mogeneous prevents formation of the bis product. For example, overnight heating of a solution of 33 g of tosylate and 32 g of anhydrous hydrazine in 150 mL of triethylene glycol in a 110 °C bath affords complete conversion of tosylate to hydrazine **3** (^{19}F NMR). Under these conditions, deuterated tosylate **2d** affords hydrazine, retaining 89% of the deuterium.

(5) W. J. Le Nobel, *Prog. Phys. Org. Chem.*, **5**, 207 (1967).

(6) For compounds **1**, **2**, **3**, and **6**, the isotopic shift at 84.6 MHz causes the slightly broadened singlet of the deuterated species to coincide with the upfield line of the doublet arising from the protonated species.

(7) Both water and *dry* ethanol have this effect, presumably as a consequence of solvation-altered basicity and nucleophilicity.

(8) W. H. Pirkle, D. L. Sikkenga, and M. S. Pavlin, *J. Org. Chem.*, **42**, 384 (1977).

(9) H. M. Peters, D. M. Fiegl, and H. S. Mosher, *J. Org. Chem.*, **33**, 4245 (1968).

(10) W. H. Pirkle and S. D. Beare, *J. Am. Chem. Soc.*, **89**, 5485 (1967).

(11) The simultaneous determination of two nonidentical enantiomeric purities for compounds differing only by isotopic substitution illustrates the power of chiral solvating agents for NMR determination of enantiomeric purity and absolute configuration.

(12) (a) W. H. Pirkle and J. R. Hauske, *J. Org. Chem.*, **42**, 1839 (1977); (b) W. H. Pirkle and M. S. Hoekstra, *ibid.*, **39**, 3904 (1974).

(13) W. H. Pirkle and R. W. Anderson, *J. Org. Chem.*, **39**, 3901 (1974).

(14) R. A. Grieger and C. A. Eckert, *J. Am. Chem. Soc.*, **92**, 7149 (1970).

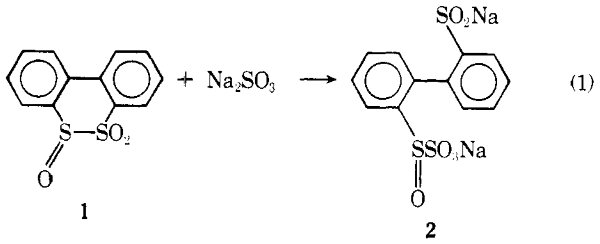
(15) Sodium borodeuteride was purchased from Ventron Corp. and was used without further purification.

Communications

Synthesis and Properties of a Bunte Salt *S*-Oxide[1]

Summary: Reaction of sulfite ion with dibenzo[*c,e*]-1,2-dithiin 1,1,2-trioxide leads to the formation of a compound having a Bunte salt *S*-oxide functional group, $-S(O)SO_3^-$, the first example of a compound with such a functionality; in acid solution the Bunte salt *S*-oxide undergoes a striking and extremely rapid decomposition to the cyclic thiolsulfonate, dibenzo[*c,e*]-1,2-dithiin 1,1-dioxide.

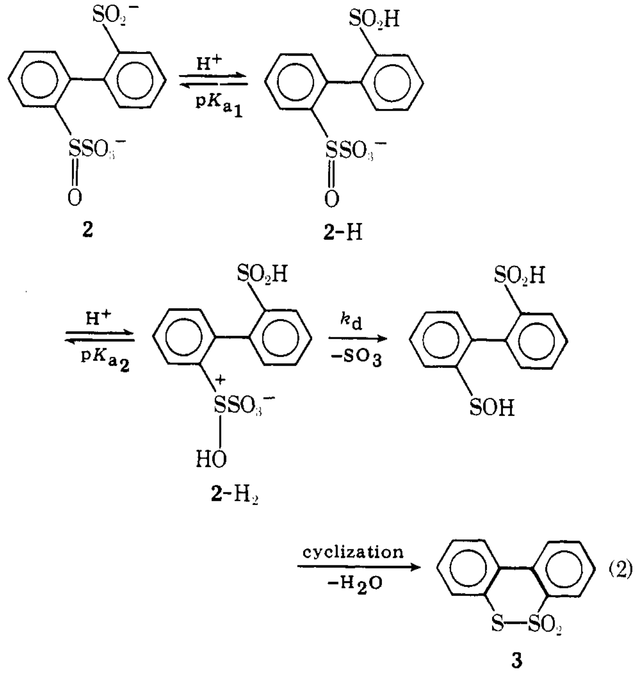
Sir: As part of a general study of the reactions of nucleophiles with oxidized derivatives of dibenzo[*c,e*]-1,2-dithiin we have examined the reaction of sulfite ion with dibenzo[*c,e*]-1,2-dithiin 1,1,2-trioxide[2] (**1**) and have been able to isolate as the exclusive reaction product the salt having structure **2** (eq 1).



