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TRAPPING OF RADICAL INTERMEDIATES IN THE PHOTOREDUCTION OF BENZOPHENONE

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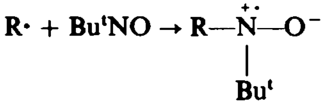
Abstract—Radical intermediates formed during the photoreduction of benzophenone by alcohols, amines, phenols, sulphides, thiols, ethers, hydrocarbons and amides have been trapped by t-nitrosobutane and the resulting nitroxide radicals characterized *in situ* by ESR. In the case of 2,6-di-t-butylphenols and aliphatic sulphides evidence was obtained for radicals other than those expected.

THE photoreduction of benzophenone has been studied with a variety of hydrogen donors viz: alcohols,[1-5] amines,[6-8] phenols,[9] sulphides,[10] thiols,[11] ethers,[12-14] and hydrocarbons.[15-19] Intermediates formed from benzophenone have been observed using spectral [20-23] and flash photolysis[5, 24-26] techniques and those formed from the donor molecules inferred from studies with deuterated[8, 14, 27] or optically active[8, 14, 27, 28] donors. We have studied these systems in the presence of t-nitrosobutane (I) which reacts (Eq 1) with the radicals formed to give more stable nitroxide radicals (II) which can be characterized using electron spin resonance (ESR).[29-34] Parameters for the signals of radicals detected are summarized in Table 1.



$$R\cdot + Bu^tNO \rightarrow R\text{—}\underset{\displaystyle Bu^t}{\underset{|}{\overset{+\cdot}{N}}}\text{—}O^- \qquad (1)$$

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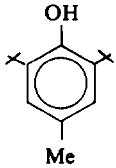
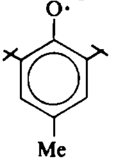
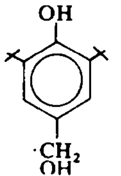
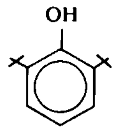
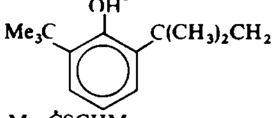
The most extensively studied hydrogen donor is isopropanol where radicals derived from benzophenone and isopropanol (III and IV resp) are formed[4] according to Eq. 2:

$$Ph_2C{=}O^* + Me_2CHOH \rightarrow \underset{III}{Ph_2\dot{C}\text{—}OH} + \underset{IV}{Me_2\dot{C}\text{—}OH} \qquad (2)$$

TABLE 1. NITROXIDE RADICALS FORMED DURING PHOTOLYSIS OF BENZOPHENONE IN VARIOUS HYDROGEN DONORS CONTAINING t-NITROSOBUTANE

Hydrogen Donor	Trapped Radical	Hfs Constants (Gauss)		g-value
Me_2CHOH	$Me_2\dot{C}OH$	$a_N = 15{\cdot}84$,		2·0059(3)
Me_2CHOH	*H·	$a_N = 13{\cdot}60$,	$a_H^{NH} = 12{\cdot}36$	2·0062(1)
EtOH	$Me\dot{C}HOH$	$a_N = 14{\cdot}88$,	$a_H^{CH} = 2{\cdot}38$	2·0061(2)
n-BuOH	$MeCH_2CH_2\dot{C}HOH$	$a_N = 14{\cdot}70$,	$a_H^{CH} = 1{\cdot}87$	2·0061(6)
MeOH	$\dot{C}H_2OH$	$a_N = 14{\cdot}79$,	$a_H^{CH_2} = 5{\cdot}07$	2·0060(8)
PhCHOH/Benzene	*H·	$a_N = 13{\cdot}74$,	$a_H^{NH} = 12{\cdot}16$	2·0061(9)
n-BuNH$_2$	$MeCH_2CH_2\dot{C}HNH_2$	$a_N = 15{\cdot}09$,	‡	2·0061(6)
Me_2CHNH_2	$Me_2\dot{C}NH_2$	$a_N = 15{\cdot}53$,	$a_N^{NH_2} = 0{\cdot}69$	2·0061(3)
Et_3N	$Et_2N\dot{C}HCH_3$	$a_N = 14{\cdot}35$,	$a_H^{CH} = 4{\cdot}06$	2·0063(5)
Bu_3N	$Bu_2N\dot{C}HCH_2CH_2Me$	$a_N = 14{\cdot}07$,	$a_H^{CH} = 3{\cdot}85$	2·0062(7)
 /Benzene		$a_H^{CH_3} = 11{\cdot}24$,	$a_H^{meta} = 1{\cdot}66$	2·0047(5)
		$a_N = 15{\cdot}27$,	$a_H^{CH_2} = 7{\cdot}46$	2·0061(9)
 /Benzene		$a_N = 13{\cdot}29$,	$a_H^{CH_2} = 1{\cdot}89$	2·0060(4)
$Me_2CHSCHMe_2$	$Me_2\dot{C}SCHMe_2$	$a_N = 14{\cdot}21$,		2·0061(5)
$Me_2CHSCHMe_2$	$Me_2CHS\cdot$	$a_N = 16{\cdot}99$,		2·0068(8)
$Me(CH_2)_3S(CH_2)_3Me$	$Me(CH_2)_3S\cdot$	$a_N = 18{\cdot}21$,		2·0070(6)
PhMe	$PhSCH_2$	$a_N = 13{\cdot}83$,	$a_H^{CH_2} = 5{\cdot}90$	2·0064(5)
PhSH/Benzene	$PhS\cdot$	$a_N = 16{\cdot}75$,		2·0066(7)
EtOEt	$Me\dot{C}HOEt$	$a_N = 13{\cdot}55$,	$a_H^{CH} = 2{\cdot}83$	2·0063(7)
$Me(CH_2)_5Me$	$Me(CH_2)_n\dot{C}H(CH_2)_{4-n}CH_3$	$a_N = 14{\cdot}22$,	$a_H^{CH} = 1{\cdot}50$	2·0062(8)
PhMe	$PhCH_2$	$a_N = 14{\cdot}98$,	$a_H^{CH_2} = 7{\cdot}27$	2·0062(5)
MeCONHMe	$MeCONH\dot{C}H_2$	$a_N = 15{\cdot}15$,	$a_H^{CH_2} = 7{\cdot}66$ $a_N^{NH} = 2{\cdot}76$	2·0062(2)

