

## Electron Spin Resonance Study of Halogenocarbonyl Nitroxides<sup>1</sup>

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**Summary** t-Butyl chlorocarbonyl and bromocarbonyl nitroxides, formed as by-products in reactions involving trihalogenomethyl radicals and nitrosobutane, have been characterised by their e.s.r. spectra, and by their reactions with primary alcohols and with dimethylamine: the e.s.r. study was facilitated by the use of a new spin trap, perdeuterionitrosobutane.

We recently pointed out<sup>2</sup> that the merits of 2-methyl-2-nitrosopropane ("nitrosobutane") as a "spin-trap"<sup>3,4</sup> should be enhanced by complete deuteration of the t-butyl group. Lines in the spectra of t-butyl nitroxides are broadened by unresolved splittings from the protons of the t-alkyl group, and this effect should be considerably reduced by complete deuteration. The account by Jakobsen and Torssell of the scavenging of 2,6-dimethoxyphenyl radicals with perdeuterionitrosobutane<sup>5</sup> prompts this description of the use of the same deuteriated scavenger to identify some unusual nitroxides encountered in an investigation of radical reactions of polyhalogenomethanes by the spin-trapping method.

It had been found<sup>6</sup> that u.v. irradiation of bromotrichloromethane solutions of nitrosobutane gives two nitroxides, one of which is t-butyl trichloromethyl nitroxide,<sup>2</sup> whilst the other, longer-lived, radical was tentatively identified as  $\text{Bu}^t(\text{Br})\text{NO}\cdot$  (Figure 1a,  $a_N = 6.65\text{G}$ ). Subsequently, however, it has been found that similar irradiation of a benzene solution of nitrosobutane saturated with carbon tetrabromide gives a new radical with a similar nitrogen hyperfine splitting ( $a_N = 6.50\text{G}$ ), but with a much larger and better resolved halogen splitting ( $a_{\text{Hal}} = 2.12\text{G}$ ).

In a second series of experiments, the "spin-adduct"<sup>3</sup> of

nitrosobutane with trichloromethyl radicals<sup>1</sup> formed by hydrogen abstraction by butoxy-radicals from chloroform<sup>2</sup>

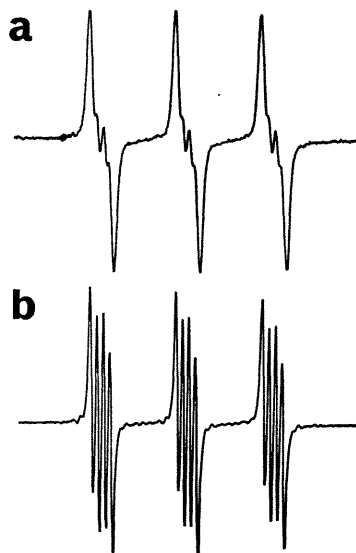


FIGURE 1. The e.s.r. spectra of (a)  $\text{CICON}(\text{Bu}^t)\text{O}\cdot$  and (b)  $\text{CICON}[\text{C}(\text{CD}_3)_3]\text{O}\cdot$  recorded under comparable conditions.

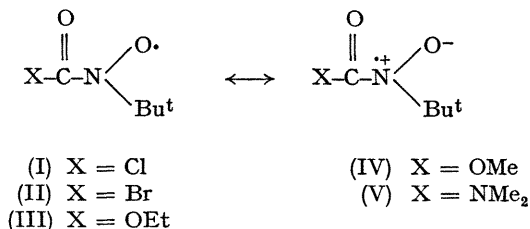
was found to be gradually replaced by a radical having a three-line spectrum with  $a_N = 8.25\text{G}$ . (Figure 2a). A similar observation has been noted previously.<sup>7</sup>

Replacement of nitrosobutane by perdeuterionitrosobutane<sup>†</sup> in the experiments with bromotrichloromethane

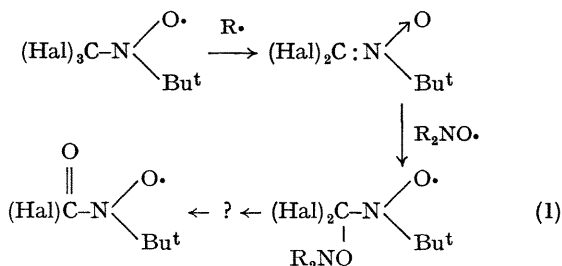
<sup>†</sup>  $[\text{D}_9]$ -t-Butylamine, prepared from  $[\text{D}_9]$ -t-butyl alcohol by a modified Ritter procedure, was oxidised to  $[\text{D}_9]$ -nitrosobutane by the method of Holman and Perkins.<sup>8</sup>

and with chloroform gives the nitroxides whose spectra are traced in Figures 1b and 2b, respectively. Both spectra show the very considerable improvement in resolution achieved by deuteration of the nitrosobutane. In addition, the secondary hyperfine structure in Figure 1b is clearly attributable to a single halogen atom ( $a_{\text{Hal}} = 0.50\text{G}$ ), and secondary structure attributable to two protons is evident in Figure 2b. The origin of this two-proton triplet ( $a_{\text{H}} = 0.45\text{G}$ ) was traced to the ethanol present in the chloroform sample employed, for when scavenging experiments were carried out with ethanol-free chloroform, the spectrum of the secondary nitroxide formed was not that of Figure 2b, but that of Figure 1b. Clearly, therefore, the halogen in this radical must be chlorine and not bromine.

