Organic Peroxides. Part 12.[1] The Preparation and Properties of Some Triazinyl Peroxides

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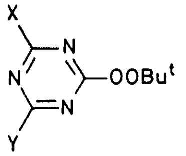
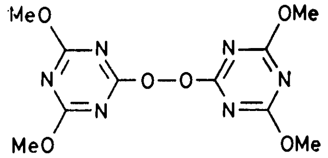
The triazinyl peroxides (*A*; X = Y = OOBu^t; X = OMe, Y = OOBu^t; X = Y = OMe; X = NEt$_2$, Y = OOBu^t; X = Y = NEt$_2$) and (*B*) have been prepared from the reaction between the appropriate peroxidic nucleophile and chlorotriazine. The structures of the peroxides are confirmed by their ^{13}C n.m.r. spectra, and by the recovery of t-butyl hydroperoxide when the peroxides (*A*; X = Y = OOBu^t; X = OMe, Y = OOBu^t) were hydrolysed.



(*A*)



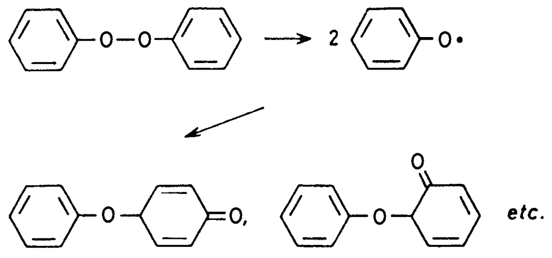
(*B*)

These peroxides are thermally stable up to *ca.* 90 °C. Photolysis of the peroxides (*A*) gives the radical Bu^{t}O· and $XYC_3N_3O\cdot$. The e.s.r. spectra of the triazinoxyl radicals could not be observed, but the adducts $XYC_3N_3OCH_2CH_2\cdot$ and $XYC_3N_3O\dot{P}(OMe)_3$, which they form with ethylene and with trimethyl phosphite, respectively, were detected. It is suggested that these properties imply that the radicals have a σ-O rather than a π-delocalised structure.

THE organic peroxides have played a major part in the development of the understanding of free radical mechanisms, because the weak oxygen–oxygen bond readily undergoes photolysis or thermolysis to give alkoxyl radicals which can be used to bring about secondary reactions. In particular, di-t-butyl peroxide has been used extensively because it is readily available, safe to handle, and otherwise fairly unreactive.[2]

There is a severe need for sources of alternative oxyl radicals, with varying electronic and steric properties, for use in studies of homolytic reactions. The perfluoro-t-butoxyl radical is useful in this respect, but its precursor, bis(perfluoro-t-butyl) peroxide, is rather hazardous and expensive to prepare.[3] More use has been made of the trimethylsilyloxyl radical whose properties are usefully different from those of the t-butoxyl radical[4] and whose precursor, bis(trimethylsilyl) peroxide, is readily available.[5,†] The protonated t-butoxyl radical, which can be prepared by photolysing di-t-butyl peroxide in the presence of trifluoroacetic acid, also shows promise of being a useful reagent.[6]

Many reports of the isolation of diaryl peroxides can be found in the older literature,[7] and some still appear, but none has yet stood up to examination. The dissociation energy of a normal peroxide bond is *ca.* 150 kJ mol^{-1}, but phenoxyl radicals are stabilised by benzylic resonance by *ca.* 67 kJ mol^{-1}.[8] In diphenyl peroxide, the dissociation energy of the peroxide bond would therefore be *ca.* 150 − (2 × 67) = 16 kJ mol^{-1}, and the peroxide would not be stable at room temperature. The phenoxyl radicals instead undergo head-to-tail and tail-to-tail dimerisation to give phenoxycyclohexadienones and bis(cyclohexadienones) [equation (1)]; in any case, resonance-stabilised phenoxyl radicals would be too unreactive to be of much use in most free radical reactions.

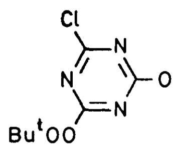


(1)

It is therefore particularly interesting that some heteroaryl peroxides appear to be surprisingly stable: it raises the question of the origin of the stability, and the possibility that these peroxides might be a source of heteroaryloxyl radicals with a useful reactivity. The peroxyazines (I)—(V) have been reported to be formed from the reaction between the appropriate chloroazines and hydroperoxides. The stability decreased as the number of nitrogen atoms in the aromatic ring decreased, and the diazine and monoazine peroxides (IV) and (V) were reported to rearrange as shown in equations (2) and (3).

We report here a study of the preparation and structure, and some of the reactions of some 1,3,5-triazinyl peroxides.

[†] *WARNING.* Dr. A. R. Forrester, University of Aberdeen, has informed us that a specimen of the hydrogen peroxide complex of diazabicyclo-octane (DABCO) prepared from concentrated hydrogen peroxide, which is used in preparing the disilyl peroxide, exploded when being dried overnight in a desiccator. The precise reason for the explosion is not clear, but suitable precautions should be taken when this compound is handled.



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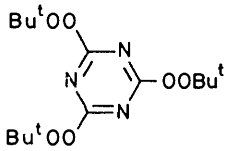

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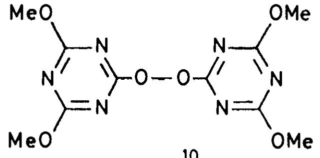

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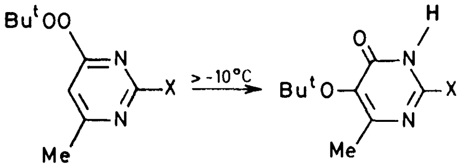
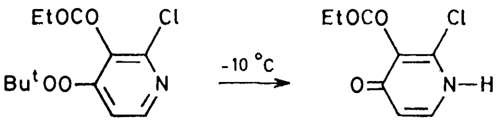


(2)

(IV)[11,12](X=H or Cl)



(3)

