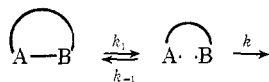


Scheme VIII

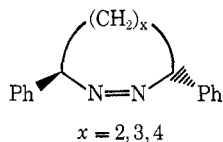


with the other reactions (k). However, the possibility that pressure effects on k_{obsd} might give clues concerning detailed mechanism (see eq 16) has led us to study a

$$\Delta V^*_{\text{obsd}} = \Delta V^*_1 + RT \partial \ln (1 + k_{-1}/k) / \partial P \quad (16)$$

series of cyclic azo compounds.

Kinetic and product studies of the six- through eight-membered ring systems shown below are in progress.²⁷



The values of ΔV^*_{obsd} for decomposition leading to expulsion of nitrogen for the six- and eight-membered ring systems are +5 and +7 cm³/mole, respectively. Together with product data, the results suggest that mechanistic differences may be present which can be probed using pressure studies.

Summary

Effects of pressure on the decomposition rates and

(27) R. C. Neuman, Jr., and E. W. Ertley, *Tetrahedron Lett.*, 1225 (1972).

products of radical initiators have provided detailed mechanistic information about these systems. Decomposition activation volumes for homolytic scission appear to be *ca.* +4 to +5 cm³/mole. Larger values indicate the presence of cage return regenerating the initiator, and smaller values can reflect polar effects in the decomposition transition state.

Cage reactions of radical pairs such as combination and disproportionation are generally favored over separative diffusion by increasing pressure. However, in spite of this, these cage bimolecular processes (combination and disproportionation) appear to be retarded by pressure because of its effect on the prerequisite rotational diffusion processes within the initial cages.

Pressure studies complement the use of solvent viscosity as a probe of initiator decomposition mechanism and provide information in cases where the latter technique cannot be used. Since diffusion rates can be altered by pressure without changes in temperature or medium, data derived from these studies may be of use in probing microscopic features of solvent structure and its interaction with solutes.

The work reported here was carried out by my able collaborators Drs. Michael Amrich, Joseph Behar, Robert Bussey, Gary Holmes, and Messrs. Ernest Ertley, George Lockyer, and Richard Pankratz. We thank the National Science Foundation for its continuing support of these studies. This account was written during the author's tenure as an NIH Special Research Fellow at Princeton University, 1971-1972.

Bimolecular Homolytic Substitution at a Metal Center

ALWYN G. DAVIES* AND BRIAN P. ROBERTS

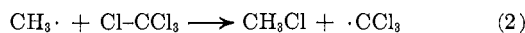
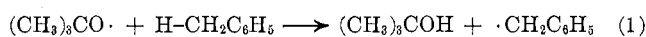
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Received March 13, 1972

Bimolecular heterolytic substitution reactions (S_N2 and S_E2) at a saturated center have been investigated intensively in recent years, principally by kinetic and stereochemical methods, and a great deal of information is now available on the way in which constitutional and environmental factors affect these processes.

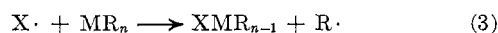
Much less is known about bimolecular homolytic substitution (S_H2), largely because there is as yet no firmly established example of this reaction taking place at a simple saturated carbon center. Such reactions occur usually at the peripheral monovalent hydrogen or

halogen atoms in an organic compound (*e.g.*, eq 1 and 2),



and infrequently at bivalent oxygen or sulfur. This severely limits the context within which the process can be studied and the techniques that can be employed.

Since 1966, however, it has become apparent that S_H2 processes can occur, often extremely rapidly, at the metallic center of an organometallic compound (eq 3).¹



This process provides a wide new context for studying the behavior of free radicals, and it supplies the key to the interpretation of many familiar organometallic reactions and the prediction of new ones. The kinetics of a number of these reactions have been studied, and

(1) K. U. Ingold and B. P. Roberts, "Free Radical Substitution Reactions," Wiley-Interscience, New York, N. Y., 1971.

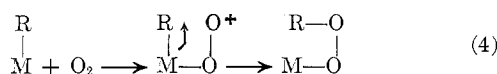
Alwyn Davies received his undergraduate training at University College London, and worked for his Ph.D. degree under the supervision of Professors E. D. Hughes and C. K. Ingold. From 1949 to 1953 he was a lecturer at Battersea Polytechnic under Joseph Kenyon, and then returned to the staff at University College. His research interests have moved from organic peroxides, through organometallic chemistry, to homolytic reactions.

Brian Roberts studied as an undergraduate at University College and obtained his Ph.D. degree in 1968 after working with Professor A. G. Davies on the mechanism of autoxidation of organometallic compounds. He is now Lecturer in Chemistry at University College.

before long our understanding of these processes should bear comparison with that of the heterolytic equivalents.

