The Thermal Rearrangement Of Nitrogen Ylids

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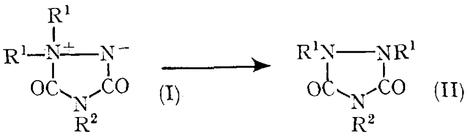
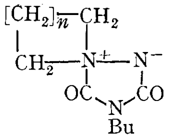
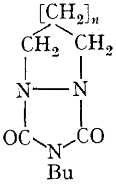
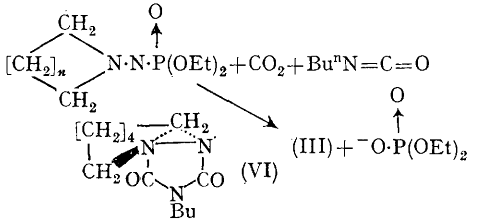
RECENTLY, it was shown that cyclic nitrogen ylids (I) undergo an alkyl shift when heated above their melting points.[1] It was of interest to extend the synthesis of the ylids to include spiro-analogues (III) and to study the rearrangement of the latter as a function of ring size.

The spiro-ylids were prepared as previously described for compounds of this class.[1] The anion of the appropriate diethyl *N*-alkylaminophosphoramidate (V) was treated with CO_2 in the presence of n-butyl isocyanate. Both (IIIa), m.p. 164—165°, and (IIIb), m.p. 124—125°, gave characteristic carbonyl bands (1810, 1670 cm.$^{-1}$). The elemental analysis of each was in agreement with calculated values.


(I) (II)


(IIIa)n=3
(IIIb)n=4


(IVa)n=3
(IVb)n=4


(VI)

Upon heating (IIIa) to 200° only recovered reactant resulted, no triazole (IVa) was detected. In contrast, solid (IIIb), when heated above its melting point, gave a distillable liquid, b.p. 158—160° at 0·5 mm., in quantitative yield. The product exhibited carbonyl-stretching frequencies (1690, 1750 cm.$^{-1}$) which are characteristic of triazoles, (II). Elemental analysis and other spectral data were consistent with the assigned structure.

Our preliminary results indicate that a seven-membered ring is the minimum size for rearrangement. The alkyl shift must be intramolecular for the reaction does not produce high-boiling products which might result if a free carbonium ion was involved. It is logical to assume that because of the dependency on ring size, the migrating carbon approaches the negative nitrogen on the same side from which it leaves. If so, the transition state (VI) must have the large ring in a *trans*-configuration which, by analogy with carbocyclics, can be accommodated only by an eight-membered, or larger, ring.

Acid hydrolysis of the rearranged product (IVb) with aqueous hydrochloric acid gave butylamine hydrochloride and dark intractable material. Reduction of the N–N bond to give macroheterocyclics is under investigation.

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[1] W. S. Wadsworth, jun., and W. D. Emmons, *J. Org. Chem.*, 1967, **32**, 1279.