Thermal Isomerisation of Inner Salts of Allylic Amido-ammonium Compounds

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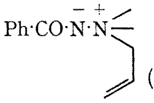
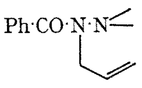
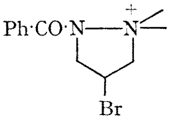
Summary Inner salts of allylic amido-ammonium compounds are readily converted into derivatives of *N*-allyl-*N'N'*-dialkylhydrazine, and to 4-bromo-2,2-dialkylpyrazolidinium salts.

CONVERSION of $R^1\cdot CO\cdot\overset{-}{N}\cdot\overset{+}{N}R^2R^3R^4$ into the tertiary amine, $NR^2R^3R^4$, and the isocyanate, $R^1\cdot NCO$, or artifact thereof by heating at 180—230° has been well documented since 1965.[1] Alternative reaction paths have been observed in particular cases, involving *e.g.* Stevens rearrangement,[2] or elimination of an alkyl group (R^2) as olefin;[3] the latter takes place with relative ease in cases where *cis*-elimination *via* a five-membered transition state is possible.[3b]


(I)


(II)


Br⁻ (III)

We now report an isomerisation typified by (I) → (II), which occurs at temperatures as low as 120—140° and with little sign of competing isocyanate formation. This reaction is considered to have affinities with the rearrangement of allylic amine oxides to *O*-allylhydroxylamines,[4] and probably proceeds through a similar five-membered transition state, though the same result would accrue if the allyl group were first transposed to oxygen (five-membered transition state) and thence to the second nitrogen (six-membered transition state). In this connection, it is interesting to note that bromination of (I) proceeds with participation and gives (III).

Satisfactory analytical and consistent spectroscopic data have been obtained for all compounds in this series.

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[1] M. S. Gibson, P. D. Callaghan, R. F. Smith, A. C. Bates, J. R. Davidson, and A. J. Battisti, *J. Chem. Soc.* (*C*), 1967, **2577**, and references cited; W. J. McKillip, L. M. Clemens, and R. Haugland, *Canad. J. Chem.*, 1967, **45**, 2613, and the two following papers; P. Robson and P. R. H. Speakman, *J. Chem. Soc.* (*B*), 1968, 463.

[2] S. Wawzonek and R. C. Gueldner, *J. Org. Chem.*, 1965, **30**, 3031.

[3] (a) W. S. Wadsworth, *J. Org. Chem.*, 1966, **31**, 1704; (b) D. G. Morris, B. W. Smith, and R. J. Wood, *Chem. Comm.*, 1968, 1134.

[4] R. F. Kleinschmidt and A. C. Cope, *J. Amer. Chem. Soc.*, 1944, **66**, 1929, and references cited.