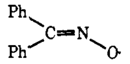
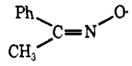
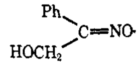
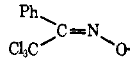
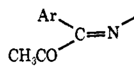
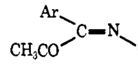
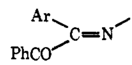
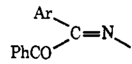
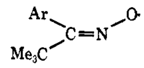
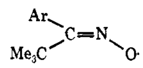
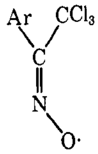
Table I. Esr Characteristics of Iminoxy Radicals from Nitrile *N*-Oxides

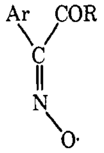
Radical[a]	a^{N}, mT	a^{H}, mT	g
	3.15	0.135 (2 H)	2.0059
	3.16	0.135 (5 H)	2.0055
 [b]	3.02	*c*	2.0057
	3.27	*d*	2.0048
	3.16	0.130 (2 H)[e] 0.075 (3 H)[f]	2.0048
	2.94	0.038 (5 H)[g]	2.0051
	3.27	0.130 (2 H)[h] 0.055 (2 H)	2.0045
	2.96	0.038 (2 H)[i]	2.0051
	3.15	0.135 (2 H)	2.0057
	3.07	0.090 (9 H)	2.0057

[a] Ar = p-ClC$_6$H$_4$. [b] Stereochemistry not determined. [c] Proton hyperfine splittings were not resolved; the line width was unusually large (0.17 mT). [d] a^{Cl}(3Cl) = 0.05 mT. [e] Attributed to the ortho protons; *cf.* ref 3 and 5. [f] Attributed to the methyl protons; *cf.* ref 5. [g] $a^{CH_3} = a^{o\text{-}H}$; *cf.* ref 5. [h] The larger and smaller proton splittings are attributed, respectively, to the ortho protons in Ar and Ph; *cf.* ref 5. [i] Attributed to the ortho protons in Ar by analogy with the data for **2** (R = CH$_3$).

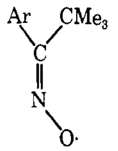
trum from acetaldehyde showed the presence of **2** (R = CH$_3$) and its geometrical isomer; an identical spectrum was obtained by treating benzyl methyl ketone with nitrogen dioxide,[6] although in this case the signals were less well resolved. Likewise, benzaldehyde gave the radical **2** (R = Ph) and its geometrical isomer[3] (Figure 1). With trimethylacetaldehyde, the spectrum showed the presence of **3** and its isomer (previously observed during the oxidation of pivalophenone oxime[7]), from which we infer that the radical Me$_3$CCO· from the aldehyde decarbonylates readily.



1



2



3

Ar = Ph or p-ClC$_6$H$_4$

The long-range electron–nucleus interactions such as those involving the methyl protons in **2** (R = CH$_3$), the ortho protons in the benzoyl fragment in **2** (R = Ph), and the *tert*-butyl protons in **3** are characteristic of iminoxy radicals.[3,5,7] Thus, the esr spectra of many iminoxy radicals from nitrile *N*-oxides (particularly those with acyl fragments) can give direct information about the structure of the addend (which is rarely true for nitrone adducts or for acyl adducts of nitroso compounds). Spectral complication which results from the occurrence of geometrical isomerism might prove a disadvantage if more than one radical is trapped; however, nitrogen splittings vary sufficiently for separate resonances to be resolved in most cases and, in addition, the observation of two isomers from a given adduct can provide extra evidence for the nature of the trapped species. It is notable that, in the nitrile oxide reaction, spin adducts from alkoxy radicals (*e.g.*, *tert*-BuO· from di-*tert*-butyl peroxide) are not detected, in contrast with the use of nitrones and nitroso compounds.

