A Probe for Homolytic Reactions in Solution. Part VI.[1,2] Reactions of Polyhalogenomethyl Radicals with Nitrosobutane

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Spectroscopic evidence (e.s.r.) has been obtained to show that the spin-adduct of a radical $\cdot CX_2Y$ (where X is Cl or Br) with nitrosobutane is converted into a carbonyl nitroxide $(YC{:}O)N(Bu^t)O\cdot$. A radical mechanism is outlined which can accommodate this.

When Y in the carbonyl nitroxide is F, Cl, or Br, it can be displaced by methanol, ethanol, or dimethylamine to give alkoxycarbonyl or aminocarbonyl nitroxides. The structure of these is compared with that of vinyl nitroxides.

Attempts to trap propenyl radicals from crotonyl peroxide using nitrosobutane led to a dialkyl nitroxide tentatively formulated as (7).

In our earliest investigations[3] of the use of nitrosobutane (2-methyl-2-nitrosopropane) as a 'spin trap',[4,5] it was noticed that u.v. irradiation of bromotrichloromethane in the presence of this scavenger gave two long-lived radicals. One of these was identified[3] as t-butyl trichloromethyl nitroxide,[4,5] but the second, more persistent ‡ species ($a_N = 6{\cdot}65$ G), whose spectrum is traced in Figure 1a, was not identified, although on the basis of the poorly resolved quartet splitting, it was tentatively suggested that this might be the spin-adduct of nitrosobutane and bromine atoms, *i.e.* $Bu^tN(Br)O\cdot$. This idea had to be discarded when it was found that irradiation of benzene solutions of carbon tetrabromide containing nitrosobutane gave a new radical with a very similar nitrogen splitting ($a_N = 6{\cdot}5$ G), but with a clearly resolved halogen quartet ($a_{Hal} = 2{\cdot}1$ G). If, as suggested

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‡ Little decay of the radical signal had occurred after one week in a sealed tube (N_2, dark, room temperature).

[1] Part V, R. J. Holman and M. J. Perkins, *J. Chem. Soc.* (*C*), 1971, 2324.

[2] A preliminary report of part of this work has appeared: R. J. Holman and M. J. Perkins, *Chem. Comm.*, 1971, 244.

[3] G. R. Chalfont, Ph.D. Thesis, London, 1968.

[4] I. H. Leaver, G. C. Ramsay, and E. Suzuki, *Austral. J. Chem.*, 1969, **22**, 1891.

[5] M. J. Perkins, P. Ward, and A. Horsfield, *J. Chem. Soc.* (*B*), 1970, 395.

by the nitrogen splitting constants, the structures of these radicals are similar, the halogen in the second case must be bromine, and in the former case it must therefore be chlorine.

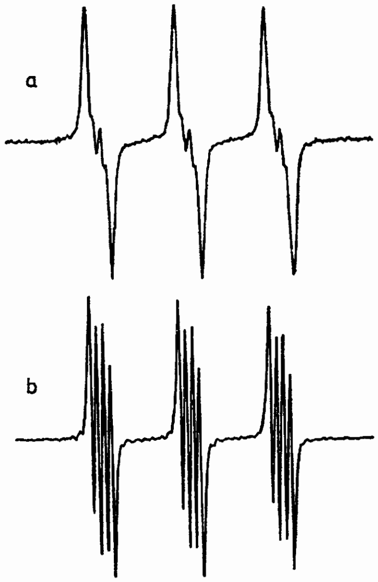

FIGURE 1 Spectra attributed to t-butyl chlorocarbonyl nitroxide: (a) $^1H_9$; (b) $^2H_9$

Subsequently, we[5] and others[4,6] have generated t-butyl trichloromethyl nitroxide by hydrogen abstraction from chloroform in the presence of nitrosobutane, and have noted that the spectrum of the nitroxide is replaced by one consisting of three lines with a relatively small nitrogen splitting. In our early experiments this splitting was found to be $a_N = 8{\cdot}25$ G. Nitrogen hyperfine splittings of this magnitude are encountered in acyl alkyl nitroxides, and indeed Torssell[6] has commented that the secondary radicals formed subsequent to the trapping of trichloromethyl radicals * by nitrosobutane may be acyl nitroxides.

We were able to investigate these reactions more closely with the aid of perdeuterionitrosobutane.[1] Replacement of protium by deuterium in the t-butyl group permits greatly improved resolution to be achieved in the e.s.r. spectra of the spin adducts, and irradiation of bromotrichloromethane solutions of this scavenger gave the well-resolved triplet of quartets shown in Figure 1b. Repetition of the hydrogen abstraction from chloroform with the deuteriated scavenger gave the triplet of triplets traced in Figure 2 ($a_N = 8{\cdot}25$ G; $a_H = 0{\cdot}45$ G).

