has a silver-gray luster. When cyclohexene was treated with 1.25 equiv of this new reagent, the allylic sulfonamide was obtained in somewhat improved yield (~10% better than using 1.25 equiv of the reagent in ref 1). However, when only 0.63 equiv of this new reagent was employed, it gave the same yield of allylic amide as did 0.63 equiv of the original reagent (ref 1). Further comparisons are needed, but it appears that this modified reagent may also be useful for the allylic aminations of olefins.

K. Barry Sharpless,* Stephen P. Singer
Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

Received February 18, 1976

Preparative Methods for β-Acyl Vinyl Anion Equivalents from Enones or Allyl Sulfides

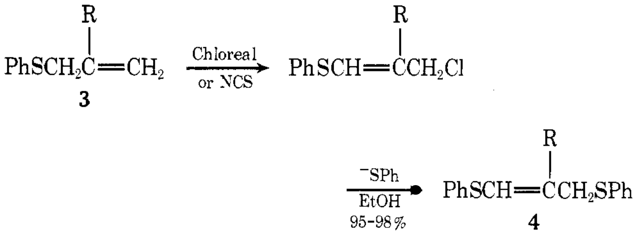
Summary: The treatment of many α,β-unsaturated aldehydes and ketones with triphenyl thioborate provides the 1,3-bis(phenylthio)alkene derivatives, the anions of which are shown to be effective β-acyl vinyl anion equivalents.

Sir: We wish to report that a variety of α,β-unsaturated aldehydes and ketones (1) can be converted directly to their 1,3-bis(phenylthio)alkene derivatives (2) by heating in hydrocarbon solvents with triphenyl thioborate (eq 1);[1] this reagent is readily prepared from B_2S_3 and thiophenol.[4] Several examples are given in Table I.

$$\underset{\mathbf{1}}{R_2CH{=}C(R_1)COR_3} \xrightarrow{B(SPh)_3} \underset{\mathbf{2}}{PhSCH(R_2)C(R_1){=}C(SPh)R_3} \quad (1)$$

This simple reaction gives a poor yield with acrolein and fails completely with methyl vinyl ketone.[5] Fortunately, the desired products from both reactions can be prepared by alternative routes. That (**4**, R = H) from acrolein can be prepared from phenyl allyl sulfide (**3**, R = H; commercially available) by the sequence in Scheme I; as pointed out elsewhere,[6] the chlorination is faster with the far less expensive reagent trichloroisocyanuric acid (Chloreal), but *N*-chlorosuccinimide can be used.[7] The bis(phenylthio) derivative (**4**, R = Me) of methacrolein can be prepared in a similar fashion; this sequence has been performed on a 20-g scale. The product **7**, expected from methyl vinyl ketone (**5**), can be prepared from the latter by treatment with thiophenol and HCl, followed by elimination of thiophenol from the condensation product (**6**) by cuprous trifluoromethanesulfonate (triflate)[8] (Scheme II).[9]

Scheme I



$$\underset{\mathbf{3}}{PhSCH_2C(R){=}CH_2} \xrightarrow[\text{or NCS}]{\text{Chloreal}} PhSCH{=}C(R)CH_2Cl \xrightarrow[\substack{EtOH\\ 95\text{-}98\%}]{^{-}SPh} \underset{\mathbf{4}}{PhSCH{=}C(R)CH_2SPh}$$

Scheme II

$$\underset{\mathbf{5}}{CH_2{=}CHCOMe} \xrightarrow[\text{HCl, 0 °C}]{\text{excess PhSH}} \underset{\mathbf{6}}{PhSCH_2CH_2C(SPh)_2Me} \xrightarrow[\substack{THF, C_6H_6,\\ 0\,°C, 2\,h}]{Cu^+} \underset{\mathbf{7}}{PhSCH_2CH{=}C(SPh)Me}$$

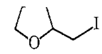
Table I. Reactions of Enones with Triphenyl Thioborate[a]

R_1[b]	R_2[b]	R_3[b]	% yield of **8**[c]
H	$CH_2CH_2CH_2$		78
H	CH_2CH_2		43
$CH_2CH_2CH_2CH_2$		Me	50[d,e]
H	Me	H	66[f]
Me	H	H	70[g]
H	H	H	35
H	H	Me	[h]

[a] Satisfactory spectral and elemental analyses were obtained on all new compounds. [b] Refers to eq 1. [c] In a typical run, 9.3 mmol of **1** was heated with 6.2 mmol of $B(SPh)_3$ at 50 °C in petroleum ether (60–110 °C) for 15 h; removal of the precipitate by filtration and evaporation of the solvent provide the isolated yields recorded. [d] Reaction performed at 150 °C for 24 h in a sealed tube; no product was obtained at 50 °C. [e] Cis–trans mixture. [f] 75% trans. [g] 50% trans. [h] Only 4-phenylthio-2-butanone produced.

Table II. Reactions of Bis(phenylthio)allyl Anions with Alkyl Halides[a]

$$PhSCH(R_2)C(R_1){=}C(SPh)R_3 \xrightarrow[\text{2. RX}]{\substack{\text{1. } sec\text{-BuLi, THF,}\\ -20\,°C,\ 45\text{ min}}} PhSC(R_2)(R)CR_1{=}C(SPh)R_3$$

R_1	R_2	R_3	RX	% yield
H	H	H	MeI	98
H	H	H	*i*-BuI	98
Me	H	H	MeI	94
Me	H	H	*n*-BuI	98
Me	H	H		94
H	$CH_2CH_2CH_2$[b]		MeI	90
H	Me[b]	H	MeI	98[c]
H	H	Me	MeI	98[c]

See footnote *a*, Table I. [b] When R_2 is alkyl, HMPA must be present to generate the anion quantitatively. [c] 90% methylation at secondary carbon, 10% at tertiary.

