That such CCl_2 addition to the C=S bond is probably a general reaction was indicated by the reaction of phenyl(bromodichloromethyl)mercury (10 mmol) with thiobenzophenone (10 mmol) in benzene (3 hr at 70°). The known 2,2-dichloro-3,3-diphenyl-1-thiirane, mp 88.5–89.5° (EtOH), lit.[7] mp 89–90°, was isolated in 75% yield. Pyrolysis of this product (4 hr at 150°) gave 1,1-dichloro-2,2-diphenylethylene, mp 79–80°, and elemental sulfur.

The reaction of diazoalkanes with thiophosgene and thioketones was reported by Staudinger and Siegwart nearly 40 years ago,[7] *e.g.*, the reaction of diphenyldiazomethane with thiophosgene, which gave 2,2-dichloro-3,3-diphenyl-1-thiirane in 68% yield. Other examples of such reactions have been described in the intervening years.[8–10] Also, the preparation of thiiranes by the reaction of diazoalkanes with elemental sulfur has been reported by Egyptian workers.[11] In all of these reactions it is, however, not clear whether it is the diazoalkane, the carbene derived from it, or, in the case of copper-catalyzed reactions, an organocopper complex, which is the reacting species. We suggest that it is the diazoalkane and not the carbene and note that in the case of $(CF_3)_2C{=}S$ the conditions (−78°, no catalyst, no irradiation) which permitted a vigorous reaction to occur with diphenyldiazomethane and ethyl diazoacetate were not those which would release the carbenes.

Although we speak in terms of CCl_2 reactions with S_8, $Cl_2C{=}S$, and $Ph_2C{=}S$ in the interactions of these sulfur compounds with phenyl(bromodichloromethyl)mercury, it is by no means clear that a free carbene intermediate is involved. We note that the available evidence suggests that the reactions of tertiary amines and triphenylphosphine with this mercurial very likely do not proceed by way of thermal CCl_2 extrusion from the mercury reagent followed by attack of CCl_2 on the nucleophilic substrate.[12,13] Instead, a direct interaction of the nucleophile with the phenyl(bromodichloromethyl)mercury was indicated as the first step in those CCl_2 transfer processes. Thus, in the case of the reactions described in this communication, it is quite possible that a free carbene mechanism is not operative. Mechanistic studies are required to answer this question.

Our studies on this new application of phenyl(trihalomethyl)mercury compounds and on related reactions are continuing.

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[7] H. Staudinger and J. Siegwart, *Helv. Chim. Acta*, **3**, 840 (1920).

[8] (a) A. Schönberg, "Houben-Weyl's Methoden der organischen Chemie" Vol. IX, G. Thieme Verlag, Stuttgart, 1955, p 158, 734; (b) M. Sander, *Chem. Rev.*, **66**, 297 (1966).

[9] A. Schönberg and E. Frese, *Chem. Ber.*, **96**, 2420 (1963).

[10] W. J. Middleton and W. H. Sharkey, *J. Org. Chem.*, **30**, 1384 (1965).

[11] N. Latif and I. Fathy, *ibid.*, **27**, 1633 (1962).

[12] D. Seyferth, M. E. Gordon, and R. Damrauer, *J. Org. Chem.*, **32**, 469 (1967).

[13] D. Seyferth, J. K. Heeren, G. Singh, S. O. Grim, and W. B. Hughes, *J. Organometal. Chem.*, **5**, 267 (1966).

[14] Postdoctoral Research Associate, 1968–1969.

Dietmar Seyferth, Wolfgang Tronich[14]
Department of Chemistry, Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

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Boryl Sulfonates, a New Class of Borylating Agents

Sir:

The synthetic usefulness of an alkyl- or arylsulfonate substituent as a good leaving group, so skillfully exploited in organic chemistry, has been largely neglected in the inorganic area, particularly in boron chemistry. We wish to emphasize the usefulness of a sulfonate group in this context[1] and to report the synthesis of a new class of boron compounds—the borylsulfonates which are convenient borylating agents. They are also the first instance of an RSO_3 group bonded to boron.

In the past, some active hydrogen compounds, notably carboxylic acids,[2] β-diketones,[3] pyrazoles,[4] *sym*-tetraalkyloxamidines,[5] and some others[6] have been borylated with trialkylboranes, but drastic conditions were required and the method was of limited applicability. The reaction of a dialkylboryl halide with anionic species, while a good route, suffered from poor availability of the dialkylboryl halide despite recent improvements in this area.[7] Dialkylboryl sulfonates, on the other hand, are easy to prepare *in situ* and require little or no purification, and their reactivities parallel those of dialkylboryl halides.

