An Unusual Ring Expansion of Lophine to 2,4,6-Triphenyl-*s*-Triazine

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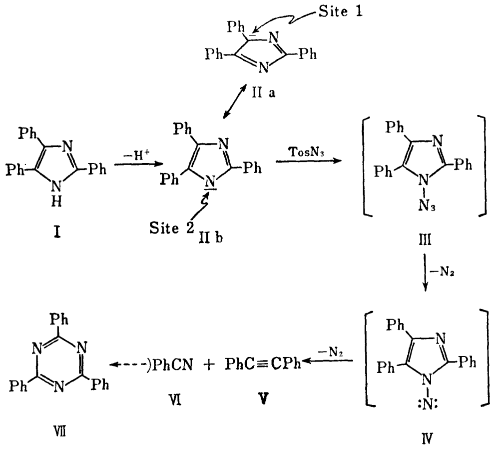
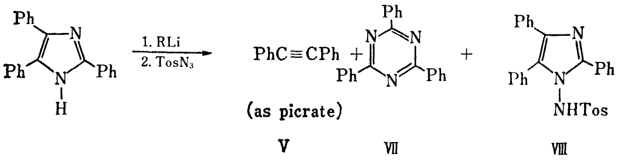
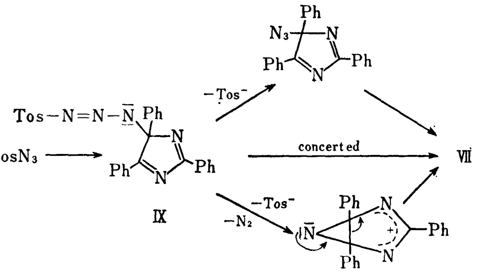
The paucity of *N*-amino imidazoles suitable for our investigation of the fragmentation of *N*-azolylnitrenes[1] prompted us to attempt the generation of these *N*-nitrenes directly *via* the *N*-azides. It has already been shown that in principle all *three* nitrogen atoms of *p*-toluenesulfonyl azide (tosyl azide) can be transferred (*azido transfer* reaction) to anions of secondary amines or imines. Although this reaction has been realized with imines,[2] difficulties arose when side-reactions became the major paths of these experiments.[2,3] These facts notwithstanding, it was anticipated that with the appropriate substrates, *N*-azidation should be possible. The ready availability of 2,4,5-triphenylimidazole (I) prompted us to explore this possibility, particularly since its anion (IIb) is symmetrical with respect to attack of tosyl azide at nitrogen (site 1); since azidation at carbon (site 2) would result in the formation of a non-aromatic ring, it was anticipated that this might favor the formation of the *N*-azide.



The anion of lophine (II), prepared by the reaction of lophine with one equivalent of methyllithium in tetrahydrofuran, was treated with a two-fold excess of tosyl azide and the reaction mixture was then heated under reflux for 12 hr; vigorous evolution of nitrogen was observed. The reaction mixture was quenched by the addition of water and the organic products were separated by chromatography on alumina. From 20.2 mmol of lophine, there was obtained 4.7 mmol of 2,4,6-triphenyl-*s*-triazine (VII), 2.7 mmol of tolan (as its picrate) and 1.0 mmol of *N*-tosylamino lophine (VIII), in addition to 10.4 mmol of unreacted lophine. Our original assumption was that the triazine arose by trimerization of benzonitrile,[4] one of the primary fragmentation products. On that basis, the yield of benzonitrile (as the triazine) would be over 160% and this coupled with the abnormally low yield of the tolan prompted us to question the fragmentation path as the source of the triazine. If the yield of tolan is taken as the extent to which fragmentation (assuming 100% conversion)[5] was responsible for triazine, then 6.1 mmol of lophine anion was converted to 3.8 mmol of triazine by another route.



(9.8 mmol) (2.7 mmol) (4.7 mmol) (1.0 mmol)



The results obtained can only be rationalized in terms of an attack of tosyl azide at carbon followed by generation of the azide or more likely a concerted ring expansion of the primary addition product (IX) perhaps *via* the highly stabilized bicyclic betaine; bond reorganization would then lead to the observed 2,4,6-triphenyl-*s*-triazine. To our knowledge, this is the first report of a nitrene ring expansion of this type of a five- to a six-membered aromatic heterocycle.[6]

The data obtained show that attack by tosyl azide at carbon is favored by almost 2 to 1 over attack at nitrogen and the ring expansion reaction proceeds in about 64% yield.

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[1] K. Sakai and J.-P. Anselme, *Tetrahedron Lett.*, **1970**, 3851.

[2] J.-P. Anselme, W. Fischer, and N. Koga, *Tetrahedron*, **25**, 89 (1969).

[3] G. Koga and J.-P. Anselme, Unpublished results.

[4] We have determined that benzonitrile trimerizes to the triazine under the reaction conditions.

[5] The serendipitous formation of VIII allowed us to ascertain that the fragmentation gave the triazine and diphenylacetylene in 48 and 60% yields respectively. *N*-Tosylaminolophine (VIII) was stable under the reaction conditions. The results of the fragmentation will be reported at a later date.

[6] For an example of another type, see H. E. Baumgarten, W. F. Wittmann, and G. J. Lehmann, *J. Heterocycl. Chem.*, **6**, 333 (1969).