The Reactivity of Organophosphorus Compounds. Part XXIX.[1] Deoxygenation of Nitroxyl Radicals by Trialkyl Phosphites: a New Route to Nitrenium Ions *via* Electron Transfer Reactions of Aminyl Radicals †

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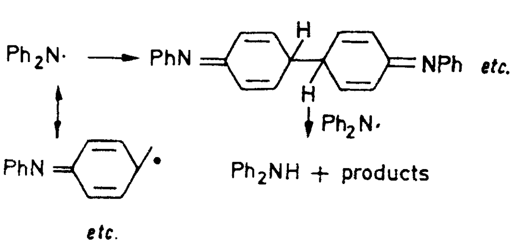
A convenient and mild route to arylnitrenium ions is described: deoxygenation of diphenylnitroxyl by triethyl phosphite in boiling ethanol under nitrogen gives diphenylamine and *p*-ethoxydiphenylamine. Thermolysis of tetraphenylhydrazine in ethanol gives the same product, thus pointing to the formation of diphenylaminyl radicals which, in part, undergo mutual electron transfer to give diphenylnitrenium ions. In accord with this phenyl-t-butylnitroxyl reacts with triethyl phosphite in methanol to give *o*- and *p*-methoxy-*N*-t-butylanilines in the same ratio as that produced *via* the authentic nitrenium ion route from *N*-chloro-*N*-t-butylaniline in methanol. Diphenylnitroxyl readily dehydrogenates 9,10-dihydroanthracene, the efficiency of the reaction being improved several fold by a cycle involving *in situ* regeneration of diphenylnitroxyl by aerial oxidation.

It is known [2] that diphenylaminyl radicals, generated in an aprotic solvent, undergo disproportionation to give diphenylamine and a polymer (*e.g.* Scheme 1). There remains, also, the previously unexploited possibility that diphenylaminyl radicals may undergo electron transfer reactions, particularly in ionising media, to give nitrenium ions [reaction (1)], species which are becoming increasingly important in organic chemistry.[3] We now report the results of experiments involving production of aminyl radicals by deoxygenation of nitroxyl radicals with trialkyl phosphites, and by thermolysis of tetraphenylhydrazine which provide strong support for such electron transfer.



SCHEME 1

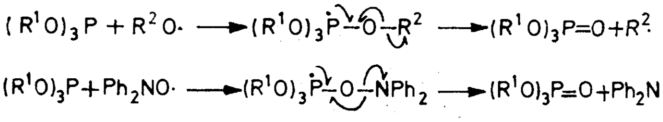
$$2R_2N\cdot \longrightarrow R_2N^+ + R_2N^- \qquad (1)$$

The versatility of triethyl phosphite as a deoxygenating agent is well known,[4] but in the series NO, RN=O, $R_2NO\cdot$, $R_3\overset{+}{N}-\bar{O}$, only reactions of the 'even' electron species, *i.e.* nitroso-compounds and amine oxides are well documented.[4] Nitric oxide has been shown to oxidise triethyl phosphite,[5,6] with the formation of nitrous oxide.[6] The suggestion that this proceeds *via* an intermediate phosphoranyl radical $(EtO)_3P(NO)\cdot$, appears to be very reasonable in view of the many examples of reaction of tervalent phosphorus compounds with radicals to give phosphoranyl radicals.[4,7,8] Reactions of trialkyl phosphites with nitroxide radicals have received almost no attention. There is one report [9] that the reaction of bis(trifluoromethyl)nitroxyl with tris(dimethylamino)phosphine proceeds as follows: $(Me_2N)_3P + 2(CF_3)_2NO\cdot \longrightarrow Me_2NON(CF_3)_2$. Though not discussed in the original paper, this reaction could proceed *via* β-fission of the intermediate radical as in reactions (2) and (3).

$$(Me_2N)_3P + (CF_3)_2NO\cdot \longrightarrow [(Me_2N)_3\dot{P}ON(CF_3)_2] \longrightarrow Me_2N\cdot + (CF_3)_2NOP(NMe_2)_2 \qquad (2)$$

$$Me_2N\cdot + (CF_3)_2NO\cdot \longrightarrow (CF_3)_2NONMe_2 \qquad (3)$$

By analogy with the reaction of trialkyl phosphites with alkoxyl radicals, which proceeds *via* β-scission of the resulting intermediate tetra-alkoxyphosphoranyl radical (Scheme 2), we expected that reaction of nitroxyl radicals, such as diphenylnitroxyl, with triethyl phosphite would give an intermediate phosphoranyl radical which would cleave, as depicted in Scheme 2, to give the long lived diphenylaminyl radical rather than an alkyl radical.



