Tetrahedron Letters No. 40, pp 4059 - 4062, 1972. Pergamon Press. Printed in Great Britain.

# THE DEOXYGENATION OF ALIPHATIC NITROSO COMPOUNDS WITH TRIALKYL PHOSPHITES: THE QUESTION OF A NITRENE INTERMEDIATE

R. A. Abramovitch, J. Court, and E. P. Kyba

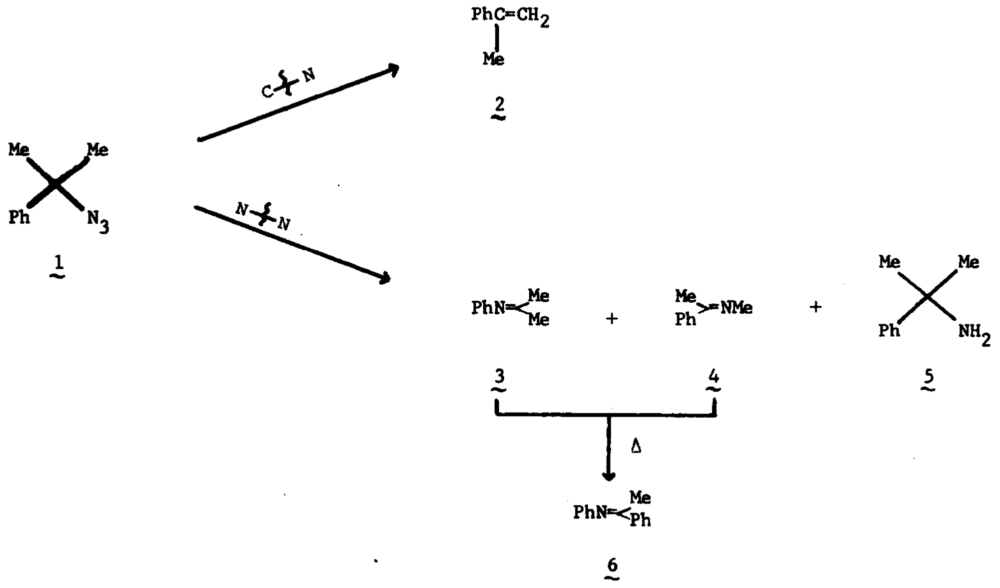
Department of Chemistry, University of Alabama
University, Alabama 35486

(Received in USA 21 July 1972; received in UK for publication 1 September 1972)

Evidence has been presented that the thermolysis of tertiary alkyl azides involves the intermediacy of alkyl nitrenes[1,2] while the photolysis does not,[2,3] migration to nitrogen beginning before N-N bond cleavage is complete. We now report related studies of the thermal deoxygenation of tertiary aliphatic nitroso alkanes with triethyl phosphite which shed light on the mechanism of this reaction.

The deoxygenation of aromatic nitro and nitroso compounds with tervalent phosphorous compounds is generally believed to involve the formation of aryl nitrene intermediates.[4] While such aryl nitrenes (or their rearrangement products) have been trapped[4a,5] a concerted loss of phosphate with attack at nitrogen could not be ruled out in some cases.[6] The reductive rearrangement of a number of tertiary nitroso alkanes with triethyl phosphite has recently been studied[7] and it was suggested that the products were formed by 1,2-alkyl shifts to the tertiary alkyl nitrene (or to its phosphate precursor). We now show that a free nitrene is *not* an intermediate in such reactions.

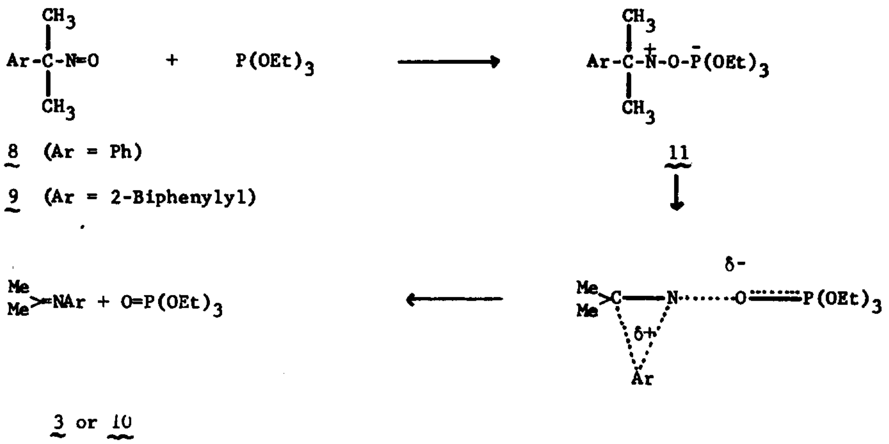
Thermolysis of 2-phenylisopropyl azide (1) at 185-190° gave[8] α-methylstyrene (2) (29%) (C-N bond fission), together with the imines 3 (12.5%) (Ph migration) and 4 (13.3%) (Me migration), and a small amount of 2-phenylisopropylamine (5) (1.6%) (H-abstraction). Under the thermolysis conditions 3 and 4 give 6 almost quantitatively. The Ph:Me migration ratio was thus 1.8. C-N bond cleavage was also observed in the thermolysis of 1-(2-biphenylyl)-1-methylethyl azide and, in this case, the 2-biphenylyl:Me migration ratio was 1.9.[1] Intramolecular aromatic substitution by the alkyl nitrene to give 6,6-dimethyl-5,6-dihydrophenanthridine (7) was observed.[1]