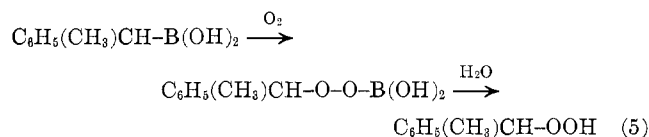
Alkylperoxyl Radicals

We were led into this field by our studies on the autoxidation of organometallic compounds.² The alkyl derivatives of many organometallic compounds, MR (M = Li, Mg, Zn, Cd, B, Al, Tl), react with oxygen to give the corresponding alkylperoxymetallic compounds as the primary products. The reactions are usually very fast and involve both a gas and a liquid phase, and are therefore difficult to study kinetically. Also, until recently no stereoisomeric compounds were available which would undergo the reaction. In 1955, more permissive criteria therefore had to be used to investigate the mechanism. It was shown that the common radical inhibitors then available did not affect the rates, and it was tentatively suggested that these reactions involved nucleophilic attack of oxygen at the metal and a 1,3-nucleophilic shift of the alkyl group from the metal to oxygen (eq 4).^{3,4}



In 1965, however, Matteson and Bowie⁵ reported the optical resolution of 1-phenylethyldihydroxyborane, providing for the first time a compound which could be used for checking the retention of asymmetry in the alkyl group, which would be expected for this mechanism.

Autoxidation of the borane, $[\alpha]_D -23.9^\circ$ (in benzene), gave, after hydrolysis, racemic 1-phenylethyl hydroperoxide (eq 5), whereas retention of optical purity



would have given a product with $[\alpha]_D 65.5^\circ$ (neat).⁶

The polar mechanism of eq 4 is therefore excluded. The racemization presumably implies the intermediacy of a species with a three-coordinate carbon atom, and, by the use of powerful inhibitors which had been recently developed, this intermediate was identified as a free radical. In particular, 1 mole % of galvinoxyl gave an induction period of several reaction half-lives; similar experiments with less efficient inhibitors 10 years earlier had given negative results simply because the alkylperoxyl radical reacted more rapidly with the organometallic compounds than with the inhibitors.

In the presence of an excess of oxygen the mechanism of the autoxidation of the organoborane (M = B(OH)₂;

(2) A. G. Davies in "Organic Peroxides," Vol. 2, D. Swern, Ed., Wiley-Interscience, New York, N. Y., 1972, Chapter 4.

(3) C. Walling and S. A. Buckler, *J. Amer. Chem. Soc.*, **77**, 6032 (1955).

(4) A. G. Davies, *Progr. Boron Chem.*, **1**, 265 (1964).

(5) D. S. Matteson and R. A. Bowie, *J. Amer. Chem. Soc.*, **87**, 2587 (1965).

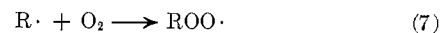
(6) A. G. Davies and B. P. Roberts, *Chem. Commun.*, 208 (1966); *J. Chem. Soc. B*, 17 (1967).

eq 6-9) is therefore similar to that of a hydrocarbon (M = H).

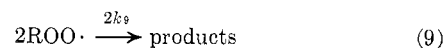
Initiation



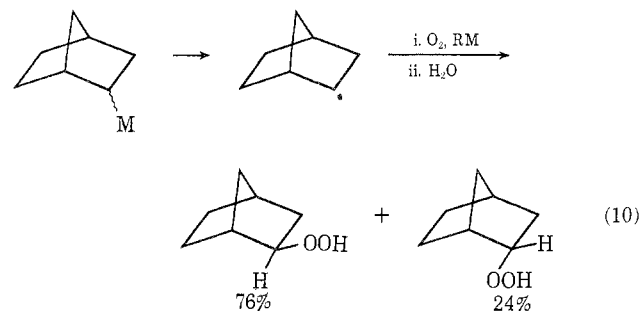
Propagation



Termination



Similar stereochemical evidence was obtained from the autoxidation of the stereoisomeric trinorborn-2-ylboranes,⁷ or norbornylmagnesium halides.⁸ Whatever the epimeric composition of the reactant, or the nature of the metal, autoxidation gave, after hydrolysis, the same mixture of *exo*- and *endo*-norbornyl hydroperoxides, implying a common, epimerizing intermediate (eq 10).



From the effect of inhibitors it has been shown that the autoxidation of organic derivatives of boron,^{7,9,10} zinc, cadmium, aluminium,¹⁰ phosphorus,¹¹ antimony,¹² and bismuth¹² follows a similar radical-chain mechanism, although this is more complex with the group V metal alkyls.¹³ This implies that an alkylperoxyl radical brings about an SH2 reaction at these various metal centers (reaction 8) much more rapidly than at the numerous hydrogen centers in the alkyl groups or in the solvent. Clearly it was important to measure these rates and to investigate the factors which governed them.

