N-Ylides from Carbenes and Amines

By Irene B. M. Band, Douglas Lloyd, M. I. C. Singer, and F. I. Wasson (Department of Chemistry, United College, University of St. Andrews, St. Andrews, Fife)

REACTIONS between carbenes and amines presumably proceed by electrophilic attack of the carbene at the nitrogen atom of the amine, giving rise to an N-ylide; the product isolated has normally undergone either proton migration or other molecular rearrangement.¹

Pyridinium tetraphenylcyclopentadienylide (II)² has now been produced, in almost theoretical yield, by heating 2,3,4,5-tetraphenyldiazocyclopentadiene (I) under reflux in pyridine with an atmosphere of nitrogen for ten minutes. The identity of the product follows from its ultraviolet spectrum and the melting point of its picrate, which are identical with those of authentic specimens, and from a mixed melting-point determination on the ylide itself.

Ylides were similarly obtained in high yield when the diazo-compound (I) was heated to reflux in α -, β -, or γ -picoline, or in 2,6-lutidine. It is noteworthy that α -picoline and 2,6-lutidine also gave ylides in excellent yield, for these ylides are virtually unobtainable by the alternative method of

preparation starting from bromotetraphenylcyclopentadiene and an amine. It seems that steric hindrance all but prevents the substitution reaction between the bromo-compound and α -substituted pyridines from taking place, whereas there is no such inhibition of the attack by the carbene on these pyridines.

When the parent diazocyclopentadiene (III) was heated in pyridine no ylide could be isolated from the reaction mixture.

(Received June 13th, 1966; Com. 401.)

¹ See, inter alia, W. R. Bamford and T. S. Stevens, J. Chem. Soc., 1952, 4675; Re. Danils and O. Le Roy Salerni, Proc. Chem. Soc., 1960, 286; A. Ledwith, Roy. Inst. Chem. Lectures, Monographs, Reports, 1964, No. 5.

² D. Lloyd and J. S. Sneezum, Tetrahedron, 1958, 3, 334.