2-Nitroso-2-phenylpropane (8) and 2-(2-biphenylyl)-2-nitrosopropane (9) were prepared by oxidation of the corresponding tertiary amines: 8 by persulfate oxidation at pH$\sim$7 or by *m*-chloroperbenzoic acid oxidation, as was 9. These compounds are extremely susceptible to atmospheric oxidation to give mostly the nitro-compound. Deoxygenation of 8 at 10° in cyclohexane with triethyl phosphite in the absence of oxygen gave mainly *N*-isopropylidene aniline (3) together with a trace of *N*-($\alpha$-methylbenzylidene) methylamine (4) and a 90% yield of triethyl phosphate. Hydrolysis of the reaction mixture followed by quantitative analysis gave aniline (79%) and acetophenone (0.5-1%). Consequently, the minimum Ph:Me migratory ratio is 160:1. If any unreacted nitroso derivative was present, 2-phenylisopropanol, bicumyl, and some 2-nitro-2-phenylpropane were observed on gas chromatography. Since these have been shown to be products of thermolysis of 8 at 225° it seems likely that they are formed from unreacted 8 in the injection port of the gas chromatograph.

Deoxygenation of 9 with $(EtO)_3P$ under the same conditions gave *N*-isopropylidene 2-aminobiphenyl (10) mainly and only traces of the methyl migration product. Quantitative analysis following hydrolysis gave 2-aminobiphenyl (82%) and 2-acetylbiphenyl ($<$0.1%). No trace of the intramolecular cyclization product (7) was detected. The 2-biphenylyl:methyl migratory ratio is, therefore, >1600.

If a stoichiometric amount of triethyl phosphite is added to a solution of 8 or 9 in cyclohexane at 22$^{\circ}$ the blue colour due to the monomer has virtually disappeared after 5 min. and no phosphite is left. On the other hand, the quantities of imines and $(EtO)_3PO$ formed after that time are less than half those obtained after a 3 hr. reaction time.[9] These results are in agreement with a fast reaction of phosphite with nitroso compound to give 11, followed by a slower, anchimerically assisted elimination of triethyl phosphate and



migration. The observed migratory ratios are close to those expected for a concerted process in which the partial positive charge is delocalized over the migrating aromatic nucleus cf. the formolysis of neophyl derivatives in which Ph:Me~10$^3$,[10] in contrast to the ratios of 1.8-1.9 found when a free alkyl nitrene is formed.

We thank the National Science Foundation (Grant #GP 18557) for support of this work.

## REFERENCES

1. R. A. Abramovitch and E. P. Kyba, J. Chem. Soc. Chem. Comm., 265 (1969).
2. R. A. Abramovitch and E. P. Kyba, "The Chemistry of the Azido Group," (S. Patai, Ed.), Ch. 5, Interscience Publishers, London, 1971, p. 221.
3. R. A. Abramovitch and E. P. Kyba, J. Amer. Chem. Soc., 93, 1537 (1971).
4. (a) J. I. G. Cadogan, Quart. Rev., 22, 222 (1968).
   (b) R. J. Sundberg, B. P. Das, and R. H. Smith, jun., J. Amer. Chem. Soc., 91, 658 (1969).

(c) P. J. Bunyan and J. I. G. Cadogan, *J. Chem. Soc.*, 42 (1963).

(d) R. A. Abramovitch and S. R. Challand, *J. Chem. Soc. Chem. Comm.* in the press.

5. (a) R. Huisgen, D. Vossuis, and M. Appl, *Chem. Ber.*, **91**, 1 (1958).

(b) W. v. E. Doering and R. A. Odum, *Tetrahedron*, **22**, 81 (1966).

(c) R. A. Odum and A. M. Aaronson, *J. Amer. Chem. Soc.*, **91**, 5680 (1969).

(d) R. A. Abramovitch, S. R. Challand, and E. F. V. Scriven, *J. Org. Chem.* in the press.

6. J. H. Boyer, "Nitrenes," (W. Lwowski, Ed.), Ch. 5, Interscience Publishers, New York, 1970, p. 163.

7. B. Sklarz and M. K. Sultan, *Tetrahedron Lett.*, 1319 (1972).

8. All quantitative analyses were carried out by glc using the internal standard technique. Products were compared with authentic samples.

9. The disappearance of phosphite and the lag in the appearance of **3** were followed by nmr.

10. W. H. Saunders, Jr. and R. H. Paine, *J. Amer. Chem. Soc.*, **83**, 882 (1961).