addition, a rough ordering of the relative ease of the intramolecular reactions of these carbenes is possible. Insertion into the carbon–hydrogen bonds of the neighboring *O*-methyl group is most favored, and Wolff rearrangement appears to be preferred to carbon–oxygen insertion, as **3** forms methyl acetate slightly faster than methyl pyruvate.

At temperatures at which products attributed to **2** appeared so did a white polymer. Formation of the polymer set in at about 280° and ceased by 360°. The material is not polyacrylate and has only methoxy signals in its nmr spectrum. It is tempting to speculate that it is poly-**2**, but so far all our attempts to isolate the monomer have been futile.

(20) National Science Foundation Predoctoral Fellow, 1967–1971.

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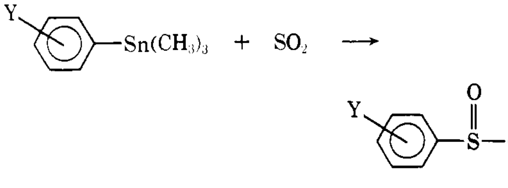
Kinetics and Mechanism of Sulfur Dioxide Insertion into Carbon–Tin Bonds

Sir:

Although sulfur dioxide has been demonstrated to be a remarkably versatile inserting agent into carbon–metal bonds,[1] almost no information is available concerning the mechanistic details of these reactions.[2] We now wish to present the results of the first kinetic study of SO_2 insertion, which strongly supports the view that insertion into aryl carbon–tin bonds is an electrophilic sulfidestannylation.

The rates of insertion of a series of meta- and para-substituted phenyltrimethylstannanes in anhydrous methanol at 30° were measured by observing the decrease in intensity with time of the sharp $(CH_3)_3Sn$ resonance (*ca.* τ 10) of the starting compound, and the concomitant appearance of the lower field (by *ca.* 18 Hz at 60 MHz) $(CH_3)_3Sn$ resonance of the product. Details of such spectra and other physical properties of the insertion products have been previously described.[3]



For all compounds studied, clean second-order kinetics, first order in stannane and in SO_2, were observed for at least two half-lives, and for the parent compound phenyltrimethylstannane, at 30°, $k_2 = 1.97 \times 10^{-3}$ l. mol^{-1} sec^{-1}. From the temperature dependence of k_2, $\Delta S^{\ddagger} = -31$ eu and $\Delta H^{\ddagger} = 7.38$ kcal mol^{-1} were derived. The pronounced negative character of $\Delta S^{\ddagger}$ is expected for an insertion reaction, where considerable loss of vibrational and translational freedom occurs on passing to the transition state.[4] Solvent reorganization could contribute significantly to this term. The rate of SO_2 insertion can be directly compared with values for protodestannation[5,6] and halodestannation[7,8] in the same solvent, $CH_3COOH < SO_2 < HCl \ll I_2 \ll Br_2$, and on this basis SO_2 exhibits moderate electrophilic capability.

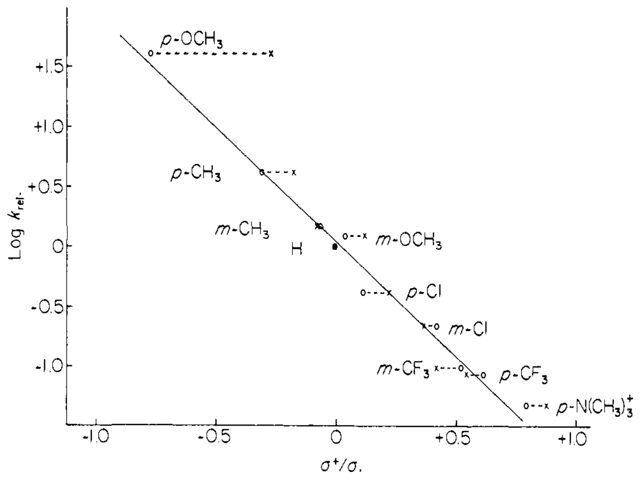


Figure 1. Plot of log k_{rel} *vs.* σ^+ (O) and σ (X).