SCHEME 2

We now report experiments which support this prediction and also provide evidence which strongly points to the novel conclusion that the resulting aminyl radicals, under certain circumstances, undergo electron transfer reactions to give a useful new source of nitrenium ions.

RESULTS AND DISCUSSION

Reaction of triethyl phosphite (2·5 mol. equiv.) with diphenylnitroxyl in carefully deoxygenated boiling

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† Preliminary communication, J. I. G. Cadogan and A. G. Rowley, *J.C.S. Chem. Comm.*, 1974, 179.

[1] Part XXVIII, J. I. G. Cadogan, J. Challis, A. Cooper, and D. T. Eastlick, *J.C.S. Perkin I*, 1973, 1798.

[2] H. Musso, *Chem. Ber.*, 1959, **92**, 2881.

[3] P. G. Gassman, *Accounts Chem. Res.*, 1970, **3**, 26.

[4] J. I. G. Cadogan and R. K. Mackie, *Chem. Soc. Rev.*, 1974, **2**, 87.

[5] R. Longli, R. O. Ragsdale, and R. S. Drago, *Inorg. Chem.*, 1962, **1**, 768.

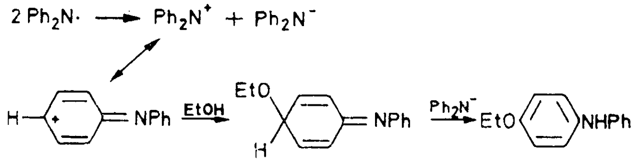
[6] L. P. Khun, J. O. Doali, and C. Wellman, *J. Amer. Chem. Soc.*, 1960, **82**, 4792.

[7] J. I. G. Cadogan, *Adv. Free Radical Chem.*, 1967, **2**, 203.

[8] A. G. Davies, D. Griller, and B. P. Roberts, *J.C.S. Perkin II*, 1972, 2224.

[9] Y. O. El. Nigumi and H. J. Emeleus, *J. Inorg. Nuclear Chem.*, 1970, **32**, 3213.

benzene gave, after 48 h under nitrogen, a quantitative yield of triethyl phosphate, diphenylamine (44%), and a tar. This indicated complete deoxygenation of the nitroxyl, as predicted by Scheme 1, to give diphenylaminyl radicals, which are known [2] to undergo disproportionation into diphenylamine (1 equiv.) and a polymer (1 equiv.). The same reaction carried out in ethanol instead of benzene gave triethyl phosphate (100%), diphenylamine (65%), tar, and 4-ethoxydiphenylamine (19%), the 2- and 3-isomers being absent (<0·5%). This suggested that in addition to the normal disproportionation reaction (Scheme 1), some diphenylaminyl radicals were being diverted to diphenylnitrenium ions, subsequently trapped by reaction with ethanol (Scheme 3), the quantitative conversion of triethyl phosphite into phosphate clearly implicating ethanol as the source of *p*-ethoxydiphenylamine. Reaction as in Scheme 3 is strongly supported by the results of corresponding experiments using tetraphenylhydrazine, which is an authentic source of diphenylaminyl radicals.[10] The close similarity of the results of experiments in three different solvents (Table 1), using the hydrazine and diphenylnitroxyl–triethyl phosphite is noteworthy.



SCHEME 3

Reactions of diphenylaminyl radicals

Solvent	Products	From $(EtO)_3P$–$Ph_2NO\cdot$	From $(Ph_2N)_2$
EtOH *	Ph_2NH	65	67
	$4\text{-}EtOC_6H_4NHPh$	19	17
PhH *	Ph_2NH	44	43
PhMe	Ph_2NH	48	44

* At the b.p. † At 80°.