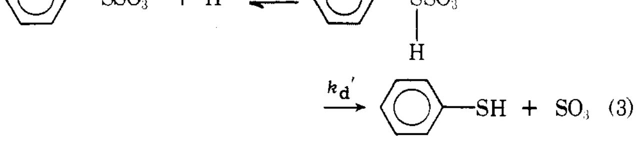
Salt **2** contains a Bunte salt *S*-oxide functional group, $-S(O)SO_3^-$, and is the first reported example of a compound containing this functionality. It exhibits some striking and interesting chemical behavior in acid solution.

Bunte salt *S*-oxide **2** was prepared by rapidly adding a 0.05 M solution of **1** in anhydrous dioxane to an equal volume of 0.05 M aqueous sodium sulfite at room temperature. Kinetic studies had shown that the reaction of **1** with sulfite is extremely rapid, $k_2 = 3 \times 10^5\ M^{-1}\ s^{-1}$, and is characterized in the ultraviolet by the disappearance of the absorption maximum at 310 nm characteristic of **1** and the appearance of a new maximum at 280 nm (ϵ 6400) due to **2**. As soon as the addition of **1** to the sulfite solution was complete, the solution was frozen and the solvent was removed by lyophilization to give **2** as a white, powdery solid.[3] The infrared spectrum of **2** (KBr) showed a strong band at 1220 cm^{-1} ($-SO_3^-$) and a series of strong absorptions in the 950–1050-cm^{-1} region (>S=O, $-SO_2^-$, $-SO_3^-$) consistent with structure **2**, but not with any possible isomeric structure.

The stability of **2** in solution and the nature of its decomposition products vary dramatically with the pH of the solution. At 25 °C in 60% dioxane containing 0.01 M $HClO_4$ **2** (10^{-4} M) disappears *extremely rapidly* ($k_1 = 1.2\ s^{-1}$) and yields the cyclic thiolsulfonate **3**[4] as the exclusive organic product. In contrast, in a 1:1 acetate/acetic acid buffer **2** disappears much more slowly ($k_1 = 2.2 \times 10^{-4}\ s^{-1}$, rate independent of total buffer concentration) and yields *none* of the cyclic thiolsulfonate [the major organic product under these conditions is diphenyl 2,2′-disulfinate[2] (**4**)[5]]. Study of the rate and products of the disappearance of **2** in trifluoroacetate, dichloroacetate, and chloroacetate buffers in 60% dioxane indicates that the facile decomposition of **2** to give thiolsulfonate **3** is acid catalyzed and takes place by the mechanism shown in eq 2. The key steps in this mechanism are the reversible protonation of the sulfinyl group of the Bunte salt *S*-oxide (K_{a_2}) and the loss of sulfur trioxide from the sulfinyl-protonated form (k_d).



Ordinary Bunte salts undergo acid-catalyzed decomposition by an analogous mechanism[6] (eq 3), but at a rate which is



about 3×10^8 *slower* under the same conditions (k_1 for acid-catalyzed decomposition of $PhSSO_3^-$ in 60% dioxane containing 0.01 M $HClO_4$ at 25 °C is calculated[6] to be only 4×10^{-9} s^{-1}). The Bunte salt *S*-oxide is thus *over 10^8 less stable* in acid solution than a similar Bunte salt. One important contributor to this phenomenal difference in stability is almost certainly the much greater basicity of the sulfinyl function in the *S*-oxide as compared to the sulfide sulfur in the Bunte salt, i.e., K_{a2} in eq 2 $\ll K_a'$ in eq 3. Sulfinyl groups are known to be much more basic than analogously substituted sulfide groups.[7]

Given the interesting chemical behavior and high reactivity shown by **2**, we are now searching for a synthetic route that will permit the preparation of a simple Bunte salt *S*-oxide containing no other functional group than the $-S(O)SO_3^-$ function.

References and Notes

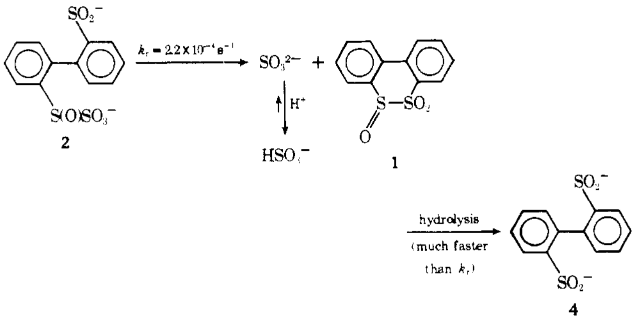
(1) This research supported by the Robert A. Welch Foundation (Grant D-650).