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[*] See equation (3) in text.

[†] The 2,6-di-t-butyl-4-methylphenoxy radical is not trapped by t-nitrosobutane.

[‡] Not calculated (see Fig. 1b).

When this photolysis was carried out in the presence of t-nitrosobutane (I) an ESR spectrum (Fig. 1a) arising from two nitroxide species was obtained. The parameters of one signal, a triplet of doublets, are similar to those published[35] for t-butyl nitroxide (V) and we envisage its formation from the benzophenone derived radical (III)

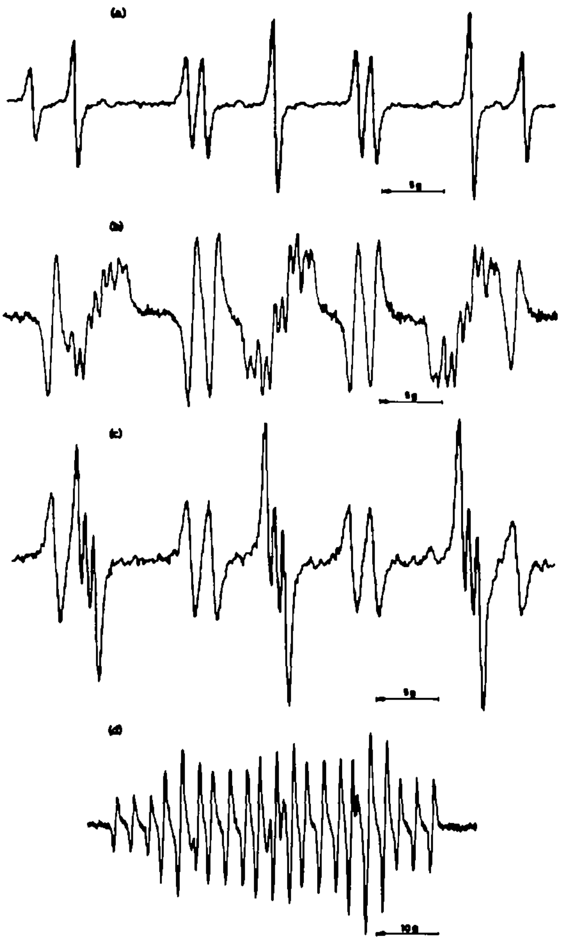
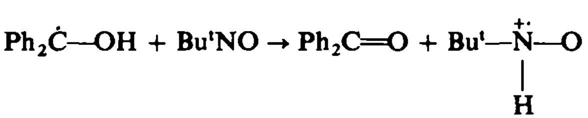


FIG. 1 ESR spectra of nitroxide radicals formed during photolysis of benzophenone solutions containing *t*-nitrosobutane. (a) iso-propanol, (b) n-butylamine, (c) iso-propylamine, (d) N-methylacetamide.