Alternative, and discounted, explanations for the formation of *p*-ethoxydiphenylamine are as follows: first, that diphenylaminyl radicals could react with ethanol to give an ethanol radical cation, and hence the ethoxyl radical, and that either of these species could couple with a diphenylaminyl radical to give the product [reactions (4) and (5)]. This would be analogous to the

$$Ph_2N\cdot + EtOH \longrightarrow Ph_2N^- + EtOH^{\cdot +} \longrightarrow EtO\cdot + Ph_2NH \quad (4)$$

$$EtO\cdot + Ph_2N\cdot \longrightarrow p\text{-}EtO\cdot C_6H_4NHPh \quad (5)$$

known [11] one electron oxidation of methanol to methoxyl radicals by the persulphate ion and would be in accord with the known extensive delocalisation of spin into the benzene rings of diphenylaminyl radicals.[12] We were unable to find experimental support for this suggestion in, for example, thermolysis of tetraphenylhydrazine in 2-phenylethanol. This gave no products ascribable to benzyl radicals, which would have been formed from any 2-phenylethoxyl radicals present [reaction (6)], as shown recently.[13] Similarly the addition of benzyl diethyl phosphite to the reaction of diphenylaminyl radicals in

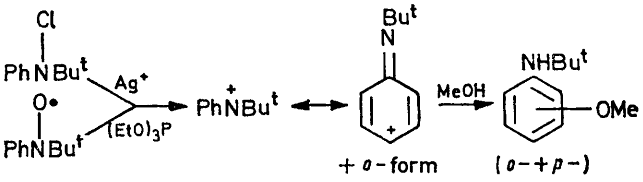
$$PhCH_2CH_2O\cdot \longrightarrow PhCH_2\cdot + CH_2O \quad (6)$$

ethanol gave no products ascribable to the intermediacy of benzyl radicals, which would be expected by trapping of ethoxyl radicals by benzyl diethyl phosphite [reaction (7)].

$$EtO\cdot + (EtO)_2POCH_2Ph \longrightarrow (EtO)_3\dot{P}OCH_2Ph \longrightarrow (EtO)_3PO + PhCH_2\cdot \quad (7)$$

A second alternative explanation of the formation of *p*-ethoxydiphenylamine involves ethoxylation of preformed diphenylamine by an ethoxylating species. This is discounted because such a species would be expected to be trapped not only by diphenylamine but also by *NN*-dimethylaniline added to the reaction mixture. Such a reaction led to no ' crossed ' products; hence no species capable of directly ethoxylating electron-rich aromatic compounds is directly responsible for the formation of 4-ethoxydiphenylamine. In accord with this are the observations that electrophilic attack on diphenylamine would be expected to give *ortho*- and *para*-isomers, *cf.* nitration,[14] and that *ortho*-, *meta*- and *para*-isomers would be expected from radical attack, *cf.* hydroxylation.[15]

Further strong support for our preferred mechanism (Scheme 3) arises from the deoxygenation of phenyl-t-butylnitroxyl by trimethyl phosphite in methanol to give a mixture of *o*- and *p*-methoxy-t-butylanilines of isomer ratio ($p : o = 6{\cdot}6 : 1$) identical with that produced by reaction in methanol of authentic *N*-t-butylphenylnitrenium ions, produced by silver induced dechlorination of *N*-t-butyl-*N*-chloroaniline.[16] (Scheme 4).



SCHEME 4

Finally, we record attempts to provide further evidence of the intermediacy of diphenylaminyl radicals in the above reaction, which led to the discovery that diphenylnitroxyl is a potentially useful dehydrogenating agent. The genesis of these experiments lies in Jackson and

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[10] C. H. Cain and F. Y. Wiselogle, *J. Amer. Chem. Soc.*, 1940, **62**, 1163.

[11] A. Ledwith, P. J. Russell, and L. H. Sutcliffe, *Chem. Comm.*, 1971, 964.