If the radicals responsible for the spectra of Figures 1 and 2 are to be identified as acyl nitroxides, their full structures must account satisfactorily for splitting patterns observed in the spectra. It seems clear that one nitrogen substituent must in each case be t-butyl, in view of the greatly improved resolution with the deuteriated scavenger. The presence of fine structure in the spectra in addition to the nitrogen splitting is surprising in view of the absence of splitting other than that due to nitrogen in the spectra of acetyl t-butyl nitroxide and benzoyl t-butyl nitroxide:[8] nor were we able to detect additional fine structure in the spectrum of acetyl $[^2H_9]$t-butyl nitroxide.

The secondary triplet structure in the spectrum of Figure 2 is clearly due to hyperfine interaction with two equivalent protons; that these originated in the ethanol present in the chloroform samples used for the initial experiments became apparent when hydrogen abstraction from ethanol-free chloroform was investigated. In such experiments, using deuteriated nitrosobutane, the spectrum of the trichloromethyl nitroxide is gradually replaced not by that shown in Figure 2, but by that shown in Figure 1b. This confirms that the halogen splitting in Figure 1b must be due to chlorine. It also suggests that the halogen-containing nitroxides with a_N *ca.* 6·5 G might be the halogenocarbonyl nitroxides (1) and (2), because in the presence of ethanol, nucleophilic displacement of chloride from (1) could give (3), with the α-methylene protons of the ethoxy-group responsible for the two proton triplet in Figure 2.

Evidence that (3) is indeed the structure of the radical responsible for the spectrum shown in Figure 2 was obtained by examining hydrogen abstraction from ethyl formate by t-butoxyl radicals in the presence of nitroso-$[^2H_9]$butane. A strong e.s.r. signal identical with that in Figure 2 was recorded.

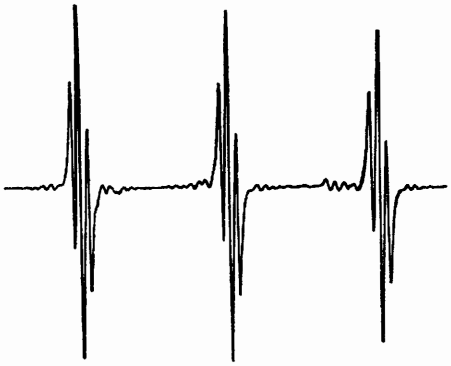

FIGURE 2 Spectrum of $EtO{\cdot}CO{\cdot}NC(CD_3)_3{\cdot}O{\cdot}$

Evidence for the nucleophilic substitution reaction was secured by repetition of the photochemical experiments with $BrCCl_3$, and, after discontinuing irradiation, by adding ethanol to a solution containing the radical believed to have structure (1). The spectrum of (1) was rapidly replaced by the spectrum of (3). Similar results

$$XCO{\cdot}NBu^t{\cdot}O{\cdot} \xrightarrow{EtOH} EtO{\cdot}CO{\cdot}NBu^t{\cdot}O{\cdot}$$

(1) X = Cl (3)

(2) X = Br

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* In one report[7] the spectrum with $a_N = 6{\cdot}5$ has been mistakenly attributed to t-butyl trichloromethyl nitroxide.

[6] K. Torssell, *Tetrahedron*, 1970, **26**, 2759.

[7] J. W. Hartgerink, J. B. F. N. Engberts, Th. A. J. W. Wajer, and Th. J. de Boer, *Rec. Trav. chim.*, 1969, **88**, 481.

[8] (*a*) A. Mackor, Th. A. J. W. Wajer, and Th. J. de Boer, *Tetrahedron*, 1968, **24**, 1623; (*b*) E. G. Janzen and B. J. Blackburn, *J. Amer. Chem. Soc.*, 1969, **91**, 4481.

were obtained when a solution of the nitroxide obtained by irradiating carbon tetrabromide in the presence of nitroso[$^2H_9$]butane, and now believed to have structure (2), was treated with ethanol.

Nucleophilic displacement of halogen from (1) and (2) by methanol and by dimethylamine similarly gave spectra of nitroxides believed to be (4) and (5).* These structures were supported by the observation that the same nitroxides could be obtained by hydrogen abstraction from methyl formate and from dimethylformamide respectively.

