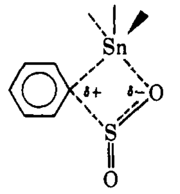
While disfavoring a highly perturbed π-electron system, solvent and salt effects could suggest a somewhat polar transition state. Thus the reaction is much faster in methanol than in benzene,[10] and although part of this acceleration could be ascribed to nucleophilic assistance by methanol at tin, some 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 We thank Professor Wojcicki for disclosing unpublished data to us.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-$C_5H_6Fe(CO)_2R$ 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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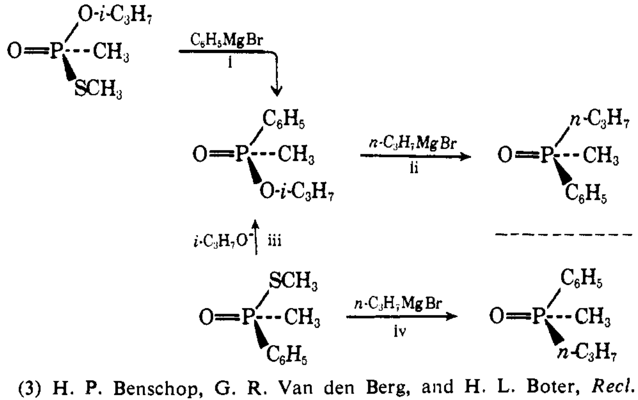
(1) This work was supported by grants from the National Science Foundation (GP-22542 and GP-15781) and the Advanced Research Projects Agency.

(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.



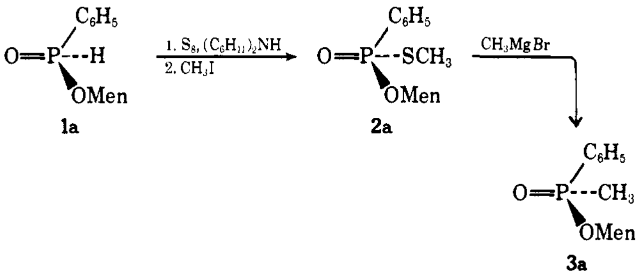
(3) H. P. Benschop, G. R. Van den Berg, and H. L. Boter, *Recl. Trav. Chim. Pays-Bas*, **87**, 387 (1968).

(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).

the resultant menthyl *S*-methyl phenylphosphonothioate (**2a**) with methylmagnesium bromide to give menthyl $(R)_P$-methylphenylphosphinate (**3a**), proceeds with *overall* retention of configuration.[7a] An X-ray analysis, described below,[7b] establishes the chirality at phosphorus in the intermediate phosphonothioate **2a** as *S*. It follows that the Grignard displacement reaction **2** → **3** and the thiomethylation **1** → **2** must both proceed with retention of configuration at phosphorus.[8,10]



Crystals suitable for X-ray analysis were obtained by slow evaporation of a 2,2,4-trimethylpentane solution of **2a**, mp 76.5°, $[\alpha]_D$ $-141°$ (benzene).[7a] Precession photographs on a crystal of dimensions *ca.* $0.15 \times 0.45 \times 0.10$ mm showed that the diastereomer crystallizes in the monoclinic system; the only extinction observed was $0k0$ with k odd. Least-squares refinement of the observed spacings of eight hkl reflections measured on a Picker automatic four-circle diffractometer gave lattice constants of $a = 18.076 \pm 0.013$, $b = 6.763 \pm 0.003$, $c = 8.509 \pm 0.010$ Å, $\beta = 102.30 \pm 0.01°$. The experimentally determined density of 1.15 g cm^{-3} agrees well with the value 1.10 g cm^{-3} calculated for two molecules of **2a** per unit cell. Since the molecule is chiral, the space group is determined uniquely as $P2_1\text{-}C_2^2$. A total of 1519 reflections above background up to $2\theta = 120°$ was observed with Cu Kα radiation using the θ–2θ scan mode on the above diffractometer. Monitoring of three standards during the data collecting showed no significant decay. The structure was solved by Patterson and Fourier methods. The final value of R in least-squares refinement which allowed for anisotropic thermal motion of the four heaviest atoms and for isotropic motion of the 17 carbon atoms, and which ignored the hydrogen atoms, is 10.3%. A view of the molecule along the b axis is shown in Figure 1. The configuration of (−)-menthol, used in the preparation of **2**, is 1*R*, 3*R*, 4*S*,[11] and it follows that the configuration at phosphorus is *S*.