$$\underset{\text{III}}{Ph_2\dot{C}\text{—}OH} + Bu^tNO \rightarrow Ph_2C\text{=}O + \underset{\text{V}}{Bu^t\text{—}\overset{+\cdot}{\underset{\substack{|\\ H}}{N}}\text{—}O} \quad (3)$$

according to Eq. 3. This nitroxide (V) was the sole radical formed when benzhydrol was used as hydrogen donor (the radical derived from benzhydrol is the same as that from benzophenone (Eq. 2) and was formed when many other hydrogen donors were used. Furthermore, this nitroxide (V) was also formed when acetophenone was used instead of benzophenone; oxidation of the ketyl radical derived from acetophenone in a manner analogous to Eq. 3 is possible. The other signal in Fig. 1a (a simple triplet) may be assigned to a nitroxide radical formed by scavenging of the C-centred radical (IV) derived from isopropanol (Table 1).

With ethanol and methanol, the nitrogen hyperfine component of the signals derived from these hydrogen donors was further split into a doublet and triplet respectively, due to the interaction of the unpaired electron with the $-\mathrm{CH}<$ and $-\mathrm{CH_2}-$ protons adjacent to the N atom. This indicates scavenging of radicals formed by abstraction of α—CH protons.

Primary amines with an α—CH proton available for abstraction gave rise to ESR signals indicating the formation of C-centred radicals as well as the benzophenone derived t-butyl nitroxide (V). Isopropylamine (Fig. 1c) gave a triplet signal further split into a 1:1:1 triplet presumably due to the amino nitrogen.[36] Both n-butylamine and n-propylamine gave similar signals (Fig. 1b) in which each of the nitroxide ^{14}N hyperfine components was apparently split into nine components (intensity ratios 1:2:3:4·5:4:4·5:3:1:1, and separation 0·60 g, determined using an iterative least squares procedure[37] for resolving the overlapping bands). This signal might arise from trapping of a radical formed by H-abstraction from the α-C atom; the observed splittings could be due to the superimposition of the amino ^{14}N and β-$\mathrm{CH_2}$ triplets on the larger α-CH doublet. t-Butylamine which lacks α-CH protons did not give rise to a hydrogen donor derived radical; only a strong triplet of doublets due to t-butyl nitroxide (V) was observed indicating that photoreduction of benzophenone had occurred.

FIG. 2 ESR spectra of the 2,6-di-*t*-butyl-4-methylphenoxy radical (a) and the trapped benzyl nitroxide (b) obtained during photolysis of benzophenone in the presence of 2,6-di-*t*-butyl 4-methylphenol and *t*-nitrosobutane. Spectrum (a) appears first, and then spectrum (b).

As secondary amines only gave rise to weak, broad spectra no conclusions could be drawn about the nature of the trapped radicals. Tertiary amines (e.g. triethylamine and tri-n-butylamine) gave a triplet of doublets indicating that abstraction of an α-CH proton occurred.

In the case of 2,6-di-t-butylphenols well resolved spectra were obtained. For 2,6-di-t-butyl-4-methylphenol the initial signal (4 triplets in the ratio 1:3:3:1)

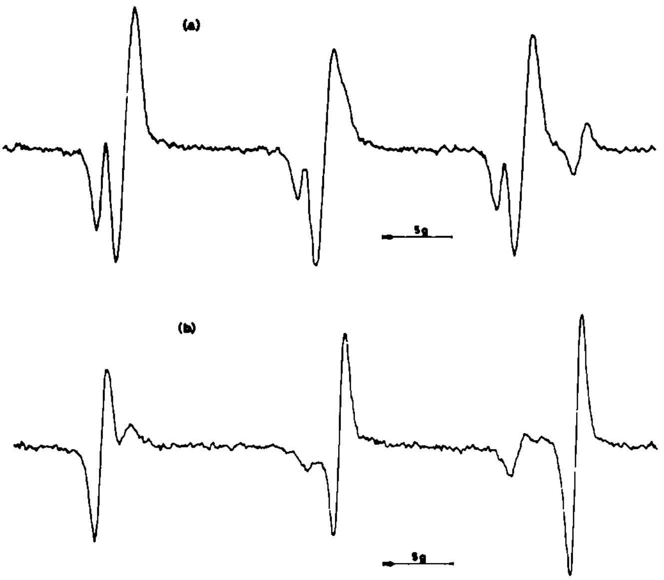


FIG. 3 ESR spectra of nitroxide radicals formed during photolysis of benzophenone in the presence of di-isopropyl sulphide and *t*-nitrosobutane. (a) Spectrum observed during photolysis, (b) spectrum observed directly after photolysis.