The results of these experiments gave a clue to the transmission of hyperfine interaction from the α-protons of the ethyl group in (3). This secondary splitting is

$$\mathrm{Me_2N{\cdot}CO{\cdot}NBu^t{\cdot}O{\cdot}} \qquad \mathrm{MeO{\cdot}CO{\cdot}NBu^t{\cdot}O{\cdot}}$$

(5) (4)

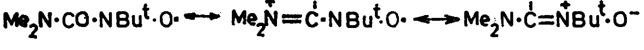
particularly pronounced in the spectrum of the aminocarbonyl nitroxide (5) ($a_{\mathrm{N(nitroxide)}} = 11{\cdot}75$ G; $a_{\mathrm{N(amino)}} = 0{\cdot}45$ G; $a_{\mathrm{H(N\text{-}methyl)}} = 0{\cdot}60$ G †). Furthermore, the nitrogen splittings in nitroxides of general formula $\mathrm{XCO{\cdot}N(Bu^t)O{\cdot}}$ increase in the order: X = alkyl $<$ X = alkoxy $<$ X = dimethylamino (data are summarised in Table 1). We therefore suggest that interaction with the protons on the α-carbon of the alkoxy- or alkylamino-groups occurs by way of the π-electron structure of what is essentially an ester or amide function. The effect is most pronounced for the aminocarbonyl nitroxide (5) in which a significant contribution from the structure (5a) is suggested by the relatively large splitting due to nitroxide nitrogen. This signifies a relatively small contribution from valence structures such as (5b), in which the amide carbonyl conjugates with the nitroxide function. The situation with alkoxycarbonyl nitroxides is intermediate between this and that for simple acyl nitroxides.‡

TABLE 1

Summary of splitting parameters for t-butyl carbonyl nitroxides [a,b]

Radical ($\mathrm{XCO{\cdot}NBu^t{\cdot}O{\cdot}}$)	Solvent	a_N(G)	a_{other} (G)
X = Cl [c]	$BrCCl_3$	6·65	$a_{Cl} = 0{\cdot}5$
X = Br	C_6H_6	6·50	$a_{Br} = 2{\cdot}1$
X = OMe [c]	$BrCCl_3$	8·20	$a_H = 0{\cdot}45$
X = OEt [c]	$CHCl_3$	8·25	$a_H = 0{\cdot}45$
X = NMe_2 [c]	$BrCCl_3$	11·75	$a_N = 0{\cdot}45$, $a_H = 0{\cdot}6$ [d]
X = Me [e]	C_6H_6	8·0	
X = Ph [f]	C_6H_6	7·7	

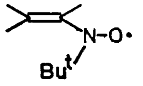
[a] Data recorded at room temperature (*ca.* 15°). [b] All the t-butyl carbonyl nitroxides had *g*-values lying between 2·0069 and 2·0073. [c] [$^2H_9$]Bu^t. [d] Splitting with only one methyl group (3H). [e] Data from ref. 8*a*. [f] Data from ref. 8*b*.



$$\mathrm{Me_2N{\cdot}CO{\cdot}NBu^t{\cdot}O{\cdot}} \longleftrightarrow \mathrm{Me_2\overset{+}{N}{=}\overset{O^-}{C}{\cdot}NBu^t{\cdot}O{\cdot}} \longleftrightarrow \mathrm{Me_2N{\cdot}\overset{O\cdot}{C}{=}\overset{+}{N}Bu^t{\cdot}O^-}$$

(5) (5a) (5b)

A logical comparison of the splitting constant data for (3) and (5) would be with figures for t-butyl vinyl nitroxides (6). However little seems to be known about such radicals, although the well documented aryl alkyl nitroxides[10] usually have a nitrogen splitting of *ca.* 11—13 G (in benzene), and similar values might be anticipated for vinyl analogues. We have made a number of attempts to generate t-butyl vinyl nitroxides by addition of vinyl radicals and vinyl carbanions to nitrosobutane, the original intention being to probe the stereochemistry of substituted vinyl radicals. Reagents investigated included acryloyl peroxides, vinyl-lithium derivatives, and vinyl iodides (with u.v. irradiation).[11] In several experiments weak spectra with a_N *ca.* 12·5—13 G were observed, but in no instance was an unambiguous structural assignment possible. For example a spectrum tentatively assigned to unsubstituted t-butyl vinyl nitroxide consisted of three broad doublets with a_N = 12·5 and a_H = 1·1 G, leading to the surprising conclusion that interaction with only one proton could be resolved. No improvement was obtained with nitroso[$^2H_9$]butane.



(6)

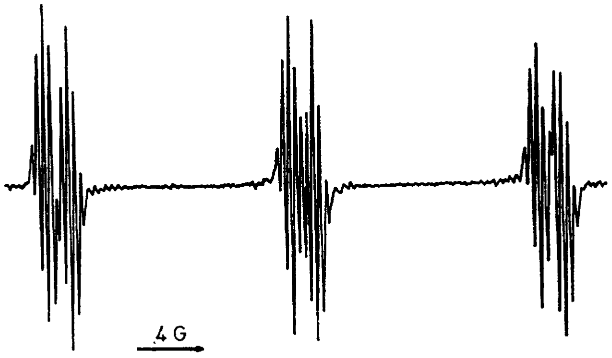


FIGURE 3 Spectrum attributed to radical (7). The slight irregularity in the spectrum is probably due to the presence of di-t-butyl nitroxide

With *trans*-crotonyl peroxide and nitroso[$^2H_9$]butane a more complex and better resolved spectrum was obtained. This showed three doublet quintets with a_N = 14·75, a_N = 1·41 (doublet), and a_N = 0·37 G (quintet) (Figure 3). The large nitrogen splitting is characteristic

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* Attempts to displace halogen using phenols or thiols were unsuccessful. The nitroxides were destroyed, presumably by reduction.[9]

† Splitting by the protons of only one *N*-methyl group were resolved.