The chain sequence of eq 6-9 should result in the same kinetic behavior as that of the autoxidation of a hydrocarbon, *i.e.*

$$-d[\text{O}_2]/dt = k_8[\text{RM}](R_i/2k_9)^{1/2}$$

This was confirmed by K. U. Ingold for a series of

(7) A. G. Davies and B. P. Roberts, *ibid.*, 311 (1969).

(8) A. G. Davies and B. P. Roberts, *ibid.*, 317 (1969).

(9) P. G. Allies and P. B. Brindley, *Chem. Ind. (London)*, 319 (1967); 1439 (1968); *J. Chem. Soc. B*, 1126 (1969).

(10) A. G. Davies and B. P. Roberts, *ibid.*, 1074 (1968).

(11) S. A. Buckler, *J. Amer. Chem. Soc.*, **84**, 3093 (1962).

(12) A. G. Davies and S. C. W. Hook, *J. Chem. Soc. C*, 1660 (1971).

(13) One limitation to this technique is that the organometallic compound may rapidly react with, and thereby deactivate, the inhibitor. For example, no inhibitor has yet been found which is resistant to organomagnesium halides¹⁰ or trialkylthalliums,^{16a} although the autoxidation of these reagents in all probability follows a radical-chain mechanism.

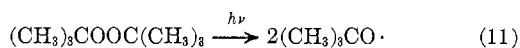
organoboranes,^{14-16a} and absolute values for k_s , the bimolecular rate constant for the SH2 reaction of the alkylperoxyl radical at the metal center, were obtained. For example, the rate constant for the abstraction of a hydrogen atom from toluene at 30° by an alkylperoxyl radical is $0.24 M^{-1} \text{sec}^{-1}$, whereas the corresponding figure for the SH2 reaction at the boron center in tri-*n*-butylborane is $2 \times 10^6 M^{-1} \text{sec}^{-1}$.^{15,16b}

This very high reactivity presumably results from the fact that a weak M-C bond (*e.g.*, B-C ~ 83 kcal mole⁻¹) is being broken, and a strong M-O bond (*e.g.*, B-O ~ 120 kcal mole⁻¹) is being formed. Other oxygen-centered radicals, and radicals centered on other elements such as nitrogen or sulfur, would be expected to react in the same way. An attempt was therefore made to establish other SH2 reactions at metal centers.

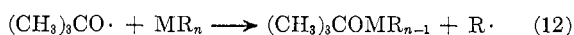
Alkoxy Radicals

There was already a suggestion in the literature that alkoxy radicals would take part in an SH2 reaction at a boron center. Matteson had attempted to chlorinate the methyl groups of trimethylboroxine, (MeBO)₃, with *tert*-butyl hypochlorite, but had found *t*-BuOB groups, and methyl chloride, in the products, and had proposed this mechanism.¹⁹

Nonchain Reactions. This process was confirmed independently by two groups of workers in 1969.^{20,21} If *tert*-butoxy radicals are generated photolytically from di-*tert*-butyl peroxide in the presence of a variety of organometallic compounds in an esr cavity (eq 11),



the SH2 reaction (eq 12) produces an alkyl radical



whose spectrum can be observed. The organometallic compounds which have been subjected successfully to this technique, at the time of writing, are: Li, Zn, Cd, Hg, B, Al, Ga, Sn (see below), P, As, Sb, Bi. In a few cases, the alkoxy radical was generated thermally from *tert*-butyl hyponitrite because the organometallic compound was photosensitive.

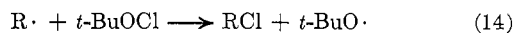
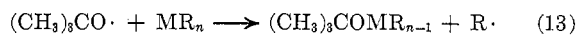
Organometallic compounds which are known not to undergo this type of SH2 process are the tetraalkyl-

silanes and tetraalkyltin compounds, which instead undergo α -hydrogen abstraction to yield radicals of the type $\text{R}_3\text{M}\dot{\text{C}}\text{HR}'$,²² but alkyltin chlorides do undergo substitution at the metal center.²³ A few other organometallic compounds, particularly the Grignard reagents, cannot be studied by this method because they react directly with di-*tert*-butyl peroxide, even at low temperature.

Rates of these reactions have been determined by causing the alkylmetallic compounds to compete with, say, cyclopentane for reaction with the alkoxy radical, and monitoring by esr the relative concentrations of the alkyl and cyclopentyl radicals. Typical results are presented under Kinetics.

Chain Reactions. If the alkyl radical which is displaced can be caused to regenerate an alkoxy radical, a chain process, which may be preparatively useful, will result. This regeneration can be brought about by either a substitution or an addition reaction.