observed was due to the phenoxy radical[38] (Fig. 2a) itself: no trapping by t-nitrosobutane (I) occurred. On further irradiation a second signal of the benzyl nitroxide type (cf. toluene as hydrogen donor—Table 1) appeared and this presumably results from abstraction of hydrogen from the 4-Me group. Fig. 2b shows the spectrum of the two radicals. With 2,6-di-t-butylphenol itself no phenoxy radical was detected but on continued irradiation a triplet of triplets appeared which was presumably due to trapping of a radical formed by abstraction of a hydrogen atom from a t-butyl group.

Although quantum yields for photoreduction of benzophenone by sulphides are small,[10] strong ESR signals were obtained in the presence of the t-nitrosobutane scavenger (I). For di-isopropyl sulphide the initial signal observed (Fig. 3a) was a simple triplet which we assign to trapping of a C-centred radical. On further irradiation or removal of the irradiation source a second triplet signal, shifted appreciably downfield, appeared (Fig. 3b) which was identical to that obtained by trapping of the isopropyl thiyl radical (prepared by direct photolysis of the corresponding disulphide at 300 nm). A similar situation seemed to occur for di-n-butyl sulphide except that the nitroxide radical derived from the n-butyl thiyl radical appeared to be formed more readily (scavenging of the C-centred radical gave rise to a weak triplet of doublets). These results could indicate that the small quantum yields for benzophenone reduction are due to inhibition by thiyl radicals[39] rather than quenching by the sulphide (cf. ref. 10). For methyl phenyl sulphide a signal (a triplet of triplets in the ratio 1:2:1) was obtained which we assign to trapping of the C-centred radical formed by abstraction of a proton from the Me group. No simple triplet signal corresponding to trapping of a phenyl thiyl radical was observed. Such a signal was observed when thiophenol was used as a hydrogen donor.

Aliphatic ethers (e.g. diethyl ether) gave spectra which indicated the expected trapping of C-centred radicals adjacent to oxygen. Similarly, with aliphatic hydrocarbons (e.g. n-heptane) trapping of C-centred radicals occurred.

No signal arising from H-abstraction from acetamide could be obtained; this is possibly due to its insolubility in benzene. N-methylacetamide gave a spectrum (Fig. 1d) which may be interpreted as being due to trapping of a C-centred radical formed by abstraction of an H atom from the N-Me group; each of the nitroxide ^{14}N hyperfine components was split into a triplet of triplets resulting from the interaction of the unpaired electron with the methylene protons($a_H^{CH_2}$ = 7·66 g) and the amide nitrogen (a_N = 2·76 g). N,N-dimethylacetamide gave a similar but more complex spectrum resulting from more than one trapped radical.

Thus in most cases we have been able to demonstrate the presence of radical intermediates which are thought to occur in the photoreduction of benzophenone by various hydrogen donors. For two classes of compounds (2,6-di-t-butyl phenols and aliphatic sulphides) it appears that radicals (alkyl and thiyl respectively) additional to those expected are formed. However, the significance of these observations to the major reaction sequences has yet to be elucidated.

EXPERIMENTAL

The t-nitrosobutane dimer was prepared by oxidation of t-butyl-hydroylamine[40] with aqueous alkaline hypobromite soln[41] and had m.p. 79–80° (Lit.[41] m.p. 83–84°). Benzophenone and the hydrogen donors were commercially available samples of analytical quality.

For irradiation deoxygenated solns of benzophenone (0·05 M) and the nitrosobutane (0·01 M) in the neat hydrogen donor or benzene–hydrogen donor solns (5 to 10% donor) were prepared. The solns were transferred to a flat quartz cell and inserted in a Varian V-4531 ESR cavity. The 365 nm output from a Bausch and Lomb High Intensity grating monochromator, with a super pressure 200 W mercury lamp, was focused on the sample.

ESR spectra were measured on a Varian V-4502 X-band spectrometer employing 100 kc/s modulation, and recorded on a Moseley 7001A X-Y recorder. g-Values were obtained by comparison with the spectrum of Fremy's salt in Na_2CO_3aq. Values quoted are referred to the central hyperfine component, taken to have a g-value of 2·0057.[42] Hyperfine splittings were also measured relative to that of Fremy's salt (a_N = 13·09 g),[43] the spectrum of which was recorded simultaneously with each sample. The microwave power incident on the cavity was of the order of 20–25 dB below 100 mW, at which level saturation of the resonance did not occur.

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