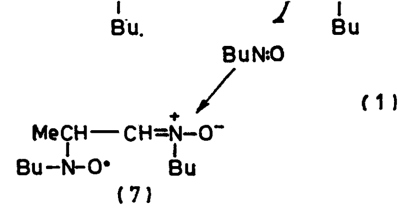
‡ As suggested by a referee, an alternative interpretation of these unexpected long-range hyperfine splittings might involve a 'through-space' interaction (*cf.* A. B. Sullivan, *J. Org. Chem.*, 1966, **31**, 2811). However, we have been unable to detect similar splitting by the methyl protons of propionyl [$^2H_9$]t-butyl nitroxide. Indeed, the long-range splittings recorded by Sullivan in substituted allyl nitroxides might be of an 'allylic' type involving interaction through the π-system (*cf.* allylic coupling in n.m.r. spectra).

[9] *E.g.* A. R. Forrester and R. H. Thomson, *J. Chem. Soc.* (*C*), 1966, 1844; see also ref. 10 p. 228.

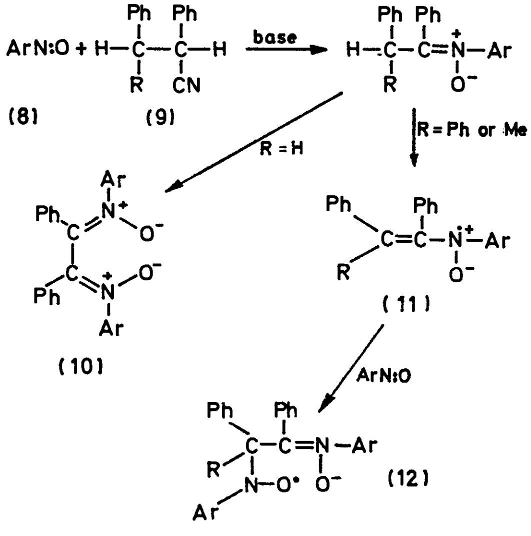
[10] A. R. Forrester, J. M. Hay, and R. H. Thomson, 'Organic Chemistry of Stable Free Radicals,' Academic Press, New York, 1968, p. 202.

[11] C. M. Camaggi and M. J. Perkins, unpublished observations.

of a dialkyl nitroxide. We suggest that the radical responsible for this spectrum may have structure (7). The vinyl group of a vinyl nitroxide would be expected to be particularly susceptible to radical attack and may be sufficiently reactive to interact with a nitroso-compound as shown in equation (1). Structure (7) accommodates the large nitrogen splitting typical of a dialkyl nitroxide, and also the large doublet (α-H) and small quintet (β-H) splittings. The α-hydrogen splitting in t-butyl isopropyl nitroxide is 1·8 G.[12]



It is interesting to re-examine the spectra of previously reported vinyl nitroxides[13] in the light of structure (7). The reaction of (8) with (9) in the presence of base gives the bis-nitrone (10), when R = H, but a nitroxide believed to be (11) when R = Ph or Me. The structural similarity between (10) and (7) suggests that the ' vinyl nitroxides ' (11) might, in fact, be the alkyl aryl nitroxides (12). In addition, a three proton quartet (a_H = 0·6 G) in the spectrum of the nitroxide with R = Me, and the absence of splitting by the phenyl ring protons, is in agreement with the alkyl aryl nitroxide formulation (12). On the other hand the nitrogen splitting of 10 G is low for (12), and favours (11).



We therefore examined the decomposition of *trans*-crotonyl peroxide in the presence of nitrosobenzene. The spectrum of the nitroxide obtained is traced in Figure 4. This can be approximated with the following parameters: a_N 10·68 G, a_H 0·27 G (3H), a_H 2·70 G (3H), a_H 0·95 G (2H), a_H 3·90 G (1H), and with a line-width of 0·15 G. These figures are inadequate to distinguish between the two alternative structures (13) and (14). The low nitrogen splitting seems more appropriate to (13) than to an alkyl aryl nitroxide, but the remaining splitting constants could be accommodated by either structure. *A priori* it might seem surprising that splittings with all the magnetic nuclei of the propenyl group in structure (13) cannot be resolved, but if the triplet of doublets mentioned previously has been correctly assigned to t-butyl vinyl nitroxide,[11] this is not unreasonable. A point against structure (13), is that the methyl splitting of 0·27 G is less than the splitting due to the methyl protons in the methoxycarbonyl nitroxide (4). If the hypothesis that this interaction is transmitted through the π-electron system is valid, the methyl splitting in (13), with a formal double bond, should greatly exceed that in (4). Finally, both structures (13) and (14) are capable of geometrical isomerism; no evidence for more than one nitroxide was obtained.