For the meta- and para-substituted $Y\text{-}C_6H_4Sn(CH_3)_3$ (Y = *m*- and *p*-OCH_3, *m*- and *p*-CH_3, *m*- and *p*-Cl, *m*- and *p*-CF_3, and *p*-$N^+(CH_3)_3$) the rate is enhanced relative to the parent by net electron-donating substituents and retarded by net electron-withdrawing groups; log k_{rel} $(= k_{Y\text{-}C_6H_4Sn(CH_3)_3}/k_{C_6H_5Sn(CH_3)_3})$ correlates well with σ^+ ($r = 0.992$), as expected for an electrophilic aromatic substitution.[9] The correlation with σ ($r = 0.929$) (see Figure 1) is clearly of a lower order. The ρ value of -1.87 is similar to but significantly lower than those found for proto ($\rho = -2.17$)[6] and iodo[7] ($\rho = -2.54$) destannylations. The ρ value indicates a very moderate sensitivity to substituents and a low level of electron demand at the reaction site, with modest perturbation of the π-electron system. It would seem that the transition state for sulfidetrimethylstannylation would poorly approximate the classical σ intermediate for electrophilic aromatic substitution being more akin to starting state.

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(1) W. Kitching and C. W. Fong, *Organometal. Chem. Rev., Sect. A*, 5, 281 (1970).

(2) Wojcicki and coworkers have synthesized optically active π-$C_5H_5Fe(CO)_2CH(CH_3)C_6H_5$, $[\alpha]^{24}_{546}$ +77.3°, which yields, on reaction with SO_2, π-$C_5H_5Fe(CO)_2\cdot SO_2\cdot CH(CH_3)C_6H_5$, $[\alpha]^{24}_{546}$ −159°. This result could indicate a substantially stereospecific insertion, but whether inversion or retention is involved is not known: A. Wojcicki, J. J. Alexander, M. Graziani, J. E. Thomasson, and F. A. Hartmann, Abstracts, Symposium on Metal Carbonyls, Venice, Italy, Sept 1968.

(3) C. W. Fong and W. Kitching, *J. Organometal. Chem.*, 22, 95 (1970).

(4) For insertion of CO into $CH_3Mn(CO)_5$ to yield $CH_3COMn(CO)_5$, $\Delta S^{\ddagger} = -21$ cal deg^{-1} mol^{-1} has been reported: F. Calderazzo and F. A. Cotton, *Inorg. Chem.*, 1, 31 (1962); but see also R. W. Glyde and R. J. Mawby, *Inorg. Chim. Acta*, 4, 331 (1970). We thank a referee for alerting us to this report.

(5) J. Nasielski, O. Buchman, M. Grosjean, and M. Jauquet, *J. Organometal. Chem.*, 19, 353 (1969).

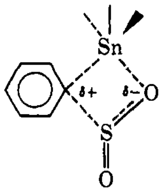
(6) O. Buchman, M. Grosjean, and J. Nasielski, *Helv. Chim. Acta*, 47, 1679 (1964).

(7) O. Buchman, M. Grosjean, and J. Nasielski, *ibid.*, 47, 1695 (1964).

(8) P. Alcais and J. Nasielski, *J. Chim. Phys. Physicochim. Biol.*, 66, 95 (1969).

(9) We have elected to use $\sigma^+ = 0.80$ for p-$N^+(CH_3)_3$, which is the σ^n value, rather than the quoted [H. C. Brown and Y. Okamoto, *J. Amer. Chem. Soc.*, 80, 4979 (1958)] value, $\sigma^+ = 0.41$, which appears unreasonably low. (See J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," Wiley, New York, N. Y., 1963, p 204.) A study of protodestannation of tricyclohexylarylstannanes [C. Eaborn and J. A. Walters, *J. Chem. Soc.*, 542 (1961)] indicates that $\sigma^+ = 0.7$ would be a better value. There appears no good reason why σ^+ should be drastically different from σ^n for $(CH_3)_3N^+$, although problems do arise for charged substituents. However, even using $\sigma^+ = 0.41$, an acceptable correlation ($r = 0.974$) is still obtained.