Alkyl radicals react rapidly with *tert*-butyl hypochlorite to regenerate the *tert*-butoxy radical. All the organometallic compounds which react photolytically with di-*tert*-butyl peroxide by reactions 11 and 12 should, therefore, given initiation, react with *tert*-butyl hypochlorite by reactions 13 and 14, unless there is a

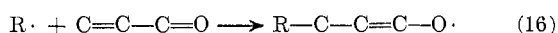
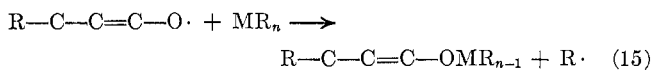


more rapid competing polar process.

The principal compounds which have been investigated thus far are the trialkylboranes,²⁴ triphenylborane,²⁵ and the alkyltin chlorides.²³ Rates for the SH2 step have been determined by causing the alkylmetallic compound to compete with some reference compound such as cyclopentane for reaction with the alkoxy radical and measuring the relative yields (by glc) of the alkyl chloride and cyclopentyl chloride. The results obtained by this method are in accord with those given by the esr technique which is discussed above.

Alkyl hypochlorites also react readily with trialkylphosphines and with the organic derivatives of the more electropositive metals (Li, Mg, Zn, Al), but it seems likely that the preferred mechanism here is heterolytic.²⁶

Alkyl radicals can also regenerate alkoxy (now vinyl-oxy) radicals by addition to an unsaturated carbonyl compound (eq 15 and 16). H. C. Brown and his co-



workers have established that the conjugative addition of organoboranes to enones proceeds by this mecha-

(14) K. U. Ingold, *Chem. Commun.*, 911 (1969).

(15) A. G. Davies, K. U. Ingold, B. P. Roberts, and R. Tudor, *J. Chem. Soc. B*, 698 (1970).

(16) (a) T. Maki, unpublished work. (b) In the early stages of the reaction, one of the initiation processes may involve an SH2 reaction of (triplet) oxygen with organoborane, *i.e.*, $\text{O}_2 + \text{BR}_3 \rightarrow \cdot\text{OOR}_2 + \text{R}\cdot$. Attempts have been made to measure rates of this process when the chain sequence is fully inhibited by iodine¹⁷ or by galvinoxyl,¹⁸ but the former method is of doubtful validity as the rates so obtained are independent of oxygen pressure over the range 15-760 mm.^{16a}

(17) H. C. Brown and M. M. Midland, *J. Amer. Chem. Soc.*, **93**, 1506 (1971); *Chem. Commun.*, 699 (1971).

(18) P. Brindley, personal communication.

(19) D. S. Matteson, *J. Org. Chem.*, **29**, 3399 (1964).

(20) (a) A. G. Davies and B. P. Roberts, *Chem. Commun.*, 699 (1969); (b) A. G. Davies and B. P. Roberts, *J. Organometal. Chem.*, **19**, P17 (1969); (c) A. G. Davies, D. Griller, and B. P. Roberts, *J. Chem. Soc. B*, 1823 (1971).

(21) (a) P. J. Krusic and J. K. Kochi, *J. Amer. Chem. Soc.*, **91**, 3942 (1969); (b) J. K. Kochi and P. J. Krusic, *ibid.*, **91**, 3944 (1969).

(22) J. K. Kochi and P. J. Krusic, *Chem. Soc., Spec. Publ.*, **No. 24**, 174 (1970).

(23) A. G. Davies, B. P. Roberts, and J. C. Scaiano, *J. Organometal. Chem.*, **39**, C55 (1972).

(24) A. G. Davies, T. Maki, and B. P. Roberts, *J. Chem. Soc., Perkin Trans. 2*, 744 (1972).

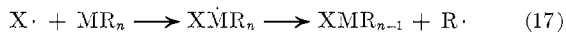
(25) R. Tudor, unpublished.

(26) C. Walling and J. Kjellgren, *J. Org. Chem.*, **34**, 1487 (1969).

nism,²⁷ and again it would be predicted to apply also to the organic derivatives of the other metals listed for reaction 12, unless there is some other faster competing process. Conjugative addition has in fact been observed with a number of other metals (*e.g.*, Mg, Zn, Mn),²⁸ but the mechanism has not been determined.

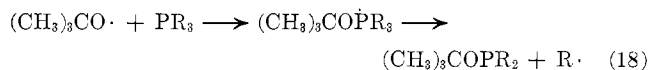
The reaction of organoboranes with quinones²⁹ and with dialkyl azodicarboxylates³⁰ both follow similar mechanisms.

The Question of a Reaction Intermediate. The question arises whether the bond-forming and bond-breaking steps of these SH2 reactions are synchronous, or whether the former precedes the latter, when the reaction will involve an intermediate (eq 17). The



nomenclature of these two reactions has been discussed;^{1,31} we have distinguished them by the names SH2 (synchronous) and SH2 (stepwise).

