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Preliminary communication

An ESR study of the reactions of t-butoxyl radicals with aminophosphines

R.W. DENNIS and B.P. ROBERTS

Christopher Ingold Laboratories, University College London, 20 Gordon Street, London WC1H OAJ (Great Britain)

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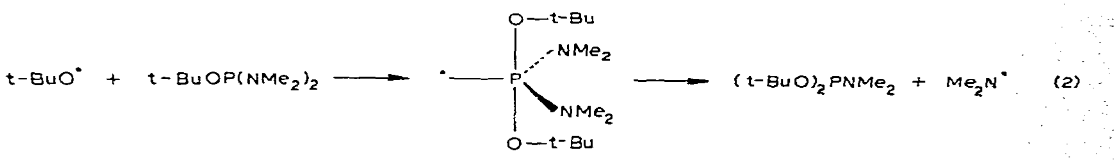
Phosphoranyl radicals have been detected by ESR spectroscopy as intermediates in the reactions of the phosphines $R_nP(OR')_{3-n}$ (n = 0–3) with alkoxyl radicals[1,2]. We now report a similar study of the aminophosphines $R_nP(NR'_2)_{3-n}$ and $(RO)_nP(NR'_2)_{3-n}$ with t-butoxyl radicals generated photolytically from di-t-butyl peroxide[1].

Tris(dimethylamino)phosphine, $(Me_2N)_3P$

When di-t-butyl peroxide was photolysed in the presence of this phosphine at −100° in cyclopropane solution a strong spectrum of the dimethylaminyl radical[3] [a(N) 14.6 G, a(H) 27.0 G at −90°] was immediately apparent. After a few minutes' irradiation a phosphoranyl radical (II) [a(P) 771 G at −100°] was also detectable and its concentration increased as the photolysis progressed. These results are consistent with reactions (1) and (2), (II) being a secondary product.

$$t\text{-BuO}^{\bullet} + (Me_2N)_3P \longrightarrow [t\text{-BuO}\dot{P}(NMe_2)_3] \longrightarrow t\text{-BuOP}(NMe_2)_2 + Me_2N^{\bullet} \qquad (1)$$

(I)

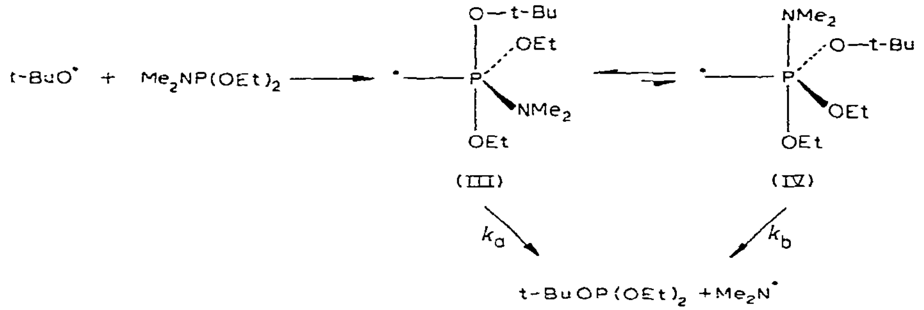


(II)

A similar phosphoranyl radical, $t\text{-BuO(EtO)}\dot{P}(NMe_2)_2$ [a(P) 785 G], was detected as a primary product from $EtOP(NMe_2)_2$ and t-butoxyl radicals. At −120° (II) decayed with first-order kinetics ($t_{1/2}$ ca. 10 s) when the light was shuttered.

Dimethylaminodiethoxyphosphine, $Me_2NP(OEt)_2$

In cyclopropane at −120° a phosphoranyl radical (III) [a(P) 841 G] was immediately apparent and a second phosphoranyl radical (V) [a(P) 885 G] appeared as the photolysis progressed. The spectrum of (III) showed a further splitting into a very poorly resolved 1/1/1 triplet [a(N) 2.8 G]. The dimethylaminyl radical was detected in addition to these phosphoranyl radicals.