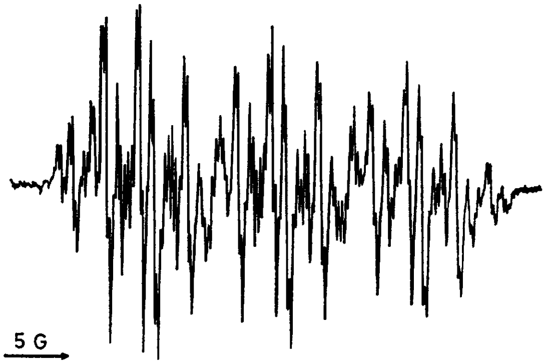
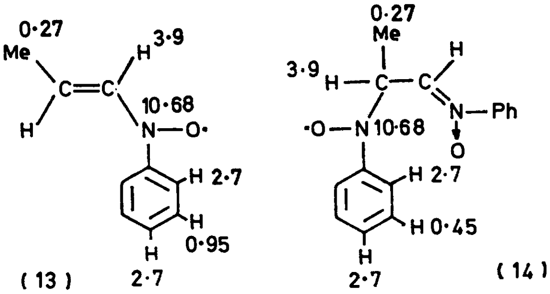


FIGURE 4 Spectrum obtained from thermolysis of *trans*-crotonyl peroxide in benzene containing nitrosobenzene

Returning to our original problem, there remains the question of the origin of the halogenocarbonyl nitroxides. It seemed probable from the high intensity of the e.s.r. signals, and from the manner in which the chlorocarbonyl nitroxide replaced t-butyl trichloromethyl nitroxide in the experiments with chloroform, that they are derived from trihalogenomethyl nitroxides. The possibility that they are formed by spin-trapping of bromocarbonyl or chlorocarbonyl radicals cannot be completely discounted, but seems unlikely in view of our failure to obtain similar spectra on irradiation of, or attempted



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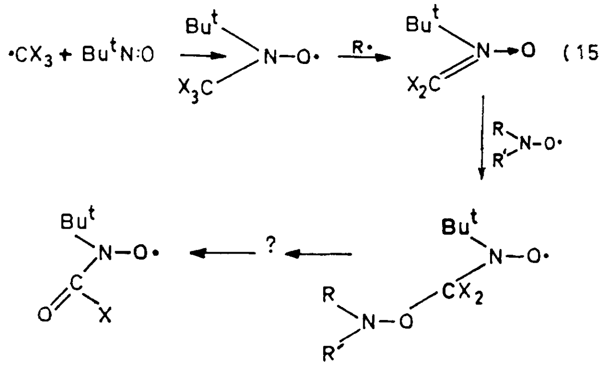
[12] H. Lemaire, R. Ramasseul, and A. Rassat, *Mol. Phys.*, 1964, **8**, 557.

[13] H. G. Aurich and F. Baer, *Angew. Chem. Internat. Edn.*, **1967**, **6**, 1080.

halogen abstraction from, phosgene or carbonyl bromide in the presence of nitrosobutane.

In a preliminary account of this work [2] we suggested that the halogenocarbonyl nitroxides might arise by the following sequence:



Abstraction of α-hydrogen from a nitroxide to give a nitrone is well documented, and formation of the dihalogenomethylene nitrone (15) by abstraction of α-halogen seems equally reasonable (a plausible alternative is spontaneous loss of a halogen atom; *cf.* ref. 14). We consider it probable that the dichloromethylene nitrone (16), recently isolated from pyrolysis of trichloronitrosomethane,[15] similarly arises by loss of chlorine from bistrichloromethyl nitroxide (a known decomposition product of trichloronitrosomethane [16]), and not by alternative routes involving dichlorocarbene.[15]

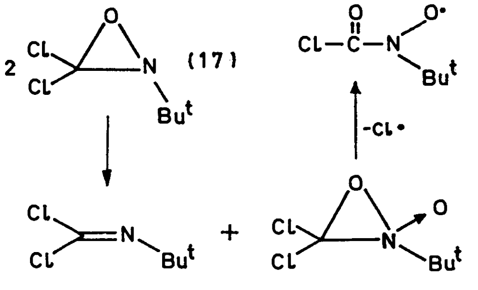
$$\mathrm{Cl_3CN{:}O \longrightarrow Cl_3C{\cdot} + NO}$$

$$\mathrm{Cl_3C{\cdot} + Cl_3CN{:}O \longrightarrow (Cl_3C)_2NO{\cdot}}$$

$$\mathrm{(Cl_3C)_2NO{\cdot} \xrightarrow{-Cl\cdot} Cl_2C{:}N(\rightarrow O)CCl_3}$$