While disfavoring a highly perturbed π-electron system, solvent and salt effects could suggest a somewhat polar transition state. Thus the reaction is much faster in methanol than in benzene,[10] and although part of this acceleration could be ascribed to nucleophilic assistance by methanol at tin, some part could be a medium effect. The effect of increasing $LiClO_4$ concentration on the rate in methanol is significant and correlates well with ionic strength.[11] Although a closed (SEi) transition state is favored, this could be sufficiently polar to respond to medium and salt effects.[12] The wide rate difference on progressing from C–Si to C–Pb bonds may indicate significant C–M bond rupture in the transition state, but other factors such as the electropositive nature of the metalloids and the differing polarizabilities of the C–M bonds may contribute not only to the rate difference among the metalloids, but also reduce π-electron involvement at the reaction site.



SEi

The present results coupled with the reactivity order, allyl ∼ allenyl ∼ propargyl > phenyl > benzyl > methyl, constitute good evidence that SO_2 insertion into carbon–tin bonds is an example of electrophilic substitution at carbon.[13] Extrapolation of these views to insertions into other main-group metal–carbon bonds is very tempting.[14] However, the kinetic and reactivity characteristics of insertion into transition metal–carbon bonds, where metal–sulfur π bonding could be quite important, may be different and highly interesting.[15]

Acknowledgments. This work was supported in part by the Australian Research Grants Committee, to whom we are grateful. We thank Professor Wojcicki for disclosing unpublished data to us.

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(10) The kinetic situation in benzene as solvent is more complex, and while being strictly first order in stannane, the second-order constants vary with $[SO_2]$ and analysis suggests both second- and third-order components. We attribute this behavior to either coordination of SO_2 to tin in the transition state (*cf.* methanol assistance) or prior π complexation of SO_2 with the arylstannane, yielding an overall third-order component.

(11) For example, with $[C_6H_5Sn(CH_3)_3] = 0.0995$ *M*, $[SO_2] = 0.720$ *M*, and $[LiClO_4] = 0.5410$ *M*, a 64% rate increase is observed. This may be compared with data in ref 5 for iododestannation, where the relative effect on $NaClO_4$ was much smaller. Lithium chloride, while still leading to a rate acceleration, is less effective than perchlorate, and although the hydrogen-bonding effect of methanol could have a leveling effect on anions, specific halo coordination at tin may be of very marginal importance, and the solvent and salt effects appear to be related to stabilization of a polar transition state. See A. A. Frost and R. G. Pearson, "Kinetics and Mechanisms," 2nd ed, Wiley, New York, N. Y., 1961, p 150, for a discussion of salt effects at moderately high ionic strengths.

(12) For a relevant discussion of salt effects, see F. R. Jensen and B. Rickborn, "Electrophilic Substitution of Organomercurials," McGraw-Hill, New York, N. Y., 1968, pp 180–181, particularly.

(13) Although the *a priori* stereochemical outcome of the SEi pathway is retention at a suitable carbon center, as yet we have been unable to confirm this, since in cyclohexyl- and norbornyltrimethylstannanes, insertion into the $Sn-CH_3$ bonds is heavily predominant. Our general experience has been that SO_2 insertion is sensitive to α-substitution. However, in the cases of *cis*- and *trans*-styryltrimethylstannanes, insertion proceeds stereospecifically with retention at the vinylic carbon.

(14) In such systems, studied in any breadth, the general rate sequence quoted above among alkyl groups appears to hold. In the group IVb metalloid–carbon bonds, the sequence of increasing rate from C–Si to C–Pb is also in line with other electrophilic cleavages.