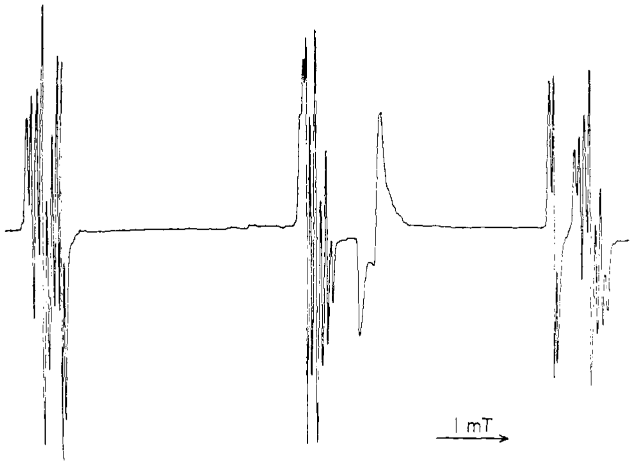


Figure 1. Esr spectrum of the radical **2** (Ar = p-ClC$_6$H$_4$, R = Ph) and its geometrical isomer; the asymmetric resonance is from irradiated quartz.

Since nitrile *N*-oxides are readily prepared, we believe that they constitute a useful addition to the types of spin trap available. In addition, the spectra of the iminoxy radicals we have obtained have narrower line widths (*e.g.*, for the radicals in Figure 1, 0.030 mT) than those of the same radicals obtained by the oxidation of oximes with, for example, lead tetraacetate; consequently, very small splittings can be resolved, and this should enable further information to be gained about long-range effects in these radicals and the factors on which they depend. Finally, our esr observations support the suggestion[8] that iminoxy radicals are intermediates in some radical-catalyzed reactions of nitrile *N*-oxides which lead to oximes.

---

[6] W. M. Fox, J. McRae, and M. C. R. Symons, *J. Chem. Soc. A*, 1773 (1967).

[7] B. C. Gilbert and R. O. C. Norman, *ibid.*, *B*, 123 (1968).

[8] T. Caronna, A. Quilico, and F. Minisci, *Tetrahedron Lett.*, 3633 (1970).

B. C. Gilbert,* V. Malatesta, R. O. C. Norman
Department of Chemistry, The University of York
Heslington, York, United Kingdom

Received December 24, 1970

The Facile Photochemical or Oxygen Initiated Free-Radical Chain Reactions of Trialkylboranes with Organic Disulfides. Convenient New Synthesis of Organic Sulfides *via* Hydroboration

Sir:

Trialkylboranes readily participate in free-radical chain reactions with organic disulfides. The reactions

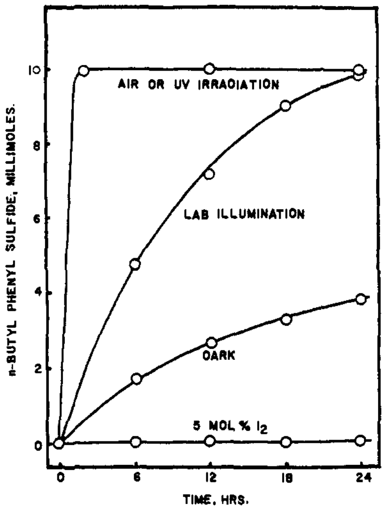


Figure 1. The reaction of tri-*n*-butylborane with phenyl disulfide in hexane.

are readily initiated by oxygen or light and are strongly inhibited by iodine. These chain reactions provide a convenient new synthetic route to a wide variety of alkyl and aryl sulfides.

Convenient methods for the conversion of organoboranes into the corresponding sulfides have been lacking. In the course of searching for such methods, we observed that phenyl disulfide and methyl disulfide undergo a slow reaction with trialkylboranes at room temperature, forming the corresponding alkyl methyl sulfide or alkyl phenyl sulfide (eq 1). We soon became convinced that these new reactions must proceed through chains involving free radicals (eq 2, 3). Such

$$R_3B + R'SSR' \longrightarrow RSR' + R_2BSR' \qquad (1)$$

$$R\cdot + R'SSR' \longrightarrow RSR' + R'S\cdot \qquad (2)$$

$$R'S\cdot + BR_3 \longrightarrow R'SBR_2 + R\cdot \qquad (3)$$

free-radical reactions of organoboranes are the subject of great current interest.[1] Accordingly, we undertook to explore the reaction in detail.

Tri-*n*-butylborane (10 mmol) was placed in 20 ml of dry *n*-hexane in a dry flask maintained under nitrogen. Phenyl disulfide (20 mmol) was added. A slow reaction was observed at room temperature with the formation of *n*-butyl phenyl sulfide. In 24 hr there was realized a 98.5% conversion of one alkyl group of the borane to *n*-butyl phenyl sulfide. A similar reaction in tetrahydrofuran (THF) required 72 hr to achieve a 77.5% conversion.