(16)

The identity of the radicals formed during irradiation of solutions of nitrosobutane in polyhalogenomethanes has independently been recognised by de Boer *et al.*,[14] thus correcting an earlier suggestion.[7] These workers have, in addition, proposed an ingenious mechanism for the formation of the carbonyl nitroxides which requires photoisomerisation of the dihalogenomethylene nitrone, *e.g.* (15), to give the oxaziridine (17), followed by oxygen transfer and subsequent loss of halogen. Although such a mechanism might be operative in the photochemical system, it cannot accommodate the results of our ground state experiments involving hydrogen abstraction from chloroform, which are successful in the absence of light.



de Boer's group have studied the irradiation of several polyhalogenomethanes,[14] and, from chloroform ($\longrightarrow \cdot\mathrm{CHCl_2}$) they obtained t-butyl formyl nitroxide, the spectrum of which has a well-resolved doublet splitting of 1·4 G due to the formyl proton. The structure of this nitroxide was confirmed by scavenging formyl radicals with nitrosobutane.*

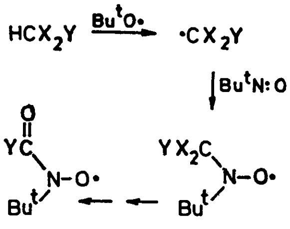
In our work the emphasis has been on hydrogen abstraction from halogenomethanes rather than on photolysis. In every case examined, radicals believed to be carbonyl nitroxides have been detected. For example, with bromoform the expected bromocarbonyl nitroxide (2) is produced; with 1,1-dichloroethane and αα-dichlorotoluene nitroxides are obtained whose spectra show the characteristic nitrogen splittings of acetyl and benzoyl t-butyl nitroxide respectively. All the results, which are summarised in Table 2, are accommodated by the general reaction sequence:

TABLE 2

Splitting parameters (in Gauss) for nitroxides formed by hydrogen abstraction from polyhalogenomethanes $\mathrm{HCX_2Y}$ in the presence of nitrosobutane [a,b]

	$\mathrm{YX_2C{\cdot}NBu^t{\cdot}O\cdot}$	$\mathrm{YCO{\cdot}NBu^t{\cdot}O\cdot}$
X = Y = Cl [c]	$a_N = 12{\cdot}5$, $a_{Cl} = 2{\cdot}2$ [d]	$a_N = 6{\cdot}65$, $a_{Cl} = 0{\cdot}5$
X = Y = Br	n.d.	$a_N = 6{\cdot}5$, $a_{Br} = 2{\cdot}2$
X = Cl, Y = H	$\left\{ a_N = 11{\cdot}7_5,\ a_{^{35}Cl} = 4{\cdot}8,\ a_{^{37}Cl} = 4{\cdot}05 \right\}$ [e]	$a_N = 7{\cdot}0$, $a_H = 1{\cdot}41$
X = Cl, Y = Me	n.d.	$a_N = 8{\cdot}0$
X = Cl, Y = Ph	n.d.	$a_N = 8{\cdot}0$ [f]
X = Cl, Y = $\mathrm{CHCl_2}$	$a_N = 12{\cdot}75_5$, $a_{Cl} = 4{\cdot}5$ and 1·1	$a_N = 6{\cdot}8$
X = Cl, Y = F [c]	n.d.	$a_N = 12{\cdot}1_5$, $a_F = 0{\cdot}7$

[a] Experiments employed butoxy radicals from the thermolysis of di-t-butyl peroxyoxalate as the hydrogen abstracting species. The appropriate halogenomethane $\mathrm{HCX_2Y}$ was the solvent, and reactions were run, and spectra obtained at 30°. [b] n.d. = Not determined. [c] Nitroso[$^2\mathrm{H}_9$]butane. [d] See ref. 5. [e] $a_{^{35}Cl}/a_{^{37}Cl} = 1{\cdot}18$ (Calc. value = 1·20). [f] This is slightly larger than the value reported in Table 1, probably as a consequence of the different solvent. When benzaldehyde was added in the present experiment the signal with a_N 8·0 became very intense.



(19) (18)

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* We have also generated t-butyl formyl nitroxide by this reaction.

[14] J. W. Hartgerink, J. B. F. N. Engberts, and Th. J. de Boer, *Tetrahedron Letters*, 1971, 2709.

[15] V. Astley and H. Sutcliffe, *Tetrahedron Letters*, 1971, 2707.

[16] H. Sutcliffe and H. W. Wardale, *J. Amer. Chem. Soc.*, 1967, **89**, 5487.

