

Homolytic Addition to *N*-Methylene-*t*-butylamine: a New Route to Aminyl Radicals

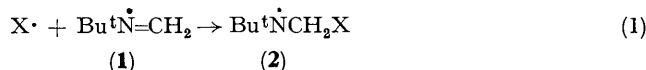
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Summary A variety of types of free radical ($X\cdot$) add to *N*-methylene-*t*-butylamine, $\text{Bu}^t\text{N}=\text{CH}_2$, to give aminyl radicals, $\text{Bu}^t\dot{\text{N}}\text{CH}_2$, the e.s.r. spectra of which have been detected.

ONLY two general methods are available for the generation of dialkylaminyl radicals in solution for study by e.s.r. spectroscopy. These involve photolysis of tetra-alkyl-tetrazenes¹ or the reaction of *t*-butoxyl radicals with dialkylaminophosphines.² Although homolytic addition to aldehydes, ketones, and alkenes is well established, very little is known about the corresponding reactions of the isoelectronic imines. An e.s.r. study of radical addition to $\text{Bu}^t_2\text{C}=\text{NH}$ has been reported,³ but only the long-lived adducts $\text{Bu}^t_2\dot{\text{C}}\text{N}(\text{H})\text{X}$ were detected.†

We report here that e.s.r. spectra of a variety of transient dialkylaminyl radicals (**2**) may be observed during photochemical generation of addenda in the presence of *N*-methylene-*t*-butylamine (**1**), which trimerises only slowly at room temperature^{4,5} [equation (1)].



Photolysis of azomethane in the presence of (**1**) (*ca.* 1 M in cyclopropane solvent) between 190 and 310 K gave rise to an e.s.r. spectrum assigned to the *t*-butyl(ethyl)aminyl radical (**2**; X=Me). The spectrum of the methyl radical was also apparent, and $[(\mathbf{2})]/[\text{Me}\cdot]$ increased with increasing temperature. Addition of *n*-propyl radicals (from photolysis of di-*t*-butyl peroxide in the presence of tripropylphosphine) to (**1**) was observed above 200 K, and the identification of (**2**; X=Prⁿ) was confirmed by generating² this radical by displacement from $[\text{Bu}^t(\text{Bu}^n)\text{N}]_3\text{P}$. The radical (**2**; X=Prⁿ) undergoes rapid self-reaction [$2k_t$, $3 \times 10^7 \text{ l mol}^{-1} \text{ s}^{-1}$ at 300 K] and hence the addition of methyl or propyl radicals to (**1**) is a relatively rapid process ($k_{\text{add}} 10^2\text{--}10^3 \text{ l mol}^{-1} \text{ s}^{-1}$ at 270 K).

Photolysis of azoisobutane in the presence of (**1**) afforded the spectra of the *t*-butyl radical and of the aminyl adduct (**2**; X=Bu^t), and these radicals were also detected during photolysis of a solution of di-*t*-butyl peroxide and (**1**) in isobutane. A number of other types of radical add to (**1**) to give aminyl adducts (**2**) and the results are summarised in the Table.

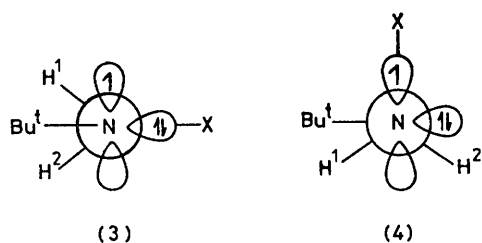
The β -proton splitting for (**2**; X=Me) is large and increases with decreasing temperature, suggesting that the most stable conformation of this radical is that shown in (**3**).