[12] F. A. Neugebauer and S. Bamberger, *Angew. Chem. Internat. Edn.*, 1971, **10**, 71.

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

[14] M. J. S. Dewar and D. S. Urch, *J. Chem. Soc.*, 1958, 3079.

[15] G. H. Williams, ' Homolytic Aromatic Substitution,' Pergamon, London, 1960.

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

Waters'[17] observations that whereas diphenylaminyl radicals are in general poor abstractors of hydrogen from C–H bonds, they convert 9,10-dihydroanthracene into an*thracene*. We were able to confirm this by adding 9,10-dihydroanthracene to the thermolysis of tetraphenylhydrazine in benzene when the yield of diphenylamine rose to 66% and anthracene was formed (56%; assuming a stoicheiometry of $Ph_2NNPh_2 + 2\,C_{14}H_{12} \longrightarrow 2\,C_{14}H_{10} + 2\,Ph_2NH$).

An attempt to use the same technique as a probe for diphenylaminyl radicals in the triethyl phosphite–diphenylnitroxyl reaction failed when it was discovered that diphenylnitroxyl will, itself, convert 9,10-dihydroanthracene into anthracene, *via* a hydrogen abstraction process of the following stocheiometry: $2\,Ph_2NO\cdot + C_{14}H_{12} \longrightarrow C_{14}H_{10} + 2\,Ph_2NOH$, the reaction being some twenty times faster than the triethyl phosphite deoxygenation of the nitroxide. Since diphenylhydroxylamine, produced in the dehydrogenation, is readily re-oxidised by air to diphenylnitroxide, the possibility was investigated of dehydrogenation of 9,10-dihydroanthracene by catalytic amounts of the nitroxyl with alternate exposures to air. In accord with this, reaction of diphenylnitroxyl with an excess of 9,10-dihydroanthracene in boiling benzene under nitrogen for 2 h led to anthracene and the equivalent amount of diphenylhydroxylamine. Passage of dry oxygen or air through the cooled system rapidly restored the colour of the nitroxyl. Reheating of the mixture under nitrogen led to a further conversion into anthracene and a regeneration of the hydroxylamine. Three such cycles led to conversion into 1 mM of anthracene by 1 mM of the nitroxyl, *i.e.* a yield of 200% based on the nitroxyl. The limitation of the method lies in the instability of diphenylhydroxylamine under the reaction conditions.

EXPERIMENTAL

Chromatography.—G.l.c. was carried out using a Pye 104 instrument with a flame ionisation detector. Columns were glass 5 ft or 7 ft × 0·4 cm i.d. packed with Chromosorb W which was treated with dimethyldichlorosilane before coating with silicones SE 30 (2·5% w/w) or OV 225 (2·5% w/w). Quantitative analysis was by the internal standard technique and all products were confirmed by comparison of retention times with authentic materials on at least two columns and by comparison of mass spectra.

High speed liquid chromatography was carried out using a Du Pont 820 liquid chromatograph. The stationary phase was Corasil II and the mobile phase 25% methylene chloride in hexane.

Materials.—Diphenylhydroxylamine from phenylmagnesium bromide and nitrosobenzene[18] had m.p. 59—61° (lit.,[19] 60°) and gave diphenylnitroxyl, m.p. 60—61° (lit.,[20] 62°), by oxidation with silver oxide.[20] Tetraphenylhydrazine, prepared by the oxidation of diphenylamine by potassium permanganate,[21] had m.p. 145—146° (lit.,[19] 147°). 4-Ethoxydiphenylamine was prepared by Ullman reaction of phenacetin with iodobenzene[22] and had m.p. 72—73° (lit.,[22] 74°). 2- and 3-*Ethoxydiphenylamine* were prepared in the same manner from the corresponding *N*-acetylphenetidines and were characterised as follows: the 3-*isomer* had m.p. 59—60° (Found: C, 78·65; H, 7·0; N, 6·4. $C_{14}H_{15}NO$ requires C, 78·8; H, 7·1; N, 6·6%), δ (100 MHz) 1·38 (3H, t), 3·95 (2H, q), 5·63 (1H, s), and 6·3—7·5 (9H, m); the 2-*isomer* had m.p. 47—48: (Found: C, 79·0; H, 7·15; N, 6·7%), δ (100 MHz) 1·43 (3H, t), 4·09 (2H, q), 6·15 (1H, s), and 6·7—7·5 (9H, m). Benzyl diethyl phosphite, b.p. 84° at 0·9 mmHg (lit.,[23] 85—88° at 1 mmHg), was prepared by transesterification of triethylphosphite with benzyl alcohol.[23] 4-Ethoxy-*NN*-dimethylaniline[24] had m.p. 35—36° (lit.,[19] 35—36·5°). *NN*-Diphenylbenzylamine prepared from benzyl bromide and the sodium salt of diphenylamine had m.p. 87—88° (lit.,[19] 88°).