In only three instances have we observed spectra of the initial spin adduct (18) *and* the derived carbonyl nitroxide (19). These were with dichloromethane ($X = Cl$; $Y = H$) and chloroform, and with *sym*-tetrachloroethane. The spectrum believed to be that of the spin adduct of dichloromethyl radicals and nitroso[$^2H_9$]butane is reproduced in Figure 5. Isotopic splittings due to the $^{37}Cl_2$, $^{37}Cl^{35}Cl$, and $^{35}Cl_2$ species are clearly seen, but there is no resolvable interaction with the proton of the dichloromethyl group. This could be a consequence of a preferred conformation such as (20), in which the proton lies in the plane of the molecule, although it has already been mentioned that t-butyl isopropyl nitroxide displays an α-proton splitting of nearly 2 G.[12] The spectrum assigned to the spin adduct (18: $X = Cl$; $Y = CHCl_2$) from tetrachloroethane is particularly interesting as it reveals two non-equivalent chlorine splittings (Figure 6). These are considered to be due to the two α-chlorine atoms whose non-equivalence results from a very high barrier to rotation about the carbon–carbon bond of the tetrachloroethyl group, and consequent conformational rigidity on an e.s.r. time scale. Unfortunately the difficulties experienced in obtaining a satisfactory spectrum of this radical have so far precluded a study of its temperature dependence.

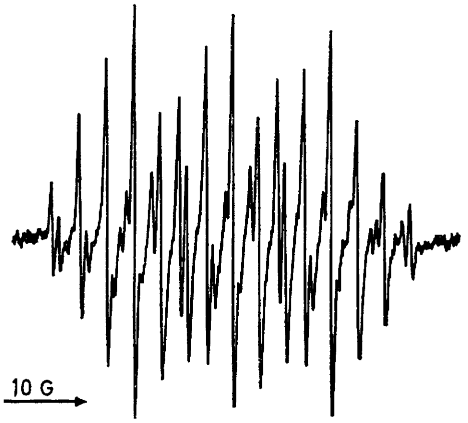
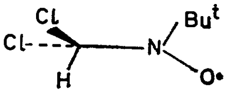


FIGURE 5 Spectrum attributed to $HCCl_2{\cdot}NC(CD_3)_3{\cdot}O{\cdot}$, showing isotopic chlorine splittings



(20)

The relative magnitudes of the hyperfine splittings due to the atoms attached to the carbonyl group in the spectra of the formyl, fluorocarbonyl, chlorocarbonyl, and bromocarbonyl nitroxides are surprising.* Possibly ' through-space ' interaction accounts for the relatively large bromine and chlorine splittings,[17a] while contributions from two coupling mechanisms of comparable magnitude but opposite sign might explain the very small fluorine splitting in the fluorocarbonyl nitroxide, which is only resolved using nitroso[$^2H_9$]butane: the structure of the radical is supported by its reaction with ethanol to give (3). A further point is that if delocalisation of the type suggested in structures (5a) and (5b) is important, we can infer from steric (and electrostatic) arguments preferred planar conformations in which carbonyl oxygen and nitroxide oxygen are *trans*-orientated, *e.g.* (5c) and (2a).[17b] Evidently the bromine in (2a) is properly placed with respect to the nitroxide group for through-space interaction to be possible. The steric argument breaks down, however, in the case of the formyl nitroxide from dichloromethane, and also in the case of the fluorocarbonyl nitroxide. Whilst the formyl nitroxide may prefer a *cis*-relationship between the oxygen atoms (21), it seems possible that the fluorocarbonyl nitroxide, which has two strongly electronegative atoms of almost equal bulk in the substituent, may spend a relatively long time in a bisected (non-planar) conformation, thus explaining the large nitrogen splitting ($a_N = 12{\cdot}15$ G).

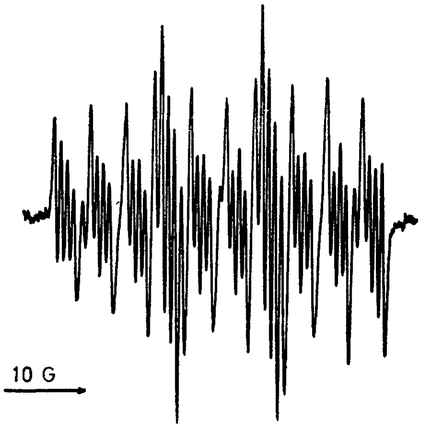
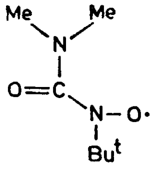
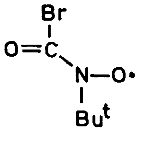


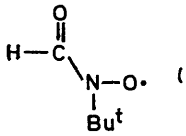
FIGURE 6 Spectrum attributed to $HCCl_2{\cdot}CCl_2{\cdot}NC(CD_3)_3{\cdot}O{\cdot}$ showing non-equivalence of the α-chlorine atoms



(5c)



(2a)



(21)

Full details of the mechanism whereby the carbonyl nitroxides are produced must await further experimentation. This should be facilitated by the availability of dichloromethylene nitrones such as (16). At present we

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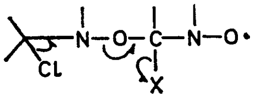
* We have been unable to detect an iodocarbonyl nitroxide in experiments involving attempted hydrogen abstraction from iodoform.