Attempts to detect by esr an intermediate in the alkoxydealkylation of organoboranes at low temperature have not yet been successful.^{32a} On the other hand, intermediate phosphoranyl radicals have been observed in the alkoxydealkylation of trimethylphosphine (eq 18, R = CH₃).^{21b,34,35} With larger alkyl



groups than methyl, no intermediate has been detected by esr, but a strong spectrum of the displaced alkyl radical R· is observed.^{21b,34,35} The higher stability of the phosphoranyl intermediate in the case of trimethylphosphine is presumably a result of the stronger CH₃-P bond.

Similar phosphoranyl species have been detected by esr in the reaction of *tert*-butoxyl and ethoxyl radicals with trialkyl and triaryl phosphites,^{21b,36} but the products can result from either α scission [*e.g.*, eq 19a, R' = (CH₃)₃C, R = C₆H₅] or β scission [*e.g.*, eq 19b, R' = (CH₃)₂C, R = C₂H₅; eq 19c, R' = C₂H₅, R = cyclo-C₅H₉] of the intermediate.

(27) (a) G. W. Kabalka, H. C. Brown, A. Suzuki, S. Honma, A. Arase, and M. Itoh, *J. Amer. Chem. Soc.*, **92**, 710 (1970); (b) H. C. Brown and G. W. Kabalka, *ibid.*, **92**, 712 (1970); (c) H. C. Brown and G. W. Kabalka, *ibid.*, **92**, 714 (1970); (d) A. Suzuki, S. Nozawa, M. Itoh, H. C. Brown, G. W. Kabalka, and G. W. Holland, *ibid.*, **92**, 3503 (1970).

(28) J. J. Eisch, "The Chemistry of Organometallic Compounds," Macmillan, New York, N. Y., 1967, p 135.

(29) G. W. Kabalka, *J. Organometal. Chem.*, **33**, C25 (1971).

(30) A. G. Davies, B. P. Roberts, and J. C. Scaiano, *J. Chem. Soc., Perkin Trans. 2*, 803 (1972).

(31) W. A. Pryor, *Nature, Phys. Sci.*, **231**, 181 (1971).

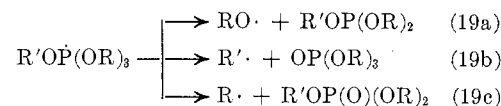
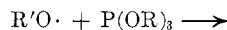
(32) (a) The suggested formation of a complex between triphenylmethyl radicals and triphenylborane has been disproved,^{32b} but a complex between a nitroxyl radical and boron trifluoride, R₂NO·BF₃, is well established.³³ (b) P. J. Moore and B. P. Roberts, unpublished work.

(33) T. B. Eames and B. M. Hoffman, *J. Amer. Chem. Soc.*, **93**, 3141 (1971).

(34) J. K. Kochi and P. J. Krusic, *Chem. Soc., Spec. Publ.*, No. 24, 147 (1970).

(35) A. G. Davies, R. W. Dennis, D. Griller, and B. P. Roberts, *J. Organometal. Chem.*, **40**, C33 (1972).

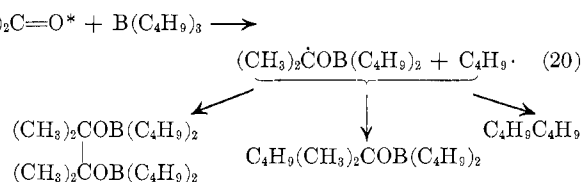
(36) (a) A. G. Davies, D. Griller, and B. P. Roberts, *Angew. Chem., Int. Ed. Engl.*, **10**, 738 (1971); *J. Chem. Soc., Perkin Trans. 2*, 993 (1972); (b) A. G. Davies, D. Griller, and B. P. Roberts, *J. Amer. Chem. Soc.*, **94**, 1782 (1972).



The interaction of *tert*-butoxyl radicals with trimethylarsine in solution gives rise to a quartet spectrum which has been tentatively assigned to the radical Me₂As(OC(CH₃)₃)₂.³⁷

Triplet Ketones

The n-π* triplet states of ketones often behave like alkoxy radicals (*e.g.*, in abstracting hydrogen), and it seemed likely that they should react in an SH2 sense with appropriate organometallic compounds. If a mixture of, for example, acetone and tri-*n*-butylborane is irradiated with uv light in the cavity of an esr spectrometer, the spectra of the two radicals which are formed (eq 20) are observed, and the products derived



from the coupling of these radicals can be isolated.³⁸

Reactions of this type have been carried out with different organoboranes, and a variety of ketones, particularly ring-substituted acetophenones, and rates have been measured by causing the borane to compete with a triplet quencher (piperylene) for reaction with the excited ketone.^{38,39} Some of the results are given under Kinetics.

