

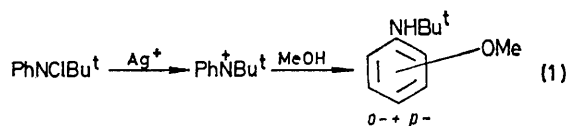
A New Route to Nitrenium Ions *via* an Electron Transfer Reaction of Aminyl Radicals

By J. I. G. CADOGAN* and ALAN G. ROWLEY

(Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ)

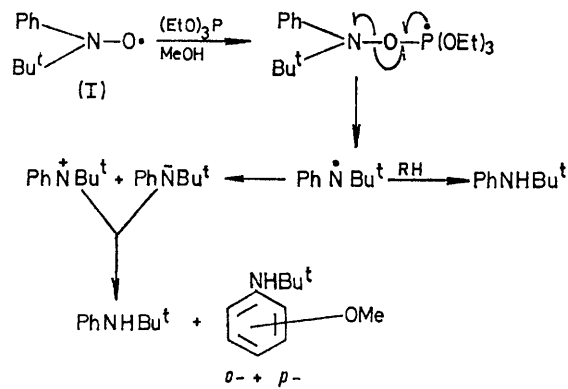
Summary A convenient and mild route to aryl nitrenium ions is described involving deoxygenation of aryl nitroxides by trialkyl phosphites in methanol or ethanol, and evidence is presented which suggests that redox transfer between arylaminyl radicals is responsible.

NITRENIUM ions are becoming increasingly important in organic chemistry.¹ The *N*-*t*-butyl-*N*-phenylnitrenium ion for example, may be conveniently produced *via* silver salt decomposition of *N*-chloro-*N*-*t*-butylaniline and detected by reaction with nucleophiles such as methanol, to give *o*- and *p*-methoxy-*N*-*t*-butylanilines [reaction (1)].² In theory this nitrenium ion may be produced by redox reaction (2) of two phenyl-*t*-butylaminyl radicals.



We report a novel route to the generation of such aminyl radicals and present evidence that such a redox reaction to give nitrenium ions occurs.

The system selected was deoxygenation of phenyl-*t*-butyl nitroxide (I) by triethyl phosphite, in methanol under



SCHEME

nitrogen. By analogy with reactions of alkoxy radicals with phosphite³ this would be expected to give the corresponding phenyl-*t*-butylaminy radical. Redox electron transfer to give the phenyl-*t*-butyl nitrenium ion would then be detectable by the appearance of *o*- and *p*-methoxy-*N*-*t*-butylanilines. The nitroxide (1 mmol) in methanol (25 ml) in the presence of the phosphite (2.5 mmol) after 48 h at the boiling point gave *N*-*t*-butylaniline and a mixture of *o*- and *p*-methoxy-*N*-*t*-butylanilines (2.3% *o*-; 15.3% *p*-), the latter in exactly the same ratio as those obtained by Gassman's nitrenium ion route involving *N*-chloro-*N*-*t*-butylaniline in methanol.² A similar result was obtained on reaction of diphenyl nitroxide with triethyl phosphite in ethanol.

The mechanism is supported by the following observations.

(1) Diphenylaminy radicals produced by an alternative and authentic⁴ route involving thermolysis of tetraphenyl-

hydrazine in ethanol under nitrogen, gave diphenylamine and ethoxylated diphenylamines of the same isomer distribution and yields as those from the reaction of triethyl phosphite with diphenyl nitroxide.

(2) No "crossed products" were obtained by carrying out the deoxygenation of diphenyl nitroxide in ethanol in the presence of *NN*-dimethylaniline, thus ruling out any mechanism involving alkoxylation of preformed diphenylamine.

(3) Thermolysis of tetraphenylhydrazine in 2-phenylethanol gave no products ascribable to the intermediacy of benzyl radicals, which would have been expected if 2-phenylethoxy radicals had been involved.⁵ This rules out mechanisms involving alkoxy radicals which might couple with the arylaminy radicals to give the alkoxyated products.

(Received, 7th November 1973; Com. 1541.)

¹ P. G. Gassman, *Accounts Chem. Res.*, 1970, **3**, 26; P. G. Gassman and G. D. Hartman, *J. Amer. Chem. Soc.*, 1973, **95**, 449.

² P. G. Gassman, G. A. Campbell, and R. C. Fredrick, *J. Amer. Chem. Soc.*, 1972, **94**, 3884.

³ C. Walling and R. Rabinowitz, *J. Amer. Chem. Soc.*, 1959, **81**, 1243; A. G. Davies, D. Griller, and B. P. Roberts, *J.C.S. Perkin II*, 1972, 2224.

⁴ C. K. Cain and F. Y. Wiselogle, *J. Amer. Chem. Soc.*, 1940, **62**, 1163.

⁵ A. Ledwith, P. J. Russell, and L. H. Sutcliffe, *J.C.S. Perkin II*, 1973, 630.