(2) M. M. Chau and J. L. Kice, *J. Org. Chem.*, in press.

(3) Upon being heated in a melting point tube a sample of **2** begins to undergo slow thermal decomposition at slightly above 40 °C. This thermal decomposition of the solid, which is rapid at 70 °C, appears to lead to the formation of significant amounts of sulfur trioxide. The other products of the decomposition have not been identified, but do not melt below 300 °C.

(4) H. J. Barber and S. Smiles, *J. Chem. Soc.*, 1141 (1928).

(5) Formation of disulfinate **4** from **2** in the acetate buffer occurs by rate-determining slow reversion of **2** to **1** plus sulfite, followed by rapid hydrolysis of **1** to **4**. In the acetate buffer sulfite is protonated to HSO_3^- as soon as it is formed, preventing the reverse reaction of **1** with sulfite.



(6) J. L. Kice, J. M. Anderson, and N. E. Pawloski, *J. Am. Chem. Soc.*, **88**, 5245 (1966).

(7) Dimethyl sulfoxide[8a] is slightly over 10^5 stronger base than dimethyl sulfide.[8b]

(8) (a) D. Landini, G. Modena, G. Scorrano, and F. Taddei, *J. Am. Chem. Soc.*, **91**, 6703 (1969); (b) P. Bonvicini, A. Levi, V. Lucchini, and G. Scorrano, *J. Chem. Soc., Perkin Trans. 2*, 2267 (1972).

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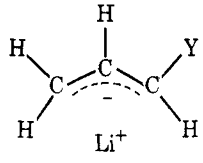
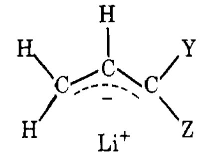
A General Route to Terminally Substituted Allylic Derivatives of Silicon and Tin. Preparation of Allylic Lithium Reagents

Summary: Wittig reactions of the appropriate *β*-trimethylstannyl- and *β*-trimethylsilylethyltriphenylphosphonium salt-derived ylides ($Ph_3P{=}CHCH_2SnMe_3$, $Ph_3P{=}CHCH_2SiMe_3$, $Ph_3P{=}C(Me)CH_2SiMe_3$ in the examples presented) with aldehydes and ketones provide a useful, general route to allylic compounds of silicon and tin.

Sir: We have reported recently concerning the synthesis and the unusual regioselectivity of *gem*-dichloroallyllithium in carbonyl addition reactions.[1] The results of this study prompted further interest in unsymmetrically substituted allyllithium reagents of general types **1** and **2**. Three major routes are available for the synthesis of allylic lithium reagents: direct lithiation of olefins,[2] allyl ether cleavage with metallic lithium,[3] and transmetalation reactions of allylic derivatives of heavy metals, principally of tin and lead.[1,4]



1



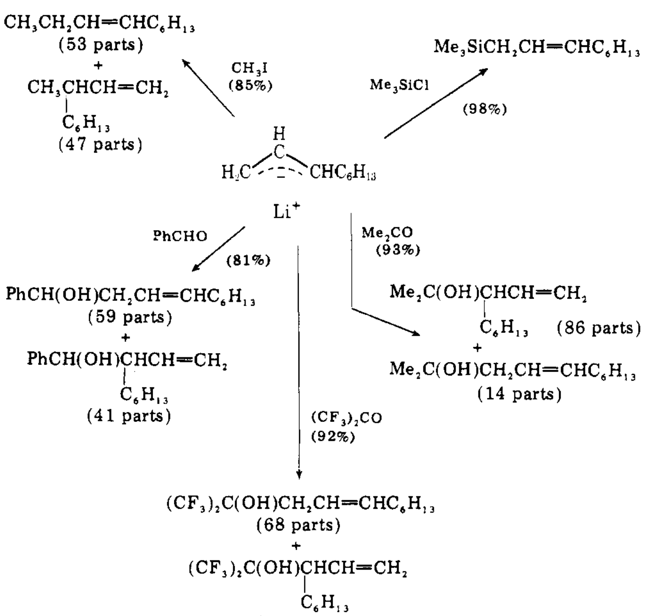
2

We describe here a new, general route to allylic derivatives of tin of types **3** and **4**. These are useful starting materials

$Me_3SnCH_2CH{=}CHR$ **3** $Me_3SnCH_2CH{=}CRR'$ **4**

for allylic lithium reagents of types **1** and **2**, where Y and Z = alkyl and aryl. Our new allyltin synthesis has added impor-

Scheme I. Reactions of *n*-Hexylallyllithium



Scheme II. Reactions of 1,1-Cyclopentamethyleneallyllithium