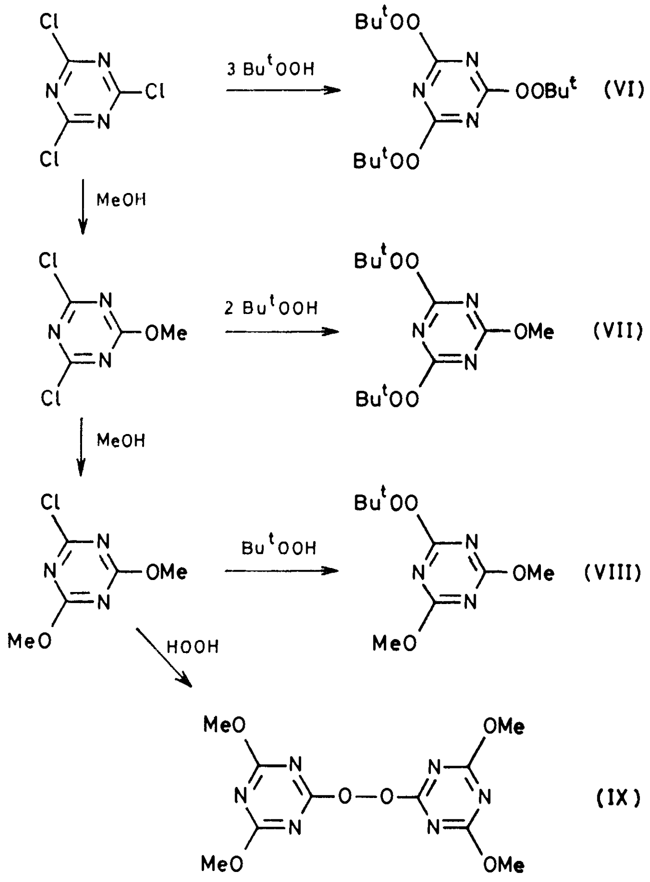
(V)[11,12]

DISCUSSION

The Preparation of Triazinyl Peroxides.—The triazinyl peroxides (VI)—(IX) were prepared by the reaction between the appropriate chlorotriazine and hydroperoxide in the presence of aqueous sodium hydroxide, as shown in Scheme 1.

Alternatively the peroxides (VIII) and (IX) were prepared using sodium t-butyl peroxide or sodium peroxide respectively in hydrocarbon suspension, and (VI) and (VIII) using t-butyl hydroperoxide in the presence of silver trifluoroacetate. No reaction occurred during 16 h between $(\mathrm{MeO})_2\mathrm{ClC_3N_3}$ and the DABCO complex of t-butyl hydroperoxide in hexane.

The products were all crystalline solids which by differential thermal analysis were found to be stable up to 90—110 °C when they decomposed by a rapidly developing, highly exothermic reaction (Table 1). The triperoxide (VI) (0.09 g) decomposed so violently that the enthalpy change could not be measured, and a sample of the monoperoxide (VIII) exploded during distillation.



Scheme 1

Much of the literature on triazines is concerned with the amino-substituted compounds because of their insecticidal activity. The peroxides $(\mathrm{Bu^tOO})(\mathrm{Et_2N})_2\mathrm{C_3N_3}$ (X) and $(\mathrm{Bu^tOO})_2(\mathrm{Et_2N})\mathrm{C_3N_3}$ (XI) were obtained

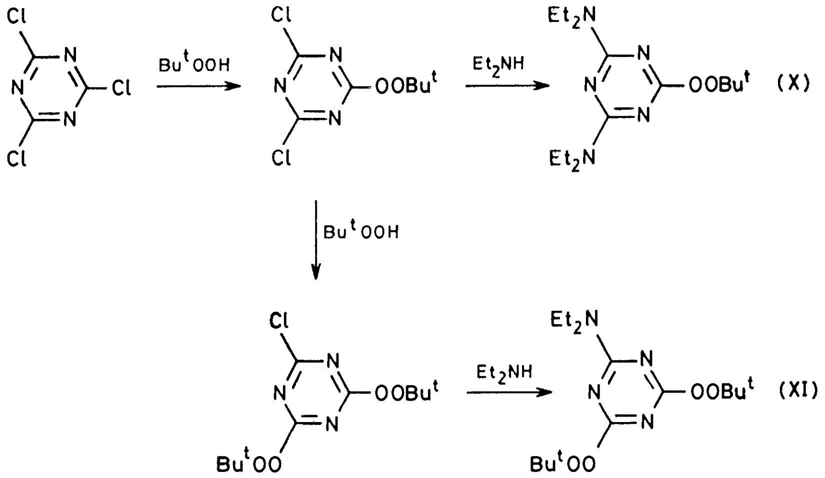
Table 1

Thermal analysis of triazinyl peroxides

Compound [Weight (g)]	Temperature at change (°C)		Differential changes			Comments
	Initial	Maximum	Wt. loss (%)	Temperature (°C)	Enthalpy ($\mathrm{kJ\ mol^{-1}}$)	
$(\mathrm{Bu^tOO})(\mathrm{MeO})_2\mathrm{C_3N_3}$	29	41	0	−0.6	−5.3	Melting
[0.0863]	107	143, 155	25	+4.6, +4.2	+54.6	*a*
$(\mathrm{Bu^tOO})_2(\mathrm{MeO})\mathrm{C_3N_3}$	61	69	0	−1.3	−8.8	Melting
[0.0981]	114	127	64	+10.0	+15.9	*b*
$(\mathrm{Bu^tOO})_3\mathrm{C_3N_3}$	38	45	0	−0.5	−8.9	Melting
[0.0908]	91	110	60	+20.0	*c*	*c*
Picric acid	38	127	0	−2.0	−8.3	Melting
[0.1327]	91	243, 287	75	+1.6, +3.2	+140	*d*

[a] Rapidly developing two-stage exothermic reaction. [b] Rapidly developing highly exothermic reaction. [c] Violent reaction, too exothermic to be measured. [d] Two-stage exothermic reaction.

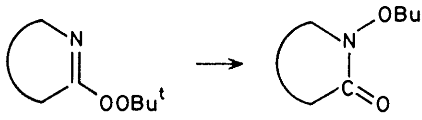
as shown in Scheme 2 by treating trichlorotriazine first with t-butyl hydroperoxide then with diethylamine and were characterised by ^{13}C n.m.r. spectroscopy.



Scheme 2

Attempts to invert the sequence of introducing the amino- and peroxy-groups were unsuccessful, because the amino-groups reduce the reactivity of the remaining chloro-substituents. Under most conditions, the compounds $(EtNH)_2(Cl)C_3N_3$ (Simazine), $(EtNH)(NCMe_2CNH)(Cl)C_3N_3$ (Bladex), $(Et_2N)(Cl)_2C_3N_3$, and $(Et_2N)_2(Cl)C_3N_3$, were recovered, and only $Cl_2(Et_2N)C_3N_3$ showed any sign of reaction with Bu^{t}OONa in benzene.

