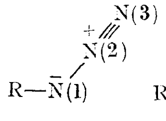
The Reaction of Azides with Dichlorocarbene: a New Route to Isocyanide Dichlorides

By J. E. BALDWIN* and J. E. PATRICK

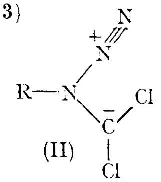
(*Department of Chemistry, Pennsylvania State University,* 212, *Whitmore Laboratory, University Park, Pennsylvania,* 16802)

A RECENT paper on the reaction of carbon monoxide and azides to yield isocyanates[1] prompts us to report some results on the reaction of azides with divalent carbon species. As a result of this study we have developed a convenient and simple synthesis of isocyanide dichlorides, which have previously been obtained by various chlorination procedures.[2]

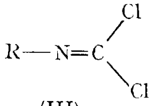
The bonding of the azido-group in alkyl azides has been suggested as possessing a large contribution from a structure formalized as (I).[3,4] It appeared possible that an electrophile such as dichlorocarbene could be added to N(1) and then subsequent elimination of molecular nitrogen, from the intermediate (II), would provide the isocyanide dichloride (III). In the event, when n-octyl azide (I; R = C_8H_{17})[5] in pentane at 0°, was stirred with an excess of potassium t-butoxide and chloroform it was smoothly transformed into the n-octyl isocyanide dichloride (89%) (III; R = C_8H_{17}) isolated by distillation. This compound, b.p. 95—100° (2·5 mm.), n_D^{27} 1·4617, ν_{max} 1650 and 875 cm.$^{-1}$, δ (deuteriochloroform) 3·47 (2 H, t) and 1·65—0·85 (15 H, m), was identical in all respects (g.l.c. behaviour, i.r. and n.m.r. spectra) with a sample obtained by the more usual method of direct chlorination of the isocyanide.[6] This procedure then is a useful and convenient extension of the presently available routes[2] in those cases where the azide is available.



(I)



(II)



(III)

For the reaction of carbon monoxide with azides[1] one possible mechanism could involve a prior formation of a nitrene. In the reaction described here this is an unlikely possibility since it proceeds at 0°; we prefer the mechanism involving the intermediate (II).

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