(3)

$$t\text{-}BuO^{\bullet} + t\text{-}BuOP(OEt)_2 \longrightarrow \underset{(V)}{(t\text{-}BuO)_2\dot{P}(OEt)_2} \longrightarrow t\text{-}Bu^{\bullet} + OP(OEt)_2O\text{—}t\text{-}Bu \qquad (4)$$

In propane at −150° the spectrum of the dimethylaminyl radical was weak and a third phosphoranyl radical (IV) [a(P) 697 G, a(N) 12.7 G] was detected as soon as the irradiation was begun, although by −120° it was undetectable. The most probable structure of (IV) and the route by which it is formed are shown in eqn. (3). It seems likely that k_b is greater than k_a; that is, departure of the dimethylaminyl radical from an apical position in the thermodynamically less stable isomer is favoured[1,2].

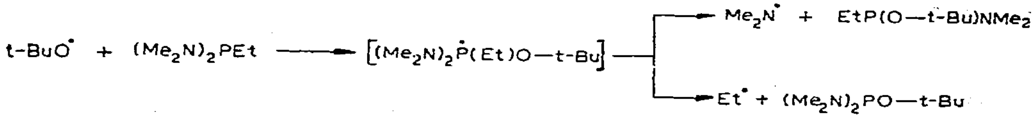
Photolysis of di-t-butyl peroxide in the presence of $(EtO)_2PNEt_2$ or $(EtO)_2PN(i\text{-}Pr)_2$ gave qualitatively similar results to the dimethylamino analogue, and the application of these reactions to the generation of specific aminyl radicals for ESR and kinetic studies should prove fruitful.

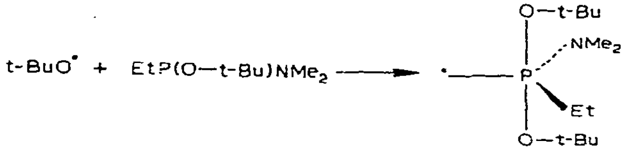
Bis(dimethylamino)ethylphosphine, $(Me_2N)_2PEt$

At −115° in cyclopropane no phosphoranyl radicals were immediately apparent. Both ethyl and dimethylaminyl radicals were, however, detected at once in the concentration ratio $[Et^{\bullet}]/[Me_2N^{\bullet}] = 0.6$, which did not change significantly with time. The phosphoranyl radicals (II) [a(P) 771 G at −100°] and (VI) [a(P) 740 G at −100°] were detected as secondary products.

Dimethylaminodiethylphosphine, Me_2NPEt_2

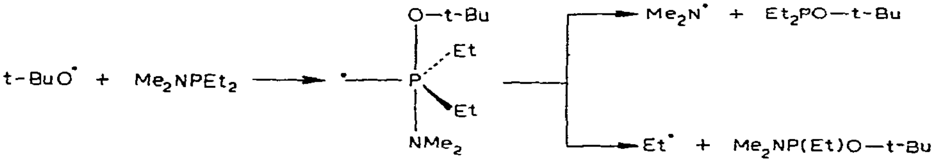
With this phosphine a phosphoranyl radical (VII) [a(P) 581 G, a(N) 12.6 G] was detected as a primary product at −120°, although the spectrum had disappeared above about −90°. On commencing photolysis the ratio $[Et^{\bullet}]/[Me_2N^{\bullet}]$ was 1.8 at −80°.





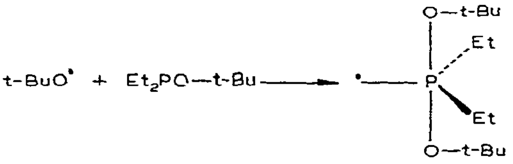
(6)

(VI)



(VII)

(7)



(VIII)

(8)

The spectrum[2] of (VIII) [a(P) 704 G at −120°] became apparent as a secondary product.

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