Iodine is a powerful inhibitor of free-radical reactions of organoboranes.[2] When the reaction was repeated in *n*-hexane with 5 mol % iodine added, no reaction was observed even after 72 hr. Consequently, the reaction must proceed through a free-radical chain.

Many of the new free-radical reactions of organoboranes may be initiated by light[3] or oxygen.[4] An investigation of the effect of these initiators on the reaction with disulfides revealed that the reaction rate is greatly accelerated by either light or air. Thus, after the addition of air at a rate of 1 ml/min to a 0.5 *M* THF solution of tri-*n*-butylborane (10 mmol) and phenyl disulfide (20 mmol), there was obtained 9.5 mmol (95%) of butyl phenyl sulfide (90% *n*-, 10% *sec*-butyl) in 1.5 hr. Similarly, treatment of such reaction mixtures in either *n*-hexane or THF (refluxing) with illumination from an external ultraviolet light source[5] results in a rapid reaction. A 98% conversion to the sulfide is realized within 1 hr for both tri-*n*-butyl- and tri-*sec*-butylborane. In the dark, the reaction proceeds only very slowly in *n*-hexane. The results are shown graphically in Figure 1. Reactions in which equimolar amounts of the organoborane and disulfide are used give somewhat slower rates and lower yields.

In contrast to the behavior of phenyl disulfide, methyl disulfide exhibits only a very slow reaction in THF or *n*-hexane at room temperature. At higher temperatures, in refluxing THF, 93% of one alkyl group on boron reacts in 24 hr. However, the reaction is greatly facilitated by the introduction of air (1 ml/min) or by illumination with an ultraviolet light.[5] Under these conditions, two of the alkyl groups on boron are utilized to form the alkyl methyl sulfide.[6]

The air-initiated reaction was studied in detail. Oxygen is a diradical and reacts with the organoborane to produce free radicals apparently by the process shown in eq 4.[2] These free radicals attack the disulfide (eq 4), forming the product and displacing methylthio radicals.[7] The methylthio radical displaces an alkyl radical on boron[1f] in the chain-carrying step (eq 6). The methylthio dialkylborinate ester[8] (**1**) may be detected by glpc. Addition of methanol to the reaction mixture causes the peak assigned to **1** to disappear and a new peak appears corresponding to the known R_2BOCH_3. Organoboranes containing secondary alkyl groups readily undergo utilization of a second alkyl group (eq 7). Organoboranes containing primary alkyl groups also undergo utilization of two alkyl groups, but the reaction is somewhat slower. The bis(methylthio)alkylboronate ester[8] (**2**) may also be identified by glpc and converted to the known methyl boronates by addition of methanol. The overall reaction may thus be written as

$$R_3B + O_2 \longrightarrow RBO_2\cdot + R\cdot \qquad (4)$$

$$R\cdot + CH_3SSCH_3 \longrightarrow RSCH_3 + CH_3S\cdot \qquad (5)$$

$$CH_3S\cdot + R_3B \longrightarrow \underset{\mathbf{1}}{CH_3SBR_2} + R\cdot \qquad (6)$$

$$CH_3S\cdot + CH_3SBR_2 \longrightarrow \underset{\mathbf{2}}{(CH_3S)_2BR} + R\cdot \qquad (7)$$

$$R_3B + 2CH_3SSCH_3 \longrightarrow 2RSCH_3 + (CH_3S)_2BR \qquad (8)$$

---

(1) (a) A. G. Davies and B. P. Roberts, *J. Chem. Soc. B*, 17 (1967); (b) P. J. Krusic and J. K. Kochi, *J. Amer. Chem. Soc.*, **91**, 3942 (1969); (c) A. G. Davies, D. Griller, B. P. Roberts, and R. Tudor, *Chem. Commun.*, 640 (1970); (d) A. G. Davies, S. C. W. Hook, and B. P. Roberts, *J. Organometal. Chem.*, **22**, C37 (1970); (e) A. G. Davies, S. C. W. Hook, and B. P. Roberts, *ibid.*, **23**, C11, 1970; (f) A. G. Davies, private communication.

(2) M. M. Midland and H. C. Brown, *J. Amer. Chem. Soc.*, **93**, 1506 (1971).