Alkylthiyl Radicals

Both nonchain and chain alkylthiyldealkylations of organometallic compounds have been established. If di-*tert*-butyl disulfide is photolyzed in the presence of an organoborane or *tert*-butylmagnesium chloride, the esr spectrum of the displaced alkyl radical can be observed (eq 21 and 22) because reaction 23 is a relatively slow



process.⁴⁰ At or above room temperature, reaction 23 becomes sufficiently rapid with dimethyl or diphenyl disulfide for a chain reaction to be established with a trialkylborane.^{40,41}

Similarly, a thiol reacts with a trialkylborane, reac-

(37) A. G. Davies, D. Griller, and B. P. Roberts, *J. Organometal. Chem.*, **38**, C8 (1972).

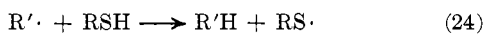
(38) (a) A. G. Davies, D. Griller, and J. C. Scaiano, *Chem. Commun.*, 196 (1971); (b) A. G. Davies, B. P. Roberts, and J. C. Scaiano, *J. Chem. Soc. B*, 2171 (1971).

(39) A. G. Davies and J. C. Scaiano, *J. Chem. Soc., Perkin Trans. 2*, in press.

(40) A. G. Davies and B. P. Roberts, *J. Chem. Soc. B*, 1830 (1971).

(41) H. C. Brown and M. M. Midland, *J. Amer. Chem. Soc.*, **93**, 3291 (1971).

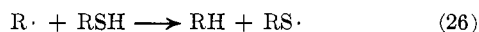
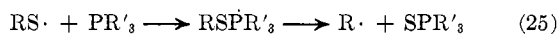
tion 22 now being followed by reaction 24, and the



appropriate alkane and thylmetallic compound can be isolated. Again, the rates of some of these reactions are presented under Kinetics.

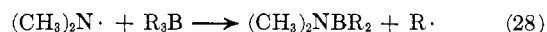
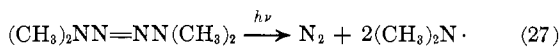
In the absence of a more rapid heterolytic reaction, thiols should react similarly with the organic derivatives of many other metals, particularly those "soft" metals which form relatively strong bonds to sulfur.

In group V, trialkylstibines and trialkylbismuthines react with thiols in the same way as trialkylboranes (eq 22 and 24, $M = Sb$ or Bi).⁴² Alkylthiyl radicals interact with trialkylarsines to show the esr spectra of the arsenanyl radical $RS\dot{A}SR'$,³⁷ but no alkyl radical appears to be displaced, and no chain reaction occurs with a thiol.⁴³ Trialkylphosphines and phosphites form phosphoranyl radicals, but exclusive β scission occurs, and a thiol is reduced to give alkane and athionophosphorus(V) compound by eq 25 and 26.⁴⁴



Dialkylaminy and Amidyl Radicals

Relatively little work has been carried out as yet in homolytic aminyldealkylation of organometallic compounds. By the esr method, the displaced alkyl radicals have been observed when dimethylaminy radicals, derived from tetramethyltetrazene, react with trialkylboranes, oxybis(dialkylboranes) (R_2BOBR_2), trialkylboroxines, and triethylstibine⁴⁵ (e.g., eq 27 and 28).



Dimethylchloramine reacts with trialkylboranes by a chain reaction, where reaction 28 is followed by reaction 29, leading to the formation of the aminoborane and

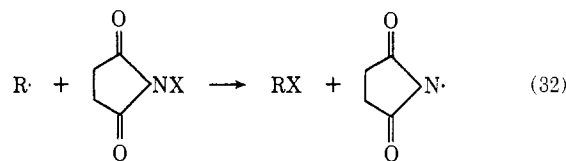
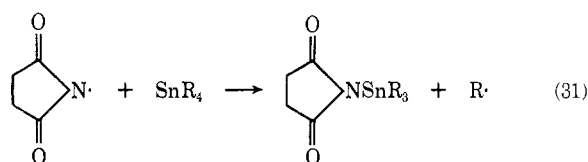


alkyl chloride.⁴⁶ This reaction, however, is accompanied by a polar process producing chloroborane and tertiary amine (eq 30), and, at room temperature in the



absence of added initiator or inhibitor, approximately equal yields of both types of products are obtained.