o- *and* p-*Methoxy*-N-*t*-*butylanilines*. 2-Methyl-2-nitrosopropane[25] (0·05 mol) in ether (100 ml) was added at −15° over 2 h to 4-methoxyphenylmagnesium bromide (0·12 mol) in ether (120 ml). After 15 h at 0° standard work up gave a mixture of *N*-t-butyl-*p*-methoxyphenylhydroxylamine (70%), anisole, and 4,4′-dimethoxybiphenyl (by n.m.r.). Reduction of the crude mixture with tin and hydrochloric acid (4N) gave *p*-methoxy-*N*-t-butylaniline, b.p. 58—59° at 0·05 mmHg (lit.,[16] 54—57° at 0·04 mmHg), δ (60 MHz) 6·67 (4H, s), 3·67 (3H, s), and 1·17 (9H, s). *o*-Methoxy-*N*-t-butylaniline, b.p. 44—45° at 0·05 mmHg (lit.,[16] 48—49° at 0·05 mmHg), was prepared similarly, δ (60 MHz 6·4—6·8 (4H, m), 3·64 (3H, s), and 1·34 (9H, s).

Phenyl-t-butylnitroxyl. This was prepared by oxidation of *N*-t-butylphenylhydroxylamine by silver oxide,[26] $\lambda_{max.}$ (C_6H_{12}) 296 nm (lit.,[26] 298 nm).

All other materials were commercially available and were redistilled or recrystallised before use. All solvents were redistilled before use. Benzene and toluene were sodium dried.

Nitrogen was British Oxygen white spot and was purified by passing successively through chromous chloride solution, concentrated sulphuric acid, and sodium hydroxide pellets. Oxygen (B.O.C.) was dried by sulphuric acid.

Deoxygenation of Diphenylnitroxyl by Triethyl Phosphite.—The nitroxyl (1 mmol) was dissolved in solvent (25 ml) and the solution purged with nitrogen for 0·5 h. Triethyl phosphite (0·5 ml) was added and the solution heated under nitrogen until the colour of the nitroxyl had been discharged. The temperature was 80° for reactions in toluene and reactions in ethanol and benzene were carried out at the b.p.

The reaction in the presence of *NN*-dimethylaniline (0·5 g) in ethanol was carried out in exactly the same manner.

The reaction mixtures were analysed by g.l.c. and t.l.c. was used to check that none of the products detected by g.l.c. had arisen from pyrolysis in the chromatograph.

It was only found possible to separate 2-ethoxydiphenylamine from the mixture of the 3- and 4-isomers by g.l.c. However 3- and 4-ethoxydiphenylamine could be separated

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[17] R. A. Jackson and W. A. Waters, *J. Chem. Soc.*, 1958, 4632.

[18] W. Wieland and A. Rosseu, *Ber.*, 1912, **45**, 494.

[19] 'Dictionary of Organic Compounds,' Eyre and Spottiswoode, London, 1965.

[20] H. Wieland and M. Offenbächer, *Ber.*, 1914, **47**, 2114.

[21] H. Wieland and S. Gambarjan, *Ber.*, 1906, **39**, 1499.

[22] M. M. Chen, A. F. D'Amado, and R. I. Walter, *J. Org. Chem.*, 1961, **26**, 2721.