Our interpretation of these observations is as follows. In view of the low nitrogen splitting constants, all of the radicals described are considered to be carbonyl nitroxides. Those from photolysis of bromotrichloromethane and carbon tetrabromide are t-butyl chlorocarbonyl and bromocarbonyl nitroxides (I and II), respectively. The larger halogen splitting in the latter is consistent with the larger nuclear moment of bromine.



The mode of formation of the halogenocarbonyl nitroxides is uncertain. It is possible that halogen abstraction from an initially-formed trihalogenomethyl nitroxide could give a dihalogenomethylene nitron. Coupling with a second nitroxide (the most plausible source of oxygen) would then give the required structural elements (reaction 1).



This reaction scheme would also accommodate formation of the chlorocarbonyl nitroxide in the experiments with

chloroform. Acylation of ethanol by this radical (I) should be facilitated by the electron-withdrawing nitroxide function, the product being the ethoxycarbonyl nitroxide (III), in which an unexpected long-range splitting by the

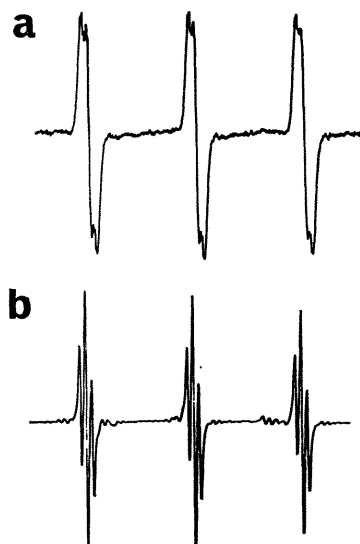


FIGURE 2. The e.s.r. spectra of (a)  $\text{EtOCON}(\text{Bu}^t)\text{O}\cdot$  and (b)  $\text{EtOCON}[\text{C}(\text{CD}_3)_3]\text{O}\cdot$  recorded under comparable conditions.

$\alpha$ -methylene protons is responsible for the secondary triplet in Figure 2b. Hydrogen abstraction by butoxy-radicals from ethyl formate in the presence of perdeuterio-nitrosobutane also gives the nine-line spectrum of Figure 2b, thus providing strong support for structure (III) [ $-\text{CO}_2\text{Et} + \text{Bu}^t\text{N}:\text{O} \rightarrow (\text{III})$ ].

Both halogenocarbonyl nitroxides produced in the photochemical reactions appeared to be indefinitely stable after irradiation was discontinued. However, both reacted with ethanol to give (III). Similarly, both reacted with methanol and with dimethylamine to give (IV) [ $a_{\text{N}} = 8.2$ ,  $a_{\text{H}}(\text{quartet}) = 0.45\text{G}$ ] and (V) [triplet of multiplets,  $a_{\text{N}} = 11.75\text{G}$ ], respectively, the structures of which were established by alternative syntheses involving hydrogen abstraction from methyl formate and dimethylformamide.

The reactions of the halogenocarbonyl nitroxides outlined here appear to be the first examples of polar reactions of nitroxides at a site which is in direct conjugation with the radical centre.

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<sup>1</sup> For the previous paper on nitroxides see G. R. Chalfont, M. J. Perkins, and A. Horsfield, *J. Chem. Soc. (B)*, 1970, 401.

<sup>2</sup> M. J. Perkins, P. Ward, and A. Horsfield, *J. Chem. Soc. (B)*, 1970, 395.

<sup>3</sup> E. G. Janzen and B. J. Blackburn, *J. Amer. Chem. Soc.*, 1969, **91**, 4481.

<sup>4</sup> M. J. Perkins, *Chem. Soc. Special Publ. No. 24*, 1970, 97; see also e.g. P. Tordo, M.-P. Bertrand, and J.-M. Surzur, *Tetrahedron Letters*, 1970, 3399; J. G. Pacifici and H. L. Browning, *J. Amer. Chem. Soc.*, 1970, **92**, 5231.

<sup>5</sup> H. J. Jakobsen and K. Torssell, *Tetrahedron Letters*, 1970, 5003.

<sup>6</sup> G. R. Chalfont, Ph.D. Thesis, London, 1968.

<sup>7</sup> J. W. Hartgerink, J. B. F. N. Engberts, Th. A. J. W. Wajer, and Th. J. De Boer, *Rec. Trav. chim.*, 1969, **88**, 481; K. Torssell, *Tetrahedron*, 1970, **26**, 2759.

<sup>8</sup> R. J. Holman and M. J. Perkins, *J. Chem. Soc. (C)*, 1970, 2195.