(3) H. C. Brown and G. W. Kabalka, *ibid.*, **92**, 712 (1970).

(4) H. C. Brown and G. W. Kabalka, *ibid.*, **92**, 714 (1970); A. Suzuki, S. Nazawa, M. Itoh, H. C. Brown, G. W. Kabalka, and G. W. Holland, *ibid.*, **92**, 3503 (1970); A. Suzuki, S. Nozawa, M. Harada, M. Itoh, H. C. Brown, and M. M. Midland, *ibid.*, **93**, 1508 (1971).

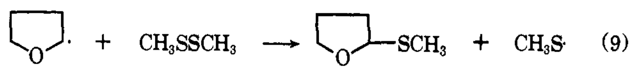
(5) A commercially available Sears 275-W sunlamp was used.

(6) However, *tert*-butyl disulfide failed to react under these conditions, probably due to its low transfer constant in free-radical reactions: W. A. Pryor and T. L. Pickering, *ibid.*, **84**, 2706 (1962).

(7) C. Walling, "Free Radicals in Solution," Wiley, New York, N. Y., 1957.

(8) Thioboronic esters are also of synthetic interest for other reactions, such as the preparation of thioacetals from aldehydes: R. H. Cragg and J. P. N. Husband, *Inorg. Nucl. Chem. Lett.*, **6**, 773 (1970).

In THF a minor reaction with solvent occurs, resulting in the formation of methyl 2-tetrahydrofuryl sulfide (**3**). (Bp 66–67° (21 mm); n^{20}D 1.4868. *Anal.* Calcd for $C_5H_{10}OS$: C, 50.80; H, 8.53; S, 27.12. Found: C, 50.86; H, 8.60; S, 27.00.) This presumably arises through hydrogen abstraction from the α position and reaction of the radical thus formed with methyl disulfide (eq 9). The side product did not interfere seriously with the reaction. Since THF is a common solvent for hydroboration,[9] it is most convenient to carry out organoborane reactions in this solvent. However, the production of **3** could be easily avoided by adopting *n*-hexane as the solvent. In this solvent the rates are approximately the same with the yields being somewhat higher.



3

The photochemical reactions are even faster than the air-induced reaction, being complete in about 2 hr. However, reactions carried out in THF give somewhat lower yields and increased formation of **3**. Thus *n*-hexane was preferred for the photochemical reactions.

Both the air-induced and photochemical reactions are synthetically useful. The reaction was applied to a representative series of olefins. The results are summarized in Table I.

Table I. The Reaction of Trialkylboranes with Methyl Disulfide

	Oxygen initiated[a]			Photochemical[b]	
Trialkylborane	Time, hr	$RSCH_3$,[c] %	**3**, %	Time, hr	$RSCH_3$,[c] %
Tri-*n*-butyl-	24	71[d]	8	2	91[d]
Triisobutyl-	20	68	30	3	91
Tri-*sec*-butyl-	10	83	13	2	95
Tri-*n*-octyl-	24	84 (75)[e]	11	2	95[c]
Tricyclopentyl-	12	81 (74)	Tr	3	93
Tricyclohexyl-	5	88 (77)	Tr	2	93
Tri-*exo*-norbornyl-	5	78 (75)	6	2	95

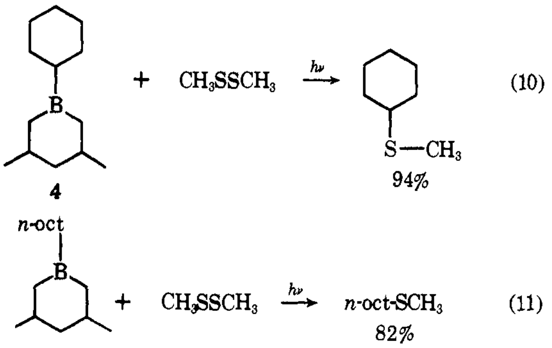
[a] In THF solution. [b] In *n*-hexane solution. [c] Yield based on methyl disulfide by gc. Isolated yields are in parentheses. [d] The product contained 15% of the *sec*-butyl isomer. [e] The product contained 10% of the *sec*-octyl isomer.