Although dimethylaminy radicals generated photochemically from tetramethyltetrazene or chemically from dimethylchloramine do not react with tetraalkyltins under mild conditions, the succinimidyl radicals derived from *N*-halogenosuccinimides do react to give the appropriate alkyl halide and *N*-trialkylstannylsuccinimide (eq 31 and 32) which will not react further with

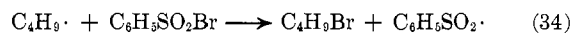
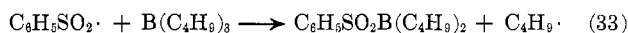


N-halogenosuccinimide.⁴⁷ This is in contrast to the alkoxydealkylations of compound R_nSnX_{4-n} discussed above,²³ where attack at tin becomes favored over hydrogen abstraction from the side chain only when $n < 4$. Benzyltributyltin reacts with *N*-bromosuccinimide to give only benzyl bromide and no butyl bromide, but tributylphenyltin and other phenyltin compounds yield aryl halides by a heterolytic process.

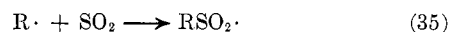
Rate constants for reactions 31 and 32 have been determined.⁴⁷ For example, for tetraethyltin in acetone at 35°, $k_{31} = 4 \times 10^4 M^{-1} \text{sec}^{-1}$.

Alkane- and Arenesulfonyl Radicals

Benzenesulfonyl bromide reacts with tri-*n*-butylborane at 70° by a radical-chain process in which the benzenesulfonyl radical displaces an alkyl radical from boron.⁴⁸



The reaction of alkyl radicals with sulfur dioxide (eq 35) is known to be fast, suggesting that sulfur



dioxide should react with trialkylboranes by a combination of reactions 33 and 35.

It is possible that some of the known insertion reactions of sulfur dioxide with other organometallic compounds may follow a similar mechanism.

Carbon-Centered Radicals and Halogen Atoms

There have been several reports from other groups of workers of homolytic displacement from organometallic compounds brought about by reaction with these radicals. Notable examples include the halogenodealkylation of organomercury⁴⁹ and organotin⁵⁰ compounds under "free-radical conditions."

An early report of an SH_2 process brought about by a carbon-centered radical at a metal center is found in the exchange reaction of methyl radicals with bis(trideuteriomethyl)mercury.⁵¹ Similar displacements have

(47) (a) A. G. Davies, B. P. Roberts, and J. M. Smith, *Chem. Commun.*, 557 (1970); (b) J. M. Smith, unpublished work.

(48) B. R. Sanderson, unpublished work.

(49) S. Winstein and T. G. Traylor, *J. Amer. Chem. Soc.*, **78**, 2596 (1956).

(50) S. Boué, M. Gielen, and J. Nasielski, *J. Organometal. Chem.*, **9**, 443, 461, 481 (1967).

(51) (a) R. E. Rebbert and P. Ausloos, *J. Amer. Chem. Soc.*, **85**, 3086 (1963); (b) R. E. Rebbert and P. Ausloos, *ibid.*, **86**, 2068 (1964).

(42) A. G. Davies and S. C. W. Hook, *J. Chem. Soc. B*, 735 (1970).

(43) S. C. W. Hook, unpublished work.

(44) (a) C. Walling, O. H. Basedow, and E. S. Savas, *J. Amer. Chem. Soc.*, **82**, 2181 (1960); (b) F. W. Hoffmann, R. J. Ess, T. C. Simmons, and R. S. Hanzel, *ibid.*, **78**, 6414 (1956).

(45) A. G. Davies, S. C. W. Hook, and B. P. Roberts, *J. Organometal. Chem.*, **22**, C37 (1970).

(46) A. G. Davies, S. C. W. Hook, and B. P. Roberts, *ibid.*, **23**, C11 (1970).

more recently been identified in the reaction of boron and tin alkyls with methyl⁵² and trifluoromethyl⁵³ radicals. When phenyl radicals are caused to react with simple alkylboron compounds, side-chain hydrogen abstraction occurs to give benzene. With tribenzylborane, however, there is also some accompanying displacement of benzyl radicals from boron to give phenylboron compounds.¹³

Kinetics

Studies of the kinetics of the SH2 process at a metal center have been carried out thus far principally on compounds of boron, phosphorus, and tin. Typical results for the reactions of organoboranes are shown in Table I. The rate constants are insensitive to small

Table I
Rate Constants^a for the Reaction
 $X \cdot + MR_n \longrightarrow XMR_{n-1} + R \cdot$