Dialkylboryl sulfonates are prepared in one step from trialkylboranes and arene- or alkanesulfonic acids; from sulfuric acid the equally useful bis(dialkylboryl) sulfate is obtained.[8] All of these compounds are soluble in aromatic hydrocarbons. Their stock solutions have long shelf-lives and may be used directly, as needed. Reactions with nucleophilic species Z^- lead readily to borylated derivatives ZBR_2.

$$R'SO_3H + BR_3 \longrightarrow RH + R'SO_3BR_2 \xrightarrow{Z^-} ZBR_2 + R'SO_3^-$$

While no elemental analyses were carried out on boryl sulfonates because of their air sensitivity, their structures are well established by (1) mode of formation, (2) stoichiometry of alkane evolution, (3) nmr spectrometry, and (4) the preparation of numerous conclusively identified derivatives.

Refluxing an equimolar mixture of anhydrous *p*-toluenesulfonic acid and triethylborane resulted in quantitative evolution of 1 equiv of ethane. Removal of the solvent *in vacuo* left a nondistillable air- and moisture-sensitive oil. Its nmr spectrum consisted of the aromatic hydrogens as a typical A_2B_2 four-peak pattern centered at τ 2.57, a methyl singlet at 7.77,

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[1] Some of the advantages of an alkane- or arenesulfonate group over a halide, traditionally used in inorganic chemistry, may be: (1) RSO_3 tends to coordinate intramolecularly rather than by formation of bridged dimers or polymers, which at times cause disproportionation in coordinatively unsaturated molecules. (2) By a suitable choice of the arene- or alkanesulfonate substituents it is possible to maintain a good leaving group at the same time effecting solubility of the compound in nonpolar solvents. (3) The alkyl or aryl group attached to the sulfonate residue may be of use as an nmr probe for the molecule.

[2] L. H. Toporcer, R. E. Dessy, and W. I. E. Green, *J. Am. Chem. Soc.*, **87**, 1236 (1965).

[3] M. F. Hawthorne and M. Reintjes, *J. Org. Chem.*, **30**, 3857 (1965).

[4] S. Trofimenko, *J. Am. Chem. Soc.*, **89**, 3165 (1967).

[5] S. Trofimenko, *ibid.*, **89**, 7014 (1967).

[6] For a comprehensive list of examples up to 1966 see ref 4.

[7] H. Nöth and H. Vahrenkamp, *J. Organometal. Chem.*, **11**, 399 (1968).

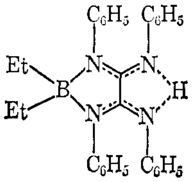
[8] Other sulfonic acids that have been used successfully in this reaction sequence include mesitylenesulfonic acid, *m*- and *p*-nitrobenzenesulfonic acids, *p*-chlorobenzenesulfonic acid, 4,4′-biphenyldisulfonic acid, and 2-naphthalenesulfonic acid.

and the BEt_2 multiplet centered at 9.1 in the correct 4:3:10 ratio.

Diethylboryl methanesulfonate was obtained similarly as a distillable pyrophoric liquid, bp 70–73° (2.5 mm). Its nmr spectrum consists of the methyl singlet at τ 7.05 and BEt_2 multiplet at 9.1 in a 3:10 ratio.

Both compounds were stored as relatively air-stable 1 *M* toluene solutions and were used as such for borylation reactions. For instance, the difficultly available N-diethylboryl-*sym*-tetraphenyloxamidine (I), mp 184–185°, was obtained in 74% yield by the reaction of $MeSO_3BEt_2$ with the monosodium salt of *sym*-tetraphenyloxamidine. *Anal.* Calcd for $C_{30}H_{31}BN_4$: C, 78.6; H, 6.77; N, 12.2. Found: C, 78.6; H, 6.57; N, 12.4. The infrared spectrum has an NH band at 3250 cm^{-1} and the nmr spectrum is likewise confirmatory with τ 0.83 s (NH), aromatic multiplet at ~3.1, and BEt_2 at ~9.3 in a 1:20:10 ratio.

Dialkylboryl sulfonates were also useful in preparing 4,4-dialkylpyrazaboles, not available by the direct route. Thus 4,4-dibutylpyrazabole (II), bp 142–144 (1.7 mm), was synthesized in 62% yield by the reaction of $MeSO_3BBu_2$, prepared *in situ*, with $KH_2B(1\text{-pyrazolyl})_2$. *Anal.* Calcd for $C_{14}H_{26}B_2N_4$: C, 61.8; H, 9.57; N, 20.6. Found: C, 61.8; H, 9.86; N, 20.6. The nmr spectrum had two overlapping doublets (J = 2.4, 0.9 Hz) centered at τ 2.52, a triplet (J = 2.4 Hz) at 3.83, and the BBu_2 multiplet around 9, with sharp peaks at 9.17 and 9.25 in the correct 2:1:9 ratio. The BH_2 hydrogens were discernible by integration.