(15) Very recently it has been reported [G. M. Whitesides and D. J. Boschetto, *J. Amer. Chem. Soc.*, **93**, 1529 (1971)] that SO_2 insertion into the Fe–C bond of *threo*-$(CH_3)_3CCHDCHDFe(CO)_2C_5H_5$ proceeds with approximately 80% inversion of configuration. Although this result excludes a frontside cyclic mechanism as the predominant pathway in the iron case, there is as yet no evidence that this stereochemistry is relevant to main-group organometallics (*e.g.*, Sn). It appears to us to be quite reasonable that substantial differences in mechanism for insertion between iron– and tin–carbon systems should exist. We recently learned (Professor A. Wojcicki, private communication) that Wojcicki and coworkers have obtained pseudo-first-order kinetic data for some π-$C_5H_5Fe(CO)_2R$ compounds in liquid SO_2 at *ca.* −40°. A point of considerable interest is that in the cases R = CH_3 or C_2H_5, the first-order constant is about 1500 times larger than for R = phenyl, and most of this difference appears to reside in the $\Delta H^{\ddagger}$ term. In authentic bimolecular electrophilic cleavage of main group–carbon bonds, alkyl is generally less reactive than aryl, and alkyl–tin bonds insert SO_2 more slowly than aryl. Substituent effects studied by Wojcicki in the phenyl series (*e.g.*, *p*-OCH_3 reacts 720 times faster than *p*-H), however, support a basically electrophilic process for the aryl–iron compounds. Large negative values of $\Delta S^{\ddagger}$ were also found.

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Retention Stereochemistry in a Grignard Displacement Reaction at Chiral Phosphorus. The Absolute Configuration of Menthyl *S*-Methyl Phenylphosphonothioate[1]

Sir:

It has been presumed heretofore that displacement reactions by Grignard reagents at chiral phosphorus in phosphonothioates occur with inversion of configuration.[2,4] We now wish to report evidence which establishes that displacement of a thiomethyl group in one such reaction surprisingly proceeds with *retention* of configuration. This result is in sharp contrast to the stereochemical course of reactions of Grignard[5] and alkyllithium[6] reagents with menthyl phosphinates, which occur with predominant inversion of configuration at phosphorus.

It has been shown that thiomethylation of menthyl $(R)_P$-phenylphosphinate (**1a**), followed by reaction of

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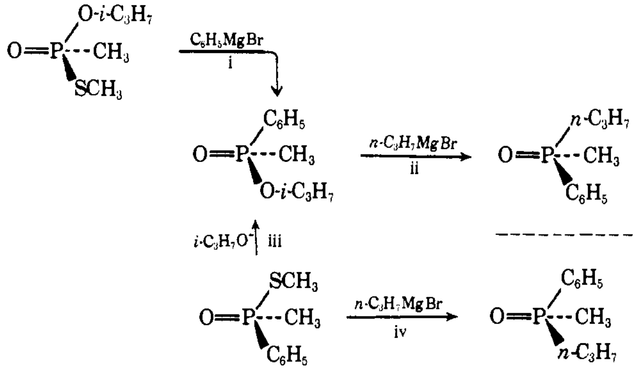
(1) This work was supported by grants from the National Science Foundation (GP-22542 and GP-15781) and the Advanced Research Projects Agency.

(2) This proposition rests on the assumptions[3] (a) that reactions i and iv proceed with the same stereochemistry, and (b) that reactions ii and iii proceed with inversion of configuration at phosphorus.



(3) H. P. Benschop, G. R. Van den Berg, and H. L. Boter, *Recl. Trav. Chim. Pays-Bas*, **87**, 387 (1968).

(4) H. P. Benschop and D. H. J. M. Platenburg, *Chem. Commun.*, 1098 (1970).

(5) (a) O. Korpiun and K. Mislow, *J. Amer. Chem. Soc.*, **89**, 4784 (1967); (b) O. Korpiun, R. A. Lewis, J. Chickos, and K. Mislow, *ibid.*, **90**, 4842 (1968).

(6) R. A. Lewis and K. Mislow, *ibid.*, **91**, 7009 (1969).