The following procedure for the preparation of methyl norbornyl sulfide is representative. A dry 200-ml flask equipped with a septum inlet and a magnetic stirrer was flushed with nitrogen. The flask was charged with 82 ml of dry THF and 14.1 g of norbornene (150 mmol) and cooled to 0°. Hydroboration was achieved by the dropwise addition of 18.6 ml of a 2.68 *M* solution of borane in THF (150 mmol of hydride) at 0° followed by stirring at room temperature for 1 hr. Methyl disulfide, 9.4 g (100 mmol), was then added. Air was introduced through a syringe needle above the THF solution at 1 ml/min. The THF solution was stirred at room temperature overnight (10 hr, 5 hr on 10-mmol scale for gc analysis) and then distilled directly. Methyl norbornyl sulfide, 10.6 g, 75%, was collected, bp 90–92° (23 mm), n^{20}D 1.5115, sulfone mp 74.5–75° (lit.[10] bp 82° (18 mm), n^{20}D 1.5118, sulfone mp 75°).

For the photochemical reactions, the THF was removed with a water aspirator after hydroboration and replaced with *n*-hexane. The methyl disulfide was then added and the resulting solution illuminated with an external ultraviolet sunlamp.[5] The *n*-hexane was allowed to reflux.

The photochemical reactions proceed faster and give higher yields but involve the extra step of solvent removal. If the alkyl group contains light-sensitive functional groups, the air-induced reaction gives satisfactory results.

It was recently pointed out that the use of *B*-alkyl-3,5-dimethylborinanes (**4**, **5**) can offer advantages in achieving high utilization of a particular alkyl group which may be a valuable intermediate in a synthesis.[11] This was tested for the present reaction. Excellent results were realized (eq 10, 11).



These results establish that organoboranes readily undergo a reaction with disulfides *via* a free-radical chain mechanism. The reaction provides a new convenient synthesis of mixed sulfides.

---

(9) H. C. Brown, "Hydroboration," W. A. Benjamin, New York, N. Y., 1962.

(10) D. I. Davies, L. T. Parfitt, C. K. Alden, and J. A. Claisse, *J. Chem. Soc. C*, 1585 (1969).

(11) H. C. Brown and E. Negishi, *J. Amer. Chem. Soc.*, in press.

(12) National Science Foundation Predoctoral Fellow.

Herbert C. Brown,* M. Mark Midland[12]
Richard B. Wetherill Laboratory
Purdue University, Lafayette, Indiana 47907

Received March 10, 1971

Phosphabenzene and Arsabenzene

Sir:

The close resemblance of benzene and its nitrogen analog, pyridine **1**, is familiar to all chemists. This resemblance in terms of structure and overall stability clearly demonstrates that the isoelectronic nitrogen atom replaces a methine group of benzene without disrupting its "aromaticity." While a formal replacement of the nitrogen of pyridine by its congeners, phosphorus and arsenic, gives phosphabenzene (phosphorin) (**2**) and arsabenzene (arsenin) (**3**), it is less clear that these materials would show aromatic properties.[1] Heavily substituted derivatives of **2**, such as

---

(1) This is rather difficult to predict since there are extremely few stable compounds of trivalent phosphorus and arsenic which are dicoordinated: see K. Dimroth and P. Hoffmann, *Chem. Ber.*, **99**, 1325 (1966); G. Märkl and F. Lieb, *Tetrahedron Lett.*, 3489 (1967); and ref **2** and **3**.

(2) G. Märkl, *Angew. Chem., Int. Ed. Engl.*, **5**, 846 (1966); G. Märkl, F. Lieb, and A. Merz, *ibid.*, **6**, 458, 944 (1967); P. deKoe and F. Bickelhaupt, *ibid.*, **6**, 567 (1967); P. deKoe, R. VanVeen, and F. Bickelhaupt, *ibid.*, **7**, 465 (1968); K. Dimroth and W. Mach, *ibid.*, **7**, 460 (1968); G. Märkl and A. Merz, *Tetrahedron Lett.*, 1231 (1969); A. I. Tolmachev and E. S. Kozlov, *J. Gen. Chem. USSR*, **37**, 1826 (1967).

(3) P. Jutzi and K. Deuchert, *Angew. Chem., Int. Ed. Engl.*, **8**, 991 (1969); H. Vermeer and F. Bickelhaupt, *ibid.*, **8**, 992 (1969).