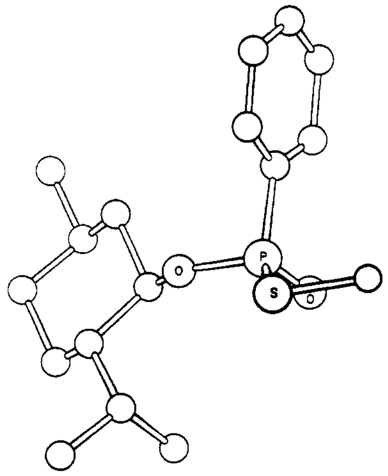


Figure 1. Menthyl *S*-methyl $(S)_P$-phenylphosphonothioate (**2a**) as viewed along the *b* axis of the crystal. Unlabeled atoms are carbon. The hydrogen atoms have been omitted.

It is reasonable to extend the present conclusions to the analogous *methyl*phosphinate systems.[12] Consequently, the absolute configuration of isopropyl *S*-methyl methylphosphonothioate (**5**)[3] is now in question, as are the underlying assumptions[2] which led to this assignment. It further follows that assignments of absolute configurations to sarin and other anticholinesterases,[3] to isopropyl methylphosphinate and its derivatives,[14] and to *O*-ethyl ethylphosphonothioic acid,[15] all of which depend upon the assignment of **5**, must now be reassessed.

Studies are underway to examine the effect of diverse nucleophilic reagents and leaving groups on the stereochemical course of displacement reactions at phosphorus in phosphonothioates and related systems.

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[7] (a) W. B. Farnham, R. K. Murray, Jr., and K. Mislow, *Chem. Commun.*, 605 (1971). Overall retention was also observed for the sequence $(S)_P$-1 (**1b**) → **2b** → $(S)_P$-3 (**3b**). (b) A listing of observed and calculated structure factors for menthyl *S*-methyl phenylphosphonothioate will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Reprint Department, ACS Publications, 1155 Sixteenth St., N. W., Washington, D. C. 20036, by referring to author, title of article, volume, and page number. Remit $6.00 for photocopy or $2.00 for microfiche.

[8] A direct configurational link between structures determined by X-ray diffraction is provided by the reaction of diastereomerically pure **2a** with *n*-propylmagnesium bromide, which gives diastereomerically pure menthyl $(R)_P$-phenyl-*n*-propylphosphinate (**4a**); similar treatment of **2b** affords **4b**. The chirality at phosphorus in **4a** is *R*, as determined by X-ray analysis.[9]

[9] E. B. Fleischer and R. Dewar, unpublished results reported in footnote 10 of ref 5a.

[10] Treatment of diastereomerically pure **2a** with methyllithium in tetrahydrofuran gives diastereomerically pure **3a**. Retention stereochemistry of the displacement reaction is therefore not limited to Grignard reagents.

[11] V. Prelog, *Helv. Chim. Acta*, **36**, 308 (1953); numbering of carbons as in *p*-menthan-3-ol. See also R. Parthasarathy, J. Ohrt, A. Horeau, J. P. Vigneron, and H. B. Kagan, *Tetrahedron*, **26**, 4705 (1970).

[12] It has been recognized,[7a,13] that transformation of menthyl methylphosphinate to **3** by way of the intermediate menthyl *S*-methyl methylphosphonothioate (*i.e.*, the *P*-methyl analog of **2**) also occurs with overall retention of configuration.

[13] G. R. Van den Berg, D. H. J. M. Platenburg, and H. P. Benschop, *Chem. Commun.*, 606 (1971).

[14] L. P. Reiff and H. S. Aaron, *J. Amer. Chem. Soc.*, **92**, 5275 (1970); L. J. Szafraniec, L. P. Reiff, and H. S. Aaron, *ibid.*, **92**, 6391 (1970); L. P. Reiff, L. J. Szafraniec, and H. S. Aaron, *Chem. Commun.*, 366 (1971).

[15] M. Mikolajczyk and M. Para, *ibid.*, 1192 (1969).

[16] Public Health Service Predoctoral Fellow, 1969–1971.

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Hydride Derivatives of Niobocene and Tantalocene

Sir:

The surprising C_6H_6–D_2 exchange catalyzed by $(C_5H_5)_2TaH_3$[1] has stimulated interest in synthesis of

[1] E. K. Barefield, G. W. Parshall, and F. N. Tebbe, *J. Amer. Chem. Soc.*, **92**, 5234 (1970).