[23] F. W. Hoffmann, R. J. Ess, and R. P. Usinger, *J. Amer. Chem. Soc.*, 1959, **78**, 5817.

[24] F. Reverdin and F. Liepl, *J. prakt. Chem.*, 1912, **86**, 200.

[25] A. R. Forrester and S. P. Hepburn, *Org. Synth.*, 1972, **52**, 77.

[26] G. Chapelet-Letourneux, H. Lemaine, and A. Rassat, *Bull. Soc. chim. France*, 1965, 444.

by high speed liquid chromatography and the absence of the former isomer was confirmed by this technique.

Blank reactions, carried out with triethyl phosphite omitted, aimed at confirming that diphenylnitroxide was thermally stable under the reaction conditions, were analysed for nitroxyl by visible spectroscopy.

For reactions from which it was desired to isolate products the above quantities were increased tenfold and the reaction mixtures analysed by column chromatography. The identity of products was confirmed by comparison of their i.r. spectra with those of authentic materials and by mixed m.p. determinations.

Thermolysis of Tetraphenylhydrazine.—The hydrazine was dissolved in solvent (25 ml) and the solution purged with nitrogen for 0·5 h. The solution was then heated to 80° under nitrogen until no hydrazine could be detected by t.l.c. (*ca.* 6 h). Analysis was exactly as described for the phosphite–diphenylnitroxyl reaction and where products were to be isolated the reaction scale was similarly increased. Reactions in the presence of 9,10-dihydroanthracene (0·5 g) and benzyl diethyl phosphite (0·5 ml and 5·0 ml) were carried out in exactly the same manner.

Reaction of Phenyl-t-butylnitroxyl with Triethyl Phosphite in Methanol.—The nitroxyl (1 mM) was dissolved in methanol (25 ml) and triethyl phosphite (0·5 ml) was added. The mixture was purged with nitrogen and then heated, at reflux, under nitrogen for 48 h when the colour of the nitroxide was discharged. Methanol was removed and the basic components isolated by standard work up. Quantitative analysis by g.l.c. and m.s.–g.l.c. established the presence of *o*-methoxy-t-butylaniline (2·3%) and the *p*-isomer (15·3%), *i.e.* an isomer ratio $p:o = 6{\cdot}6$.

Dechlorination of N-*t-Butyl*-N-*chloroaniline in Methanol by Gassman's Method.*[16]—An exact repetition of Gassman's experiment gave a mixture of *p*- and *o*-methoxy-*N*-t-butylanilines in the ratio 6·6 : 1. Gassman reported [16] $p:o = 6{\cdot}5:1$.

Reactions of Diphenylnitroxyl with 9,10-*Dihydroanthracene.*—9,10-Dihydroanthracene (1 mmol) and diphenylnitroxyl (1 mmol) were dissolved in benzene (25 ml) and after purging with nitrogen the mixture was heated at reflux under nitrogen until the colour of the nitroxyl was discharged. Benzene was then evaporated and the residue chromatographed on silica gel. The column was eluted with light petroleum (b.p. 40—60°) until no more of the anthracene–9,10-dihydroanthracene mixture was detected in the eluant by t.l.c. The eluant was then evaporated to dryness and the weighed residue analysed by n.m.r. to determine the ratio of anthracene to 9,10-dihydroanthracene present.

Where the catalytic recycling process was to be carried out molecular sieve (type 4A) (1 g) was added to the reaction mixture and after carrying out the reaction in the normal manner as described above the mixture was cooled and a stream of oxygen passed through the solution until no further change in the visible absorbance occurred. The solution was then purged with nitrogen and then heated at reflux under nitrogen until the colour was again discharged.

Added in proof: Our postulate of an electron transfer between radicals, leading to an ion-pair, is strengthened by the very recent suggestion (E. M. Kosower, A. Teuerstein, and A. J. Swallow, *J. Amer. Chem. Soc.*, 1973, **95**, 6127) that protonated pyridinyl radicals undergo analogous transformations.

We are grateful to Dr. A. R. Forrester for a sample of phenyl-t-butylhydroxylamine.

[4/158 *Received*, 28*th January*, 1974]