1; R = R' = Cl) are both stable enough compounds to be isolated by sublimation and distillation, respectively.

We now report that the dimer (4a) may be isolated[4] in 93% yield after (5a) has been heated, under reflux, in anhydrous acetonitrile solution in the presence of pyridine for 2 hr. and in 78% yield after picolinoyl azide[5] (6a) has been heated in boiling benzene solution for 2 hr. Although no intermediate may be detected by t.l.c. in the conversion of (5a) into (4a), the decomposition of (6a) may be monitored by infrared spectroscopy. When (6a) is heated in benzene solution at 80°, the intensity of the azide absorption bands at 2140 and 2192 cm^{-1} slowly decrease while a weak isocyanate absorption band at 2242 cm^{-1} soon becomes apparent. However, even after 10 min, when much picolinoyl azide (6a) still remains, a sharp absorption band of medium intensity at 1653 cm^{-1}, indicating the presence of an appreciable amount of (4a), may be observed. After 2 hr, no absorption bands assignable to (6a) or 2-isocyanatopyridine (1a) may be observed. It seems doubtful whether the latter compound (1a) accounts for more than a few percent of the products at any stage of the reaction.

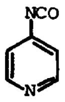


(1) a; R=R'=H

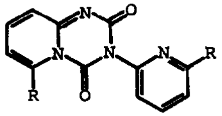
b; R=Me, R'=H



(2)

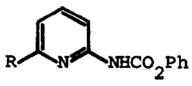


(3)



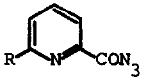
(4) a; R=H

b; R=Me



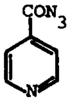
(5) a; R=H

b; R=Me

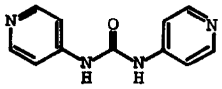


(6) a; R=H

b; R=Me



(7)



(8)

The greater stability of the above substituted 2-isocyanatopyridines (1; R = NCO, R' = H and R = R' = Cl) may be attributed either to the electronic or to the steric effect of the substituents or to a combination of both effects. In order to investigate the possible importance of the steric effect, 6-methylpicolinoyl azide (6b) was prepared[6] and its decomposition in boiling benzene solution studied. After 10 min at 80°, the intensity of the isocyanate absorption band at 2242 cm^{-1} is as strong as the azide absorption band at 2140 cm^{-1} and only weak absorption is discernable in the region of 1650 cm^{-1}. After 80 min, the isocyanate band is very strong and the azide band has almost disappeared; by this time, an absorption band of medium intensity at 1646 cm^{-1}, assignable to the dimer (4b), is apparent. However, although 2-isocyanato-6-methylpyridine (1b) is clearly formed in good yield in this reaction, it proved impossible to isolate. The residue obtained by evaporation of the solvent at room temperature contains only the dimer (4b) which may be isolated crystalline (m.p. 176-177°) in 37% yield. The ultraviolet and infrared spectra of (4b) are very closely similar to those of (4a); its ^1H n.m.r. spectrum ($CDCl_3$) displays the following signals: τ2.0 - 3.8 (6H, m), 7.17 (3H, s), 7.40 (3H, s). The dimer (4b) is not obtained when the phenyl urethane (5b) is heated either alone at 240° or in boiling pyridine solution; however, it is obtained in 16% isolated yield when 2-amino-6-methylpyridine is treated with p-nitrophenyl chloroformate in pyridine solution at 20°.

Finally, the decomposition of isonicotinoyl azide[5] (7) in boiling benzene solution was examined. The azide absorption bands at 2146 and 2196 cm^{-1} disappear slowly but, even after 10 min, a weak isocyanate absorption band at 2266 cm^{-1} is apparent. This band remains weak and virtually disappears by the time the azide (7) has completely decomposed (24 hr). The orange precipitate obtained is probably the trimeric isocyanurate[7] as it undergoes hydrolysis in hot aqueous solution to give (8)[8] and 4-aminopyridine as the sole products. Thus, 4-isocyanatopyridine (3) appears to be appreciably less stable than its 3-isomer[1] (2).

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