MR _n	X			
	ROO· (30°)	(CH ₃) ₂ CO· (30°)	C ₄ H ₉ S· (50°)	(CH ₃) ₂ CO* (20°)
(<i>n</i> -C ₄ H ₉) ₃ B	2 × 10 ⁶	3 × 10 ⁷	5 × 10 ⁷	7 × 10 ⁶
(<i>i</i> -C ₄ H ₉) ₃ B		1 × 10 ⁶	5 × 10 ⁶	8 × 10 ⁴
(<i>sec</i> -C ₄ H ₉) ₃ B	8 × 10 ⁴	3 × 10 ⁵	6 × 10 ⁵	1 × 10 ⁴
(<i>neo</i> -C ₅ H ₁₁) ₃ B		4 × 10 ⁴		
(C ₆ H ₅ CH ₂) ₃ B ^d	5 × 10 ⁶	2 × 10 ⁷ ^b		
(C ₆ H ₅) ₃ B		1 × 10 ⁷ ^c		
(<i>n</i> -C ₄ H ₉ BO) ₃	1 × 10 ³	6 × 10 ⁵		
(<i>sec</i> -C ₄ H ₉ BO) ₃	5 × 10 ⁴	6 × 10 ⁶		
(<i>t</i> -C ₄ H ₉ BO) ₃	3 × 10 ⁴	3 × 10 ⁶		
(C ₆ H ₅ CH ₂ BO) ₃ ^d	1 × 10 ⁶			

^a M⁻¹ sec⁻¹. ^b At 40°. ^c At 25°. ^d S. Korcek, G. B. Watts, and K. U. Ingold, *J. Chem. Soc., Perkin Trans. 2*, 242 (1972).

changes of temperature because the activation energies are low (*e.g.*, 0–6 kcal mole⁻¹ for *tert*-butoxydealkylation).

Homolytic dealkylations of metals by radicals centered on the electronegative elements oxygen, sulfur, nitrogen, and halogens are exothermic processes, and the metal has available orbitals of low energy to accept the incoming radical. Many of the reactions are very fast, the fastest approaching the limit of a diffusion-controlled process. Electronic factors which dictate the accessibility of the acceptor orbitals would be expected to affect the rate of the SH2 process, as well as factors which determine the strength of the bond being broken in the transition state. Steric factors would also be expected to be important, particularly at a small multivalent atom such as boron.

The data in Table I show that there is a sharp decrease in reactivity of the organoboranes when the

(52) (a) J. Grotewold and E. A. Lissi, *Chem. Commun.*, 21 (1965); (b) J. Grotewold, E. A. Lissi, and J. C. Scaiano, *J. Chem. Soc. B*, 1187 (1971).

(53) (a) T. N. Bell and A. E. Platt, *Chem. Commun.*, 325 (1970); (b) T. N. Bell and A. E. Platt, *Int. J. Chem. Kinet.*, 2, 299 (1970).

metal carries oxygen ligands. It is reasonable to associate this with the need to disrupt any p_π-p_π bonding between oxygen and boron when the transition state is formed. Similarly, the pyridine complex of tributylborane is unreactive toward butylperoxyl radicals, while the uncomplexed borane is extremely reactive.

On the other hand, the rate of *tert*-butoxydealkylation increases on going from tetrabutyltin to tributyltin chloride. The presence of halogen ligands generally stabilizes the higher coordination numbers of metals, and the chlorine facilitates the formation of five-coordinate tin in the SH2 transition state.

Cleavage of the boron-carbon bond is probably more advanced in the transition state of the reactions of boroxines than of boranes, and resonance stabilization of the incipient benzyl radical probably accounts for the relatively high reactivity of tribenzylboroxine. A similar enhanced reactivity is observed in benzyltin compounds.

Steric effects can be detected in the sequence of reactivities toward *tert*-butoxydealkylation, (*n*-C₄H₉)₃B > (*i*-C₄H₉)₃B, (*sec*-C₄H₉)₃B > (*neo*-C₅H₁₁)₃B, which can presumably be associated with the increasing repulsive forces which are encountered on proceeding from the planar three-coordinate trialkylborane to the nonplanar four-coordinate transition state. Similar steric factors appear to influence the dealkylation of tetraalkyltins by succinimidyl radicals.⁴⁷

Prognosis

As yet, the homolytic reactions of only the simple alkylboranes have been explored at all thoroughly. The extension of these studies to derivatives of other metals, particularly those of groups IV and V, and to compounds with more complex organic ligands, is in its early stages, but the whole of the field of the organic derivatives of the transition metals is as yet unexplored.

The only reaction of excited states that has been examined is that between ketone triplets and organoboranes, but preliminary studies by esr show that many other systems give rise to radicals under similar conditions; these would repay a closer study.

Kinetic investigations have again been restricted largely to the organoboranes, and here the pattern of reactivity is beginning to emerge. Similar studies may be expected in the near future on derivatives of other metals, particularly those of phosphorus and arsenic, where radical intermediates have been detected by esr.

Little attempt has yet been made to exploit these reactions preparatively, or to assess their relevance to technological applications of organometallic compounds, such as is their effect on autoxidation reactions or on the stabilization of polyvinyl chloride. Developments in these fields can confidently be expected in the near future.