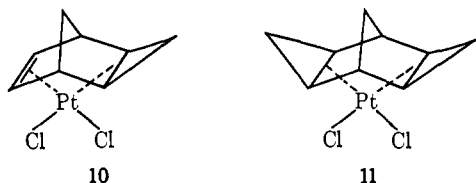


The catalytic activity of a number of other transition metal complexes was also studied. $\text{Mo}(\text{CO})_6$, $\text{W}(\text{CO})_6$, Cu_2Cl_2 , $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$, $(\text{C}_6\text{H}_5\text{CN})_2\text{PdCl}_2$, $\text{IrHCl}_2(\text{PPh}_3)_3$, and $\text{Rh}_2(\text{nor-C}_7\text{H}_8)_2\text{Cl}_2$ were found to be inactive. With $[(\text{C}_2\text{H}_4)_2\text{PtCl}_2]$ or $\text{K}[(\text{C}_2\text{H}_4)\text{PtCl}_3]$ **1** and **4** form the insoluble, stable pale yellow complexes **10** and **11**, respectively. The structures of these com-



plexes⁶ follow from elementary analyses, the absence of the uncoordinated $\text{C}=\text{C}$ stretching frequency for **10** and the presence of a terminal $\text{Pt}-\text{Cl}$ bond at 355 cm^{-1} , and from the quantitative displacement of coordinated **1** and **4** by reaction with bicyclo[2.2.1]hepta-2,5-diene.

Complex **11** did not give rise to the formation of tetracyclo[3.3.1.0^{2,8}.0^{4,6}]nonane (triansterane) upon being heated.

(6) Edgewise coordination of cyclopropane derivatives toward platinum has been reported previously by Mason⁷ and Irwin and McQuillin.⁸

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New Reactions of Phenyl(bromodichloromethyl)mercury. Preparation of Perchlorothiirane

Sir:

Dichlorocarbene is known to be an electrophilic reagent, and there are quite a few of its reactions which can be understood best in terms of initial CCl_2 interaction with a lone pair atom present in the compound undergoing reaction.¹ The previously reported² reaction of dichlorocarbene (*via* sodium trichloroacetate) with di-*t*-butyl disulfide, which gives $\text{Me}_3\text{CSSCHCl}_2$ and isobutylene, presumably *via* CCl_2 attack at sulfur, suggested to us that a study of the reactions of dichlorocarbene with other sulfur compounds, including elemental sulfur itself, might be of interest. In its reaction with sulfur, electrophilic attack by CCl_2 at a sulfur atom might be expected to result in opening of the S_8 ring and ultimately in the formation of thiophosgene.

Phenyl(bromodichloromethyl)mercury³ was used as the dichlorocarbene source^{4,5} during the present study.

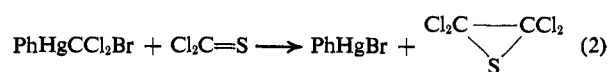
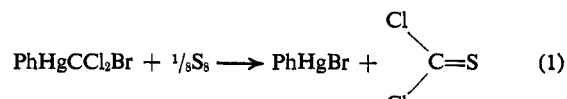
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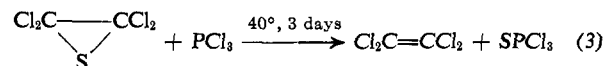
(3) D. Seyferth and R. L. Lambert, Jr., *J. Organometal. Chem.*, **16**, 21 (1969).

(4) D. Seyferth, J. M. Burlitch, R. J. Minasz, J. Y.-P. Mui, H. D. Simmons, Jr., A. J.-H. Treiber, and S. R. Dowd, *J. Am. Chem. Soc.*, **87**, 4259 (1965).