Evidence for the Peroxide Structures.—Evidence for the structure of the compounds (VI)—(XI) as heteroaromatic peroxides seems convincing. The elemental analysis, including that for 'peroxide oxygen' for compounds (VI)—(IX), is satisfactory, and the only reasonable alternative to a peroxide structure is the ketohydroxylamine structure (XII).



(XII) (4)

Moreover, hydrolysis of the compounds which we identify as the tri- (VI) and di-peroxide (VII) under acid conditions gave t-butyl hydroperoxide which was identified by g.l.c.; it is hardly conceivable that a rearranged structure such as (XII) could give t-butyl hydroperoxide on hydrolysis.

The ^{13}C n.m.r. spectra support the peroxide structures. The chemical shift of carbon atoms in the ring was 176 p.p.m., as it is in $(MeO)_3C_3N_3$, but which is far from the value of *ca.* 149 p.p.m. which is found for the keto-group in the ring in the compounds (XII).[13] Similarly, the chemical shift of the tertiary carbon atom in the t-butyl group (84—85 p.p.m.) is close to the value for other t-butyl peroxides (*e.g.* 78 p.p.m. for Bu^{t}OOBu^t), but lower than that normally found in t-butylmono-oxy-compounds.

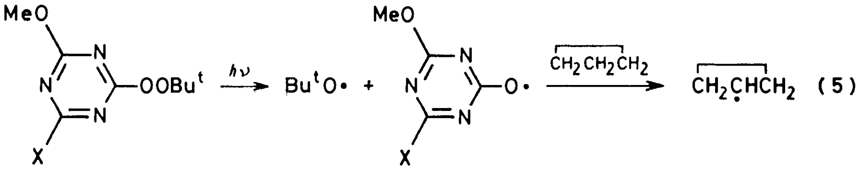
The combined techniques of i.r. and Raman spectroscopy have been applied to the peroxides $(Bu^tOO)(MeO)_2C_3N_3$ (VIII) and $(MeO)_2C_3N_3OOC_3N_3(OMe)_2$ (IX) by Bleckmann,[14] and the results have been analysed using his frequency calculation model.[15] For the compound (VIII), a Raman band at 885 cm^{-1} (calc. 886 cm^{-1}), force constant 2.70 mdyn Å^{-1}, is assigned to the O–O stretch. For compound (IX), ν(O–O) is identified with a Raman band at 895 cm^{-1} (calc. 900 cm^{-1}), force constant 3.14 mdyn Å^{-1}, and it is concluded that the molecule has a planar structure.

The same conclusion comes from preliminary results of an *X*-ray diffraction study of (IX),[16] which shows that the crystals are monoclinic, with the unit cell dimensions $a = 7.3$, $b = 3.8$, $c = 13.4$ Å. The very short b dimension suggests strongly that the molecules must be planar.

E.S.R. Study of the Photolysis of Triazinyl Peroxides.—The compounds were photolysed in solution in the presence of various reactants in the cavity of an e.s.r. spectrometer, and the spectra which were observed gave further evidence for the peroxide structures.

Unfortunately, the bistriazinyl peroxide (IX), which would give only the triazinyloxyl radical on photolysis, was too insoluble to be studied by this technique, and studies had to be limited to the triazinyl t-butyl peroxides which present the problem of distinguishing between the reactions of the triazinyloxyl and t-butoxyl radicals which are formed. The best reagents for achieving this are ethylene, which is rather unreactive towards the t-butoxyl radical,[17] and trialkyl phosphites which with oxyl radicals form adducts with characteristic e.s.r. spectra.[18]

Photolysis of the peroxides $(Bu^tOO)(MeO)_2C_3N_3$ (VIII) and $(Bu^tOO)_2(MeO)C_3N_3$ (VII) in cyclopropane alone gave a strong spectrum of the cyclopropyl radical, $a(H_\alpha)$ 6.6, $a(4H_\beta)$ 23.6 G, similar to that which is observed when di-t-butyl peroxide is photolysed under the same conditions. The significant point is that no e.s.r. spectrum, which might be ascribed to the triazinyloxyl radical (XIII) could be observed, although the observation of the cyclopropyl radical confirms that (XIII) must be formed. Either the triazinyloxyl radical (XIII) abstracts hydrogen rapidly from cyclopropane, or (like the t-butoxyl radical but unlike the phenoxyl radical) [19] it has an e.s.r. spectrum which is too broad to be observed in fluid solution.


(5)

(VII) X = Bu^{t}OO
(VIII) X = MeO
(XIII)

Photolysis of di-t-butyl peroxide in the presence of trimethoxytriazine in cyclopropane similarly showed only the spectrum of the cyclopropyl radical and there was no complication from radicals resulting from the addition of t-butoxyl radicals to the heteroaromatic ring, or from abstraction of hydrogen from the methoxy-groups; under the same conditions, anisole reacts to show the spectrum of the phenoxymethyl radical. Perhaps the reactivity of the methoxy-group in the structure $^-N{=}\overset{|}{C}{-}OMe$ is reduced as it is in esters containing the structure $O{=}\overset{|}{C}{-}OMe$.

Photolysis of the peroxides $(Bu^tOO)_n(MeO)_{3-n}C_3N_3$ (n = 1—3) [(VIII)—(VI), respectively] in a mixture of cyclopropane and ethylene at —110 to —40 °C showed e.s.r. spectra, listed in Table 2, which we ascribe to the 2-triazinyloxyethyl radicals (XIV); as expected (because the concentration of the peroxide and ethylene was low), the spectrum of the adduct formed by the t-butoxyl radical, $Bu^tOCH_2CH_2\cdot$ [$a(2H_\alpha)$ 22.0, $a(2H_\beta)$ 33.2 G, at —60 °C] [6] was too weak to be detected. The spectrum of the radical $(Bu^tOO)_2C_3N_3OCH_2CH_2\cdot$ is illustrated in Figure 1.

Over the temperature range —109 to —6 °C, the value of $a(2H_\beta)$ for the radical (XIV; X = Y = Bu^{t}OO) showed da/dT —12.6 mG K^{-1}. These radicals, like other 2-alkoxyethyl radicals,[20] are therefore most stable in the staggered conformation as shown.