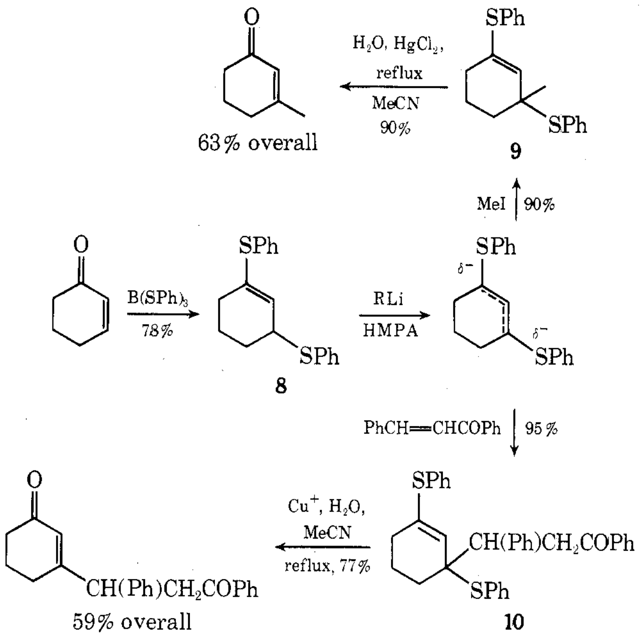
These bis(phenylthio)alkenes have many potential uses but one of the most important derives from the behavior of their lithio derivatives as β-acyl vinyl anion equivalents.[10] The results in Table II indicate that the lithio derivatives can be formed readily and alkylated efficiently. The anion of **8**, derived from cyclohexenone, also added to benzaldehyde and underwent conjugate addition to chalcone in 90 and 95% yields, respectively.

The otherwise unfunctionalized 1,3-bis(phenylthio)alkenes can be hydrolyzed to enones by mercuric chloride in wet acetonitrile as found by Corey[10] for the methylthio analogues; this was demonstrated for **2** (R_1 = Me, R_2 = *n*-butyl, R_3 = H)[11] and **9**. The ketone **10**, however, gave only a 25% yield of enone and a large quantity of insoluble material by this method. The following procedure, based on our new method of carbonium ion formation,[8] is successful for both **10** and **8**;[13] a solution of 0.20 mmol of **10** and 0.40 mmol of the benzene complex of cuprous triflate in 5 ml of acetonitrile and 0.5 ml of water[14] was heated at reflux for 10 h, cooled, and passed rapidly through a silica column and the solvent evaporated.

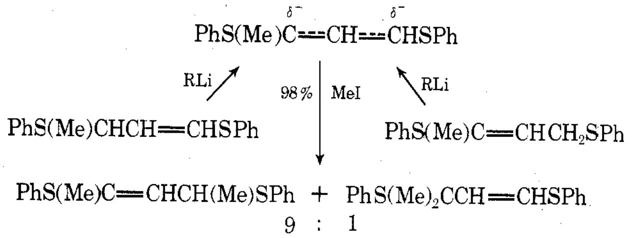
Thus, for example, the overall transformations shown in Scheme III have been realized.

It is clear that these techniques will frequently allow the replacement of a β hydrogen of a conjugated enone by an electrophilic substituent.[15] However, as implied by the last two entries in Table II (Scheme IV), in the case of enones

Scheme III



Scheme IV



which yield unsymmetrical anions, this procedure will result in a substitutive 1,3-carbonyl transposition[16] in some cases. Presumably, in the case of unsymmetrical anions with different steric requirements at the partially negative carbon atoms, the least hindered of the latter will be alkylated most readily as in Scheme IV. Methods of reversing this regioselectivity and of exploiting the interesting implications of this aspect are now under investigation, as are alternative uses of the 1,3-bis(phenylthio)alkenes.

Acknowledgment. We thank the National Institutes of Health for Grant GM20707 in support of this work. We also thank Mr. Richard Gapinski for technical assistance.

References and Notes

(1) Triethyl thioborate is reported[2] to form a normal thioacetal with α,β-unsaturated aldehydes. In view of the known allylic rearrangements of allylic thioethers,[3] we intended to perform the thermal or Lewis acid catalyzed rearrangements of these unsaturated thioacetals. However, both reactions apparently occur in the same reaction mixture with triphenyl thioborate, presumably because of the Lewis acid behavior of the latter and the superior leaving ability of thiophenoxide.

(2) R. H. Cragg and J. P. N. Husband, *Inorg. Nucl. Chem. Lett.*, **6**, 773 (1970).

(3) H. Kwart and N. Johnson, *J. Am. Chem. Soc.*, **92**, 6064 (1970); Y. Makisumi and T. Sasatani, *Tetrahedron Lett.*, 1975 (1969).

(4) A modification of the literature procedure [J. Brault and J. M. LaLancette, *Can. J. Chem.*, **42**, 2903 (1964)] consisting of heating B_2S