A reaction of 10 mmol of this mercurial with 0.16 g (5 mg-atoms of S) of S_8 in 30 ml of dry benzene under nitrogen at 70° for 1 hr resulted in the formation of phenylmercuric bromide in 93% yield. Concentration of the yellow filtrate at 14 mm to remove solvent was followed by trap-to-trap distillation of the residue *in vacuo*. Gas-liquid partition chromatographic (glpc) analysis (20% Dow Corning DC 200 silicone oil on 80-100-mesh WAW DMCS) of the distillate showed the presence of small amounts of benzene and tetrachloroethylene as well as of a third component. The latter was not the expected thiophosgene; its combustion analysis (C, Cl, S) and its mass spectrum showed it to be the as yet unknown 2,2,3,3-tetrachloro-1-thiirane (perchlorothiirane) (34% yield, by glpc). The formation of this product is understandable in terms of CCl_2 addition to the $\text{C}=\text{S}$ bond of the initially formed thiophosgene (eq 1 and 2). Perchlorothiirane is a colorless,



malodorous liquid, bp $36\text{--}38^\circ$ (0.1 mm), which is stable at room temperature for moderate lengths of time. On long standing at room temperature or on mild heating it turns yellow. It can be purified by glpc (DC 200 column at 90°). Its thermolysis at 150° (10 min) gives tetrachloroethylene and elemental sulfur. Quantitative desulfurization of perchlorothiirane is accomplished by reaction with phosphorus trichloride in slight excess under mild conditions (eq 3). On the



other hand, its reaction with triphenylphosphine in ether at room temperature was more complex. Triphenylphosphine sulfide was isolated in 46% yield, but tetrachloroethylene was formed in only trace amounts, and the reactants were converted mostly to intractable, resinous materials.

The fragmentation of perchlorothiirane in the mass spectrometer at 70 eV gave the chlorinated equivalents of thiirane itself:⁶ $\text{C}_2\text{Cl}_4\text{S}^+$ (17.5), $\text{C}_2\text{Cl}_3\text{S}^+$ (29.8), $\text{C}_2\text{Cl}_2\text{S}^+$ (62.9), CCl_2S^+ (3.2), C_2ClS^+ (12.3), CClS^+ (100.0), Cl_2S^+ (0.58), S^+ (3.2), C_2Cl_4^+ (78.8), C_2Cl_3^+ (46.2), C_2Cl_2^+ (26.8), C_2Cl^+ (8.7), CCl_3^+ (21.0), CCl_2^+ (23.5), and CCl^+ (21.7). Its infrared spectrum (liquid film) showed absorptions at 1145 (s), 1110 (w), 920 (sh), 910 (w), 835 (sh), 815 (s), 770 (w), 750 (s), 745 (sh), 705 (w), 675 (s), 670 (sh), and 650 cm^{-1} .

The ready occurrence of the reaction shown in eq 2 was demonstrated in a reaction of 27 mmol each of $\text{PhHgCCl}_2\text{Br}$ and thiophosgene under nitrogen in benzene at 40° for 3 days. The yields of phenylmercuric bromide and perchlorothiirane were 92 and 36%, respectively.

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That such CCl_2 addition to the $\text{C}=\text{S}$ 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 $88.5\text{--}89.5^\circ$ (EtOH), lit.⁷ mp $89\text{--}90^\circ$, was isolated in 75% yield. Pyrolysis of this product (4 hr at 150°) gave 1,1-dichloro-2,2-diphenylethylene, mp $79\text{--}80^\circ$, 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 $(\text{CF}_3)_2\text{C}=\text{S}$ 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 , $\text{Cl}_2\text{C}=\text{S}$, and $\text{Ph}_2\text{C}=\text{S}$ 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.

Acknowledgment. The authors are grateful to the Air Force Office of Scientific Research (SRC)-OAR for generous support of this work through U. S. Air Force Grant No. AFOSR-68-1350.

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(14) Postdoctoral Research Associate, 1968-1969.

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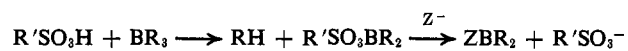
Boryl Sulfonates, a New Class of Borylating Agents

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 context¹ 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 others⁶ 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 .



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,

(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.

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(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.