TABLE. E.s.r. parameters for aminyl radicals $\text{Bu}^t\dot{\text{N}}\text{CH}_2\text{X}$ in cyclopropane

X	Temp./K	<i>g</i> -Factor	Hyperfine splittings/G		$d a(\text{H}_\beta) /dT/\text{mG K}^{-1}$
			$a(\text{N})$	$a(2\text{H}_\beta)$	
Me	309	2.0047	14.5	36.8	-24
Pr ⁿ	307	2.0047	14.5	37.3	-19
Bu ^t	311	2.0048	14.6	39.2	-8
CF ₃	227	2.0048	14.5	37.3	-17
H ₂ (HO)C	307	2.0045	15.0	36.9	-19
H ₂ (MeO)C	310	2.0049	14.6	36.0	-24
Me(H)(HO)C	282	2.0045	15.1	40.1 (1H _A) 36.2 (1H _B)	-26 (H _A) <i>ca.</i> 0 (H _B)
Me(H)(EtO)C	202	2.0047	14.7	41.1 (1H _A) 37.7 (1H _B)	-29 (H _A) <i>ca.</i> 0 (H _B)
Me ₂ (HO)C ^a	307	2.0048	15.1	39.2	-9
Et ₃ Si	307	2.0047	14.6 ^b	23.3 ^b	+14

^a This radical was also obtained by thermolysis of di-*t*-butyl hyponitrite at 340 K in the presence of (**1**) and isopropyl alcohol in *t*-butylbenzene solvent. ^b $a(^{29}\text{Si})$ 32.6 G at 304 K.

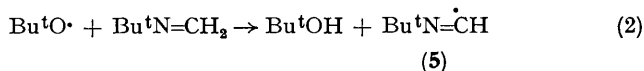
† Addition to carbon is expected to be very slow as a result of steric effects and the radical $\text{Bu}^t_2\dot{\text{C}}(\text{X})\dot{\text{N}}\text{H}$ would be much shorter lived than $\text{Bu}^t_2\dot{\text{C}}\text{N}(\text{H})\text{X}$.



The same conformation appears to be adopted by all the adducts of carbon-centred radicals, and the relatively small value of $d|a(\text{H}_\beta)|/dT$ for (2; X=Bu^t) is in accord with a greater resistance to torsional motion about the N-C_β bond than in (2; X=Me), presumably because of steric effects. However, the spectrum of (2; X=Et₃Si) shows a relatively small value of $a(\text{H}_\beta)$ which decreases with decreasing temperature. We conclude that the most stable conformation of (2; X=Et₃Si) is (4), in which hyperconjugative interaction between the unpaired electron and the Si-C_β bond is maximised and in which H¹ and H² are non-equivalent. In accord with this, lines corresponding to $M_I(\text{H}_\beta) = 0$ broaden relative to the other lines in the spectrum as the temperature is reduced, showing that rotation about the N-C_β bond is becoming slow on the e.s.r. time scale. The alkyl radicals MeCH₂ĊH₂⁶ and Et₃SiCH₂ĊH₂⁷ show similar preferences for 'staggered' and 'eclipsed' conformations, respectively.

α-Hydroxyalkyl radicals[†] appear to add more rapidly to (1) than do alkyl or α-alkoxyalkyl radicals. For example, photochemical generation of H₂ĊOH in the presence of (1) gave rise only to the spectrum of the aminyl adduct and the addendum could not be detected. The spectra of the α-hydroxyalkyl radical adducts exhibit selective broadening at low temperatures of lines corresponding to $M_I(\text{H}_\beta) = 0$. We attribute this line shape effect to restriction of rotation about C_β-C_γ, and it seems likely that intramolecular hydrogen bonding between the OH group and the radical centre may contribute to the rotational barrier, since a similar effect was not observed for the adducts of α-alkoxyalkyl radicals. The β-protons in the aminyl adducts of MeĊ(H)OH and MeĊ(H)OEt are diastereotopic and give rise to markedly different splittings.

Photolysis of di-*t*-butyl peroxide in the presence of (1) in cyclopropane solvent at low temperature does not give an aminyl adduct, but a spectrum assigned⁸ to the imidoyl σ-radical (5) [$a(1\text{H})$ 68.5, $a(1\text{N})$ 4.6 G, g 2.0018 at 210 K] is detected. This radical is presumably formed by abstraction of hydrogen from (1) [equation (2)].



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[†] Produced by photolysis of Bu^tOObu^t in the presence of the appropriate alcohol. Methanol is reported (ref. 5) to add to (1) to give MeOCH₂N(H)Bu^t, but no spectra attributable to radicals of the type ROCH₂NĊBu^t were detected in these systems.

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