The alternative of an N-adduct (XV) seems unlikely as this would be expected to show coupling to nitrogen. For example, the radical $HCONEtCH_2\dot{C}H_2$ has $a(2H_\alpha)$ 22.1, $a(2H_\beta)$ 27.2, a(N) 3.7 G.[21]

Under the same conditions, the triperoxide (VI) and propene showed only the spectrum of the allyl radical by hydrogen abstraction, and no radical resulting from addition to the double bond could be detected. t-Butoxyl radicals similarly react by hydrogen abstraction, but perfluoro-t-butoxyl and trimethylsilyloxyl radicals react only by addition.[3,4]

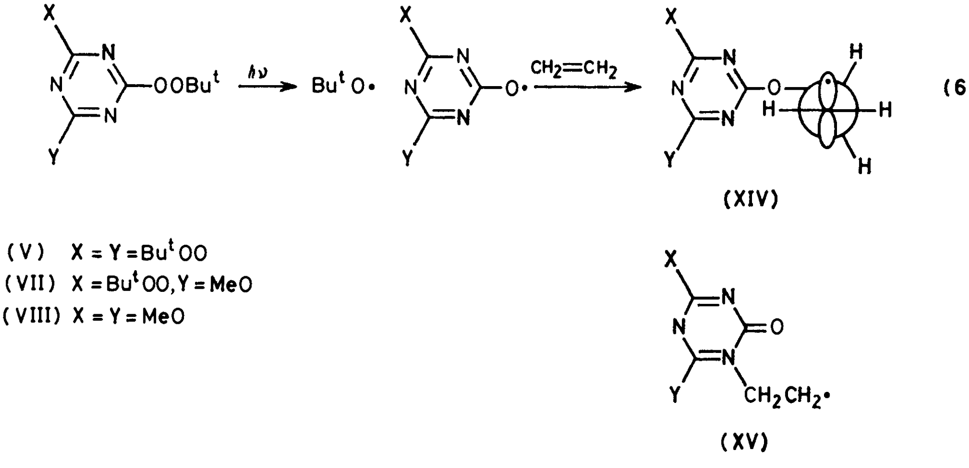
TABLE 2

E.s.r. spectra of the adducts formed between triazinoxyl radicals and ethylene or trimethyl phosphate

	$XYC_3N_3OCH_2CH_2\cdot$ [a]			$XYC_3N_3O\dot{P}$-$(OMe)_3$ [b,c]	
$(Bu^tOO)(X)(Y)C_3N_3$	T/ °C	$a(2H_\alpha)$/ G	$a(2H_\beta)$/ G	T/ °C	a(P)/ G [d]
$(Bu^tOO)(MeO)_2C_3N_3$	−43	22.0	29.0	−64	1 064
$(Bu^tOO)_2(MeO)C_3N_3$	−40	22.5	28.7	−95	1 066
$(Bu^tOO)_3C_3N_3$	−25	22.0	28.0 [e]	−108	1 089
$(Bu^tOO)(Et_2N)_2C_3N_3$ [f]				−124	1 055 [g]

[a] In cyclopropane–ethylene solvent. [b] In cyclopropane solvent. [c] In each case the spectrum of the radical $Bu^tO\dot{P}$-$(OMe)_3$ was observed at low temperature and that of $Bu^t\cdot$ at high temperature. [d] Derived by the Breit–Rabi equation. [e] da/dT = −12.6 mG K^{-1} from −109 to −6 °C. [f] Containing a small amount of $(Bu^tOO)_2(Et_2N)C_3N_3$. [g] Below −70 °C, a spectrum consisting of a broad quintet with a separation $ca.$ 22 G was also observed.

The same methoxy peroxides (VI) and (VII), and the bis(diethylamino) peroxide (X) were photolysed in the


(6)

(XIV)

(V) X = Y = Bu^{t}OO
(VII) X = Bu^{t}OO, Y = MeO
(VIII) X = Y = MeO

(XV)

presence of trimethyl phosphite. Below −70 °C, all showed the doublet spectrum of the t-butoxytrimethoxyphosphoranyl radical (XVI), a(P) 887 G,[18] and a second doublet with larger phosphorus hyperfine coupling and broader lines which we ascribe to the triazinyloxytrimethoxyphosphoranyl radicals (XVII). Details of these radicals are included in Table 1, and the spectrum of the two radicals (XVI) and (XVII; X = Y = OMe) formed from $(\mathrm{MeO})_2(\mathrm{Bu^tOO})\mathrm{C_3N_3}$ are illustrated in Figure 2. At higher temperatures, the spectrum of the tetra-alkoxyphosphoranyl radical (XVI) decreased in intensity, and the spectrum of the t-butyl radical, formed by β-scission of (XVI),[18] took its place. The spectrum of the triazinyloxytrimethoxyphosphoranyl radicals (XVII) could be observed up to *ca.* −30 °C, but no radicals resulting from their fragmentation could be detected. Below −70 °C, the peroxide $(\mathrm{Bu^tOO})(\mathrm{Et_2N})_2\mathrm{C_3N_3}$ (X) showed the e.s.r. spectra of the phosphoranyl radicals (XVI) and (XVII), and of a third species which appeared as a broad binomial quintet, with separation *ca.* 22 G. The identity of this spectrum is discussed below.

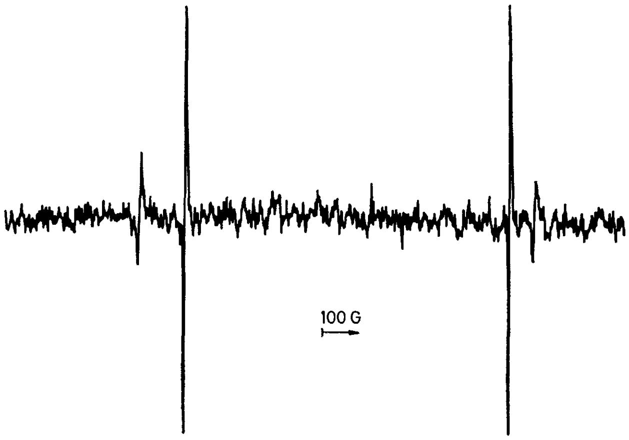
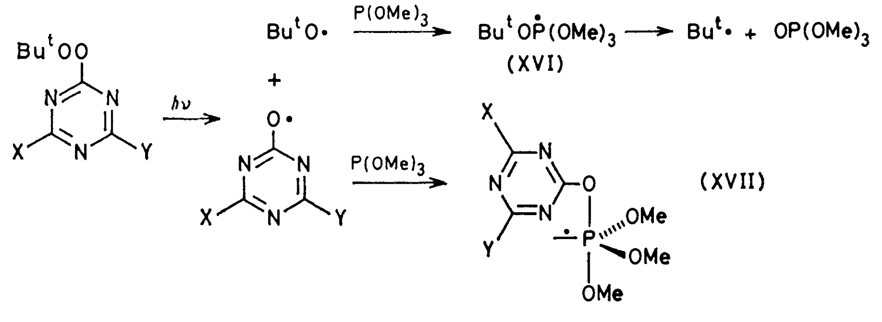


FIGURE 1 E.s.r. spectrum of the radical $(\mathrm{Bu^tOO})_2\mathrm{C_3N_3OCH_2CH_2}\cdot$ in cyclopropane at −38 °C



In phosphoranyl radicals, the value of a(P) normally increases as the electronegativity of the ligands increases; for example, in $(\mathrm{EtO})_3\dot{\mathrm{P}}\mathrm{OC(CH_3)_3}$, a(P) is 890 G, whereas in $(\mathrm{EtO})_3\dot{\mathrm{P}}\mathrm{OC(CF_3)_3}$, a(P) is 1 020 G. In this context, the triazinyloxy-groups therefore appear to be more electronegative than methoxy-groups. Phosphoranyl radicals normally adopt a trigonal bipyramidal structure with the most electronegative ligands in the apical position, and the radicals (XVII) probably assume the structure which is shown: the broadness of the lines may be caused by some unresolved coupling to the nitrogen atoms of the triazine group. If the ligand were bonded through nitrogen, a(N) would be expected to be large; for example the radical $(\mathrm{EtO})_3\overline{\dot{\mathrm{P}}\mathrm{NCOCH_2CH_2}\dot{\mathrm{C}}\mathrm{H_2}}$ shows a(N) 25.8 G.[22]

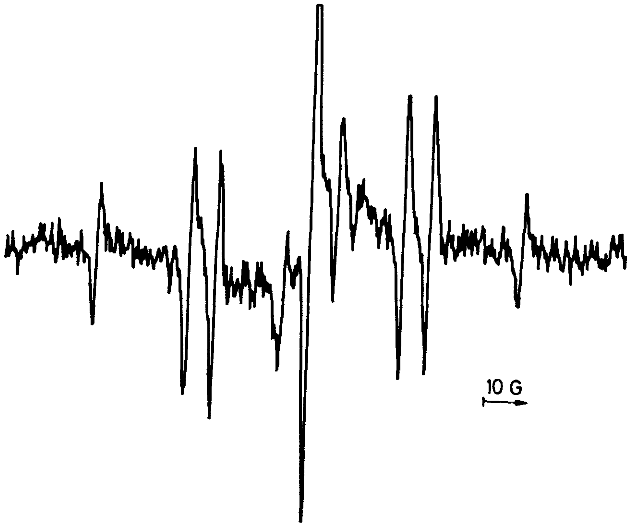
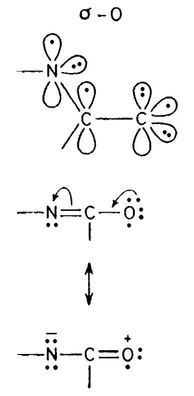


FIGURE 2 E.s.r. spectra of the radicals $(\mathrm{MeO})_2\mathrm{C_3N_3O}\dot{\mathrm{P}}(\mathrm{OMe})_3$ (outer doublet) and $\mathrm{Bu^tO}\dot{\mathrm{P}}(\mathrm{OMe})_3$ (inner doublet) in cyclopropane at −63 °C

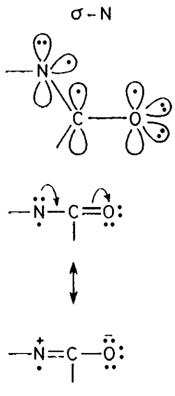
The identity of the radical which gives rise to the broad quintet spectrum from the amino peroxide (X) is not clear. This was the only spectrum which was observed when the peroxide (X) was photolysed alone in cyclopropane at −129 °C, and when di-t-butyl peroxide was photolysed in the presence of the triazine $(\mathrm{Et_2N})_2(\mathrm{Cl})\mathrm{C_3N_3}$ at −101 °C. Photolysis of di-t-butyl peroxide in the presence of tris(diethylamino)triazine, $(\mathrm{Et_2N})_3\mathrm{C_3N_3}$, gave a well resolved spectrum consisting of a quartet of doublets, a(1H) 18.9, a(3*H*) 21.5 G at −80 °C, and under the same conditions, the dimethylamino-analogue $(\mathrm{Me_2N})_3\mathrm{C_3N_3}$, showed a triplet spectrum, a(2H) 20.5 G. The simplest explanation therefore appears to be that these radicals are α-aminoalkyl radicals, $\mathrm{XYC_3N_3N(Et)}\dot{\mathrm{C}}\mathrm{HCH_3}$ and $\mathrm{XYC_3N_3N(Me)}\dot{\mathrm{C}}\mathrm{H_2}$, but in that case it is surprising that no hyperfine coupling is observed to nitrogen, as the radical $\mathrm{Me_2N}\dot{\mathrm{C}}\mathrm{H_2}$ shows $a(2\mathrm{H}_\alpha)$ 11.6,

$a(6H_\beta)$ 4.06, a(N) 7.0 G,[23] and $Et_2N\dot{C}HCH_3$ shows $a(H_\alpha)$ 14.7, $a(3H_\beta)$ 20.1, $a(2H_\gamma)$ 1.4, a(N) 5.2 G.[24] Perhaps the negative contribution to hyperfine coupling by spin polarisation, and the positive contribution by p_π–p_π overlap coincidentally cancel.

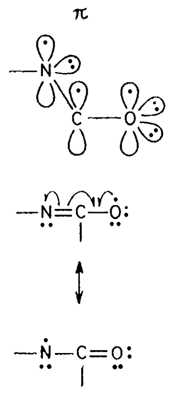
The Electronic Structure of the Triazinoxyl Radicals.—The triazinoxyl radicals may be regarded as examples of amidyl radicals, the electronic structures of which have been the subject of much discussion.[25,26] The possible electronic configurations are illustrated in formulae (XVIII)—(XX).