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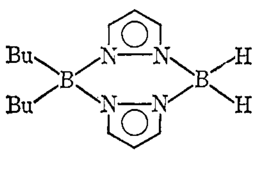


II

S. Trofimenko

Contribution No. 1537, Central Research Department
Experimental Station
E. I. du Pont de Nemours and Co.
Wilmington, Delaware 19898

Received January 13, 1969

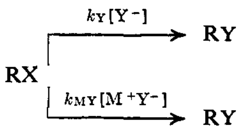
The Nonnucleophilicity of Inorganic Ion Pairs[1,2]

Sir:

For 53 years the phenomenon of decreasing second-order rate constants with increasing nucleophile concentration for bimolecular nucleophilic substitution at a saturated carbon atom has been ascribed to incomplete dissociation of the nucleophilic salt, resulting in competitive intervention with anionic nucleophile of ion-paired nucleophile. This interpretation of published data, dignified as the Acree hypothesis,[3] has been widely accepted,[4] and in fact the kinetic trend of published data *can* in general be accommodated arithmetically by a kinetic equation derived from the equilibrium and the scheme given above. That this is not

$$M^+X^- \overset{K_D}{\rightleftharpoons} M^+ + X^-$$

the explanation for the lowered rate constant with increasing salt concentration ($k_2 = 7.50 \times 10^{-4}$ l. M^{-1} sec^{-1} at 5.0×10^{-6} *M* and $k_2 = 2.34 \times 10^{-4}$ l. M^{-1} sec^{-1} at 1.24×10^{-2} *M* lithium chloride) observed in the replacement of chloride ion in methyl chloride in 95% aqueous acetone by lithium radiochloride[3b] is the subject of the present communication.



The system under discussion lends itself admirably to a study of the question at hand since concentrations of inorganic chloride as low as 10^{-6} *M* (complete dissociation) can be employed. Under conditions where [MeCl] ≫ $[LiCl]_s$ (stoichiometric concentration of inorganic chloride) the kinetic expression for the reaction becomes $kt = (2.303/a) \log (C/X)$, where a = [MeCl] and C and X are counts of inorganic radioactivity initially and at time t, respectively; thus pseudo-first-order kinetics are expected, independent of $[Cl^-]$ and thus of $[Li^+Cl^-]$.

As indicated above it is observed experimentally that second-order rate "constants" do in fact decrease with increasing chloride ion concentration by a factor of 3.22 as lithium chloride concentration (stoichiometric) increases by a factor of 2500 ($[LiCl]_s \leq 0.1$ [MeCl]). Since the rate expression for radiochloride incorporation is independent of chloride concentration this result must have its cause in something other than ion-pair association.

Substantiating this conclusion is the observation that other nonnucleophilic salts, including the perchlorates of lithium, sodium, potassium, and rubidium as well as lithium salicylate, when combined with low ($\leq 8 \times 10^{-5}$ *M*) stoichiometric concentrations of lithium chloride, accomplish similar rate depressions for the displacement of chloride ion by radiochloride, whose magnitudes can be predicted quite accurately from a knowledge of their ion-pair dissociation constants, K_D, and Debye–Hückel theory. Under these conditions a plot of log k *vs.* $(C\Theta)^{1/2}$ (C = stoichiometric concentration of salt and Θ is the degree of dissociation, determined experimentally from conductivity studies) is, according to theory, predicted to be a straight line with slope = −7.33, the deviation from constancy being ascribed to a simple medium effect. In Table I are listed the observed slopes of plots for the investigated salts.

It is of special interest and importance that lithium chloride is not exceptional, its slope being similar in magnitude to those of the other investigated salts.

An alternate way of appraising the data is to compare predicted (from Debye–Hückel theory and dissociation constants) and experimental rate constants. This is done at two levels of concentration of salt (*ca.* 0.001 and 0.005 *M*) in Table II. The agreement will be seen to be good if not excellent.

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(1) Part VIII of the series "Nucleophilic Substitution at a Saturated Carbon Atom."

(2) Supported in part by the National Science Foundation.

(3) H. C. Robertson and S. F. Acree, *J. Am. Chem. Soc.*, **39**, 1902 (1915).

(4) Representative papers include W. Bruce, M. Kahn, and J. A. Leary, *ibid.*, **87**, 2800 (1965); L. J. LeRoux and S. Sugden, *J. Chem. Soc.*, 1279 (1939); Y. Pocker and A. J. Parker, *J. Org. Chem.*, **31**, 1526 (1966); N. N. Lichtin and K. N. Rao, *J. Am. Chem. Soc.*, **83**, 2417 (1961).