

DECOMPOSITION OF AROMATIC AZIDES IN TERTIARY ALIPHATIC AMINES:

FORMATION OF AZEPINES AND o-DIAMINES

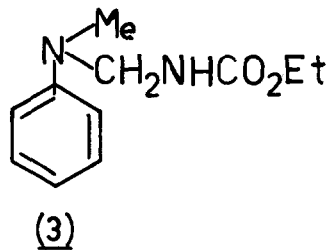
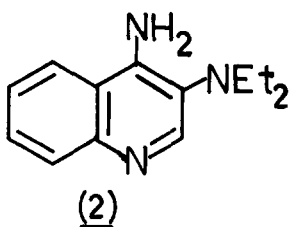
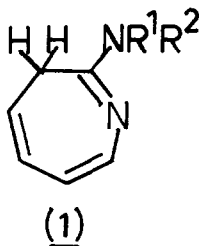
B. Nay, E.F.V. Scriven, H. Suschitzky, D.R. Thomas, and (in part) S.E. Carroll

The Ramage Laboratories, Department of Chemistry & Applied Chemistry,

University of Salford, Salford M5 4WT, Lancs.

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It is well established that primary and secondary amines react with aryl nitrenes to give azepines¹ or o-diamines², but no such reactions have been reported with tertiary aliphatic amines. We have found these to be a substitute for secondary amines in reactions with some aryl azides with the advantage that they promote the singlet nitrene³ and thereby increase yields. For instance, photolysis of phenylazide in triethylamine affords 2-diethylamino-3-H-azepine in 60% yield, whereas only a 36% yield of the same azepine may be obtained by irradiating phenyl azide in diethylamine. When phenylazide was decomposed in TMEDA (tetramethylethylenediamine), the main product isolated was the azepine (1b) on photolysis or thermolysis in ca. 40% yield.



(1a) $R^1=R^2=Et$; (1b) $R^1=Me$, $R^2=(CH_2)_2NMe_2$

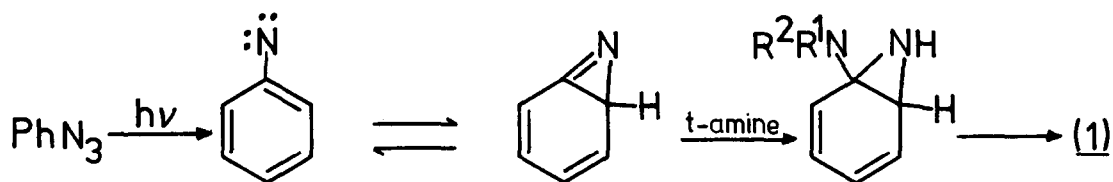
3-Diethylamino-4-aminoquinoline (2) (55% yield) is the chief product from the photolysis of 3-azidoquinoline in triethylamine, but no comparable diamine was obtained from photolysis in TMEDA. Attempts to obtain 7-amino-8-dialkylamino quinolines by irradiating 8-azidoquinoline in the above t-amines were unsuccessful, probably due to steric effect by the nitrogen lone pair preventing approach of the nucleophile.

The above photolyses were carried out using a medium pressure mercury lamp with a pyrex filter. The azepines were characterised by ^1H n.m.r., i.r., m.s., and CHN analysis. The solvents used contained no detectable amounts of primary or secondary amines.

Previous workers⁴ have found that the decomposition of ethyl azidoformate in N,N-dimethylaniline gives an ylid, which can rearrange to (3). In this work, we have shown that phenyl azide and 3-azidoquinoline prefer to rearrange to an azirine, that may be trapped by the t-amine, rather than react as the electrophilic singlet to give an ylid or hydrazine; the fate of the alkyl group lost is under investigation. Hydrazine formation is known⁵ to compete with azepine formation in the photolysis of p-cyanophenyl azide in dimethylamine, but in this case the aryl nitrene is a considerably stronger electrophile than phenyl nitrene and the solvent is a secondary amine.

t-Alkylamines may be added to the list of amines that give 2-alkylamino-3-H-azepines with phenyl azide, and o-alkylamino arylamines with a bicyclic aromatic azide.

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References

1. P.A.S. Smith in "Nitrenes", Ed. W. Lwowski, Interscience, N.Y., 1970, p.99.
2. B. Iddon, H. Suschitzky, and D.S. Taylor, J.C.S. Perkin I, 1974, 579;
S.E. Carroll, B. Nay, E.F.V. Scriven, and H. Suschitzky, Synthesis, 1975, 710.
3. S.E. Carroll, B. Nay, E.F.V. Scriven, and H. Suschitzky, Tetrahedron Letters, 1977,
accepted for publication.
4. K. Hafner, D. Zinser, and K.L. Moritz, Tetrahedron Letters, 1964, 1733.
5. R.A. Odum and G. Wolf, J.C.S. Chem. Comm., 1973, 360.