(XVIII)



(XIX)



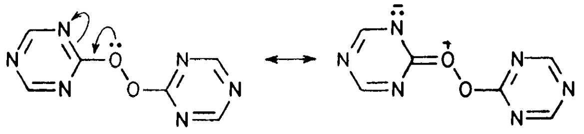
(XX)

The radicals $Bu^tCO\dot{N}Me$ and $MeCO\dot{N}Bu^t$ show values of a(N) similar to those of nitrogen-centred π-radicals (*e.g.* $Me_2\dot{N}$:) and these amidoyl radicals were suggested to have π-structures, with the odd electron localised largely on nitrogen.[27] Similar π-structures were confirmed for the radicals $EtCO\dot{N}CH_3$, $EtCO\dot{N}CH_2Me$, $EtCO\dot{N}CHMe_2$, and $EtCO\dot{N}CHBu^t_2$ from a study of the temperature coefficients of $a(H_\beta)$,[28] and CIDNP studies again favoured a π-configuration for the radical $4\text{-}MeC_6H_4CO\dot{N}Me$.[29] Reactions of the amidoyl radicals occur through the nitrogen atom, but they apparently do not add readily intermolecularly to alkenes.[26,30]

The related succinimidyl radical has been proposed to exist in distinct π and σ (probably σ-N) electronic states which are close in energy, but which are not readily interconvertible, and which show different reactivities towards, for example, alkenes and alkanes.[31]

The thermal stability of the triazinyl peroxides resembles that of the dialkyl peroxides rather than the diaryl peroxides, and implies that there can be no substantial resonance stabilization in the product radicals which is not already present in the parent peroxides. The i.r. and Raman spectra,[14] and the size of the unit cell in the peroxide (IX),[16] show that the heteroaromatic rings and the two peroxide oxygen atoms all lie in the same plane, whereas most peroxides adopt a skewed structure to minimise the destabilising overlap of the unshared pairs of electrons on the two oxygen pairs.[32]

The planarity of the peroxide (IX) in the solid state may be due in part to lattice forces, but it may also indicate that the destabilising overlap of the $2p$ electrons on oxygen is rendered unimportant by their delocalisation onto the nitrogen atoms of the rings, which can readily accommodate the negative charge [formula (XXI)]. By this process, electronegative substituents are known to increase the stability of organic peroxides.[33]

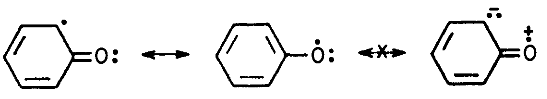


(XXI)

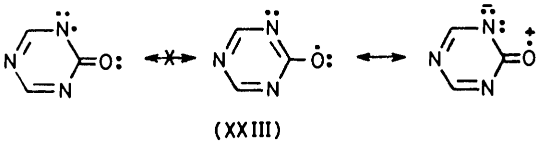
If homolysis of the oxygen–oxygen bond retained the unpaired electron in the radical in a σ-orbital on oxygen, the properties of the triazinoxyl radicals could then be accommodated. The resonance illustrated in (XVIII) would not weaken the peroxide bond because it is already present in the peroxide. The low standing concentration of the radical, and the broadening of the e.s.r. signal by spin–orbit coupling, could render the spectrum undetectable. Aryloxyl radicals on the other hand can be obtained in relatively high concentrations and spin–orbit coupling is negligible, and the e.s.r. spectra can readily be observed.

The electronegativity which the radical shows as a ligand in phosphoranyl radicals would follow from the polarity of the resonance hybrid (XVIII), and the reactivity towards ethylene which is like that of the radicals $Me_3SiO^\cdot$ and $t\text{-}C_4F_9O^\cdot$, which carry electron-attracting groups, but unlike that of $PhO^\cdot$ or $Bu^tO^\cdot$ would also be rationalised.

On this picture, the basic difference between the phenoxyl and triazinoxyl radicals would be that, in the phenoxyl radical (XXII), one electron rather than two is delocalised into the ring because the latter process would involve destabilising production of charges.



(XXII)



(XXIII)

In the triazinoxyl radical, the delocalisation of two electrons occurs to the exclusion of that of one, (XXIII), because the electronegative nitrogen can now better accommodate the negative charge.

EXPERIMENTAL

Starting Materials.—2,4-Dichloro-6-methoxy-1,3,5-triazine and 2-chloro-4,6-dimethoxy-1,3,5-triazine were prepared from the reaction between trichlorotriazine and methanol in the presence of sodium hydrogencarbonate [34] and 2,4,6-trimethoxy-1,3,5-triazine by a similar reaction in the presence of sodium hydroxide, δ_C(CHCl$_3$) 173.6 (*C*OMe) and 55.4 (CO*Me*).[34] The trimethoxytriazine was isomerised by heating into tri-*N*-methyl-1,3,5-triazin-2,4,6-one, δ_C(CHCl$_3$) 149.4 (*C*=O) and 29.4 (N*C*H$_3$).[35]

2-*t-Butylperoxy*-4,6-*dimethoxy*-1,3,5-*triazine*.—(A) A solution of t-butyl hydroperoxide (0.82 cm^3) in aqueous sodium hydroxide (0.46 g in 11 cm^3 of water) was slowly added to 2-chloro-4,6-dimethoxy-1,3,5-triazine (1.0 g) in hexane (50 cm^3) at 15 °C. The mixture was stirred for 1 h, and then the hexane layer was separated and evaporated to dryness. Crystallisation of the resulting oil from pentane at 0 °C gave the *peroxide* as crystals (0.56 g, 43%), m.p. 68 °C (Found: C, 47.3; H, 6.6; N, 17.9; O (iodimetrically) 26.2. $C_9H_{15}N_3O_4$ requires C, 47.2; H, 6.6; N, 18.3; O, 27.9%), δ_H(CHCl$_3$) 1.40 (9 H, Bu^t) and 4.05 (6 H, OMe), δ_C(CHCl$_3$) 175.7 (*C*OOBu^t), 173.6 (*C*OMe), 84.4 (OO*C*Me$_3$), 55.5 (O*C*H$_3$), and 26.2 (OOC*Me*$_3$).

When dichloromethane (30 cm^3) was used instead of hexane, the peroxide was obtained in 38% yield. On several occasions the product was purified by static distillation, but this practice was discontinued following an explosion.

(B) Silver trifluoroacetate (1.26 g) was added portionwise during 30 min to an ice-cooled stirred solution of the chlorodimethoxytriazine (1.0 g) and t-butyl hydroperoxide (1.76 cm^3) in dichloromethane (50 cm^3). The mixture was then stirred for 1.5 h at 0 °C, and 2 h at room temperature. The precipitated silver chloride was filtered off, and the filtrate was washed with sodium hydrogencarbonate (1.0 g in 25 cm^3 of water), and filtered after 20 min. The organic layer was separated and dried (MgSO$_4$), and the solvent was removed leaving an oil, which crystallised to give the peroxide (0.56 g, 43%), m.p. 67 °C.