[17] (*a*) B. C. Gilbert and R. O. C. Norman, *J. Chem. Soc.* (*B*), 1966, **86**, 722; (*b*) *cf.* H. G. Aurich and J. Trösken, *Angew. Chem. Internat. Edn.*, 1971, **10**, 819.

feel that oxygen is probably supplied to a methylene nitrone such as (15) by a second nitroxide molecule,* and that a crucial structural feature in the oxygen donor may be the presence of a chlorine or bromine atom on the α-carbon. This could facilitate fragmentation of the complex (22) to complete the oxygen transfer. Experiments designed to evaluate these ideas are in hand.



(22)

Finally, we must withdraw the suggestion hazarded in our earlier note,[2] that nucleophilic displacement of halogen from the halogenocarbonyl affords the first example of an ionic nitroxide reaction at a site in direct conjugation with the radical centre. Precedent exists in the reactions of the cyclic nitronyl nitroxides [20] and imino nitroxides [21] studied by Ullmann's group.†

EXPERIMENTAL

The general experimental procedure has been indicated.[22] Hydrogen-abstraction experiments using di-t-butyl peroxyoxalate were carried out as previously described,[5] and employed the hydrogen donor as solvent.

Compounds were mostly commercial materials purified where necessary by distillation or crystallisation. Alcohol-free chloroform was obtained by distillation from phosphorus pentoxide. Nitrosobutane [23] and nitroso$[^2H_9]$butane [1] were prepared according to recent literature procedures.

Crotonyl peroxide was prepared by the method of Fichter and Rosenzweig.[24] The decomposition of this peroxide in benzene in the presence of nitrosobutane or nitrosobenzene was effected by heating in the cavity of the spectrometer to *ca.* 50°.

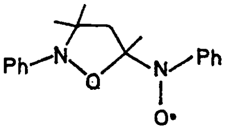
In photochemical experiments samples were irradiated in the cavity employing unfiltered light from a 100 W medium-pressure mercury arc.

No halogenocarbonyl nitroxides could be detected when benzene solutions of phosgene or bromophosgene (prepared by a modification of Schumacher and Lenher's method,[25] and distilled from mercury to remove last traces of bromine) were irradiated in the presence of nitrosobutane, or when azobisisobutyronitrile was added and the solutions were warmed.

We thank the S.R.C. for a studentship (to R. J. H.), and for a grant to purchase the spectrometer.

[1/1652 *Received, 9th September,* 1971]

* Banfield and Kenyon's radical [18] provides an interesting analogy for this. The revised [19] cyclic structure (i) is essentially an intramolecular adduct of a nitroxide and a nitrone.



(i)

† *Note added in proof:* By analogy with our proposals for reactions involving t-butyl dihalogenomethylene nitrone, it is tempting to speculate that the radical observed following reaction of nitrone (16) with chlorine may have the structure, chlorocarbonyl trichloromethyl nitroxide $ClCO{\cdot}N(CCl_3)O{\cdot}$, rather than that suggested, $Cl_2C{:}N(\longrightarrow O)CCl_2{\cdot}$ (V. Astley and H. Sutcliffe, *Chem. Comm.*, 1971, 1303). The spectral parameters are not inconsistent with the nitroxide formulation, and this would accord well with our general mechanistic hypothesis.

[18] F. H. Banfield and J. Kenyon, *J. Chem. Soc.*, 1926, 1612.

[19] R. Foster, J. Iball, and R. Nash, *Chem. Comm.*, 1968, 1414.

[20] *E.g.* E. F. Ullman and L. Call, *J. Amer. Chem. Soc.*, 1970, **92**, 7210.

[21] E. F. Ullman, L. Call, and J. H. Osiecki, *J. Org. Chem.*, 1970, **35**, 3623.

[22] G. R. Chalfont, M. J. Perkins, and A. Horsfield, *J. Amer. Chem. Soc.*, 1968, **90**, 7141.

[23] R. J. Holman and M. J. Perkins, *J. Chem. Soc.* (*C*), 1970, 2195.

[24] F. Fichter and J. Rosenzweig, *Helv. Chem. Acta*, 1935, **18**, 238.

[25] H. J. Schumacher and S. Lenher, *Ber.*, 1928, **61**, 1671.