(C) A solution of t-butyl hydroperoxide (1.7 cm^3) in dry pentane (20 cm^3) was added dropwise to a vigorously stirred suspension of finely powdered sodamide (0.70 g) in dry pentane (20 cm^3) under nitrogen. The mixture was stirred for 2 h, when a thick precipitate separated. A solution of the chlorodimethoxytriazine (1.0 g) in pentane (100 cm^3) was then added slowly, and the mixture was stirred for a further 2 h. The mixture was filtered, and the solvent was removed under reduced pressure, leaving the peroxide as an oil (1.26 g, 96%) which solidified in the refrigerator.

2,4-*Bis*-(*t-butylperoxy*)-6-*methoxy*-1,3,5-*triazine*.—t-Butyl hydroperoxide (1.64 cm^3) in 2N-sodium hydroxide (20 cm^3) was added slowly with stirring to a suspension of 2,4-dichloro-6-methoxy-1,3,5-triazine (1.0 g) in hexane (50 cm^3), below 20 °C. The solid dissolved within 30 min. Next day, the organic layer was separated and the solvent was removed to leave a solid, which was recrystallised from hexane to give the *peroxide* (1.19 g, 75%), m.p. 63 °C (Found: C, 49.8; H, 7.4; N, 14.9; O, 26.3. $C_{12}H_{21}N_3O_4$ requires C, 50.2; H, 7.4; N, 14.6; O, 27.8%), δ_H(CHCl$_3$) 1.35 (18 H, Bu^t) and 4.02 (3 H, Me), δ_C(CHCl$_3$) 175.4 (*C*OOBu^t), 84.9 (OO*C*Me$_3$), and 26.2 (OOC*Me*$_3$).

2,4,6-*Tris*-(*t-butylperoxy*)-1,3,5-*triazine*.—t-Butyl hydroperoxide (2.64 cm^3) in 2N-sodium hydroxide (33 cm^3) was added with stirring to trichlorotriazine (1.0 g) in hexane (50 cm^3) below 20 °C. After 6 h the hexane layer was separated and the solvent was removed leaving a solid which was recrystallised from hexane to give the peroxide (1.87 g, 84%), m.p. 51 °C (lit., 48—50 °C) (Found: C, 51.6; H, 7.8; N, 12.2; O, 25.7. Calc. for $C_{15}H_{27}N_3O_6$: C, 52.2; H, 7.9; N, 12.2; O, 27.8%), δ_H(CHCl$_3$) 1.40.

Bis-(2,4-*dimethoxy*-1,3,5-*triazinyl*) *Peroxide*.—(A) Hydrogen peroxide (100 vol; 0.38 cm^3) in 2N-sodium hydroxide (5.7 cm^3) was added gradually to 2-chloro-4,6-dimethoxy-1,3,5-triazine (0.5 g) in ethanol (10 cm^3) with stirring at 10—15 °C. The solid which separated was filtered off, washed with water, dried, and recrystallised from chloroform to give the peroxide (0.25 g, 35%), m.p. 145 °C (decomp.) (Found: C, 38.0; H, 3.8; N, 26.5. Calc. for $C_{10}H_{12}N_6O_2$: C, 38.5; H, 3.9; N, 26.9%), δ_C(CH$_2$Cl$_2$) 56.0 (CH$_3$) [lit.,[10] 155—158 °C (decomp.)].

(B) 85% Hydrogen peroxide (1 cm^3) was concentrated by static distillation on a vacuum line to one-third of the original volume. This material (0.2 g) was then very slowly added to a stirred suspension of finely ground sodamide (0.44 g) in ether (10 cm^3) at 0 °C. There was an instantaneous reaction; the solid coagulated, then dispersed on further stirring. After 2.5 h, a slurry of 2-chloro-4,6-dimethoxy-1,3,5-triazine (2.0 g) in ether (30 cm^3) was added, and the mixture was stirred for 5 h then left to stand overnight. Water (20 cm^3) was added, and the precipitate was filtered off, washed with water and ether, and dried, yielding the peroxide (37%), m.p. 150 °C (decomp.).

2-(t-*Butylperoxy*)-4,6-*bis*(*diethylamino*)-1,3,5-*triazine*.—t-Butyl hydroperoxide (1.53 g) in benzene (15 cm^3) was added to a stirred suspension of sodamide (0.79 g) in benzene (30 cm^3). After 1 h, a solution of trichlorotriazine (2.5 g) in benzene was added, and the mixture was stirred for 6 h. The mixture was then filtered, and the filtrate was washed with benzene, and the filtrate and washings were combined and mixed with a solution of diethylamine (1.98 g) in benzene (20 cm^3). A solution of sodium carbonate (2.87 g) in water (50 cm^3) was then added and the mixture was stirred and slowly heated to 40—45 °C during 1—2 h. The mixture was cooled, and the benzene layer was separated and dried. The solvent was removed leaving a heavy oil which, by iodimetric titration was shown to be the required peroxide in 80—81% purity, δ_H(CCl$_4$) 3.56 (2 H, q, *J* 7.0 Hz, NC*H*$_2$CH$_3$), 1.36 (9 H, s, CMe$_3$), and 1.16 (3 H, t, *J* 7.0 Hz, NCH$_2$C*H*$_3$).

2,4-*Bis*-(*t-butylperoxy*)-6-*diethylamino*-1,3,5-*triazine*.—Trichlorotriazine (2.0 g) in benzene (30 cm^3) was added with stirring to sodium t-butyl peroxide prepared from sodamide (1.33 g) and t-butyl hydroperoxide (2.57 g) in benzene (100 cm^3). The mixture was stirred for 4 h at room temperature, then filtered, and the precipitate was washed with benzene. Diethylamine (2.26 cm^3) in benzene (10 cm^3) was added to the combined filtrate and washings, and the mixture was stirred at 40 °C for 2 h. Next day, the precipitate of diethylammonium chloride was filtered off, and the solvent was removed from the filtrate leaving a yellowish oil which by titration was found to be 81% pure, δ_H(CCl$_4$) 3.61 (2 H, q, *J* 7.0 Hz, NC*H*$_2$CH$_3$), 1.39 (9 H, s, Bu^t), and 1.20 (3 H, t, *J* 7.0 Hz, NCH$_2$C*H*$_3$).

By a similar method using no inorganic base, 2-t-butylperoxy-4,6-tris(diethylamino)-1,3,5-triazine was prepared in 86% purity.

Neither of the two above diethylamino peroxides could be induced to crystallise. Chromatography of either on silica gel using a methanol–toluene solvent system gave a mixture of the two peroxides which could be differentiated by ^{13}C n.m.r. spectroscopy. (Bu^{t}OO)(Et$_2$N)$_2$C$_3$N$_3$: δ_C(CHCl$_3$) 174.5 (*C*OOBu^t), 163.6 (*C*NEt$_2$), 83.5 (*C*Me$_3$), 41.5 (N*C*H$_2$-CH$_3$), 26.4 (C*Me*$_3$), and 13.4 (NCH$_2$*C*H$_3$). (Bu^{t}OO)$_2$-

$(\mathrm{Et_2N})\mathrm{C_3N_3}$: $\delta_{\mathrm{C}}(\mathrm{CHCl_3})$ 174.0 ($C\mathrm{OOBu^t}$), 164.3 ($C\mathrm{NEt_2}$) 82.6 ($C\mathrm{Me_3}$), 41.5 ($\mathrm{NCH_2}C\mathrm{H_3}$), 26.3 ($\mathrm{C}Me_3$), and 13.4 ($\mathrm{N}C\mathrm{H_2CH_3}$).

Thermal Analysis.—Samples (*ca.* 100 mg) were submitted to thermal gravimetric and differential thermal analysis in air at a heating rate of 3 °C $\mathrm{min^{-1}}$. The results are given in Table 1.

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REFERENCES

[1] Part 11, A. G. Davies, *J. Chem. Soc.*, 1962, 4288.

[2] A. G. Davies, 'Radicaux Libres Organiques,' Editions CNRS, 1978, vol. 278, p. 399.

[3] A. G. Davies, R. W. Dennis, R. C. Dobbie, and B. P. Roberts, *J. Chem. Soc., Chem. Commun.*, 1974, 468.

[4] P. G. Cookson, A. G. Davies, N. A. Fazal, and B. P. Roberts, *J. Am. Chem. Soc.*, 1976, **98**, 616.

[5] P. G. Cookson, A. G. Davies, and N. A. Fazal, *J. Organomet. Chem.*, 1975, **99**, C31.

[6] P. G. Cookson, A. G. Davies, B. P. Roberts, and M.-W. Tse, *J. Chem. Soc., Chem. Commun.*, 1976, 937.

[7] A. G. Davies, 'Organic Peroxides,' Butterworths, London, 1961.

[8] L. A. Mahoney, and M. A. Da Rouge, *J. Am. Chem. Soc.*, 1975, **97**, 4722.

[9] N. A. Sokolov, L. G. Usova, N. N. Vyshinskii, and O. S. Morozov, *J. Gen. Chem. USSR*, (*Engl. Transl.*), 1972, **42**, 2069.

[10] P. R. H. Speakman, *Chem. Ind.* (*London*), 1977, 232.

[11] H. Kropf and M. Ball, *Liebigs Ann. Chem.*, 1976, 2331.

[12] H. Kropf and H. M. Amirabadi, *Tetrahedron*, 1978, **34**, 1231.

[13] J. B. Stothers, 'Carbon-13 NMR Spectroscopy,' Academic Press, New York, 1972.

[14] P. Bleckmann, personal communication, to be published in detail.

[15] P. Bleckmann, B. Schrader, W. Meier, and H. Takahashi, *Ber. Bunsenges. Phys. Chem.*, 1971, **75**, 1279; P. Bleckmann, *Z. Naturforsch. Teil A*, 1974, **29**, 1485.

[16] M. F. C. Ladd, personal communication.

[17] I. H. Elson, S. W. Mao, and J. K. Kochi, *J. Am. Chem. Soc.*, 1975, **97**, 335.

[18] A. G. Davies, D. Griller, and B. P. Roberts, *Angew. Chem. Int. Ed. Engl.*, 1971, **10**, 738; *J. Chem. Soc., Perkin Trans. 2*, 1972, 993.

[19] M. C. R. Symons, *J. Am. Chem. Soc.*, 1969, **91**, 5924.

[20] K. S. Chen and J. K. Kochi, *J. Am. Chem. Soc.*, 1974, **96**, 1383.

[21] H. Paul and H. Fischer, *Ber. Bunsenges. Phys. Chem.*, 1969, **73**, 972.

[22] J. W. Cooper, M. J. Parrott, and B. P. Roberts, *J. Chem. Soc., Perkin Trans. 2*, 1977, 730.

[23] P. Neta and R. W. Fessenden, *J. Phys. Chem.*, 1971, **75**, 738.

[24] D. E. Wood and R. V. Lloyd, *J. Chem. Phys.*, 1970, **53**, 3932.

[25] W. C. Danen and R. A. Neugebauer, *Angew. Chem. Int. Ed. Engl.*, 1975, **14**, 7833.

[26] P. Mackiewicz and R. Furstoss, *Tetrahedron*, 1978, **34**, 3241.

[27] W. C. Danen and R. W. Gellert, *J. Am. Chem. Soc.*, 1972, **94**, 6853.

[28] J. Lessard, D. Griller, and K. U. Ingold, *J. Am. Chem. Soc.*, 1980, **102**, 3262; R. Sutcliffe, D. Griller, J. Lessard, and K. U. Ingold, *ibid.*, 1981, **103**, 624.

[29] C. Brown and A. J. Lawson, *Tetrahedron Lett.*, 1975, 191.

[30] R. S. Neale, *Synthesis*, 1971, 1.

[31] P. S. Skell and J. C. Day, *Acc. Chem. Res.*, 1978, **11**, 381, and references cited therein.

[32] L. S. Silbert, 'Organic Peroxides,' ed. D. Swern, Wiley, New York, 1971, vol. 2, p. 637.

[33] C. G. Swain, W. T. Stockmeyer, and J. T. Clarke, *J. Am. Chem. Soc.*, 1950, **72**, 5426.

[34] J. R. Dudley, J. T. Thurston, F. C. Shaefer, D. Holm-Hausen, C. J. Hull, and P. Adams, *J. Am. Chem. Soc.*, 1951, **73**, 2986.

[35] A. Hantzsch and H. Bauer, *Chem. Ber.*, 1905, **38**, 1005; E. M. Smolin and L. Rapoport, 'The Chemistry of Heterocyclic Compounds. s-Triazines and Derivatives,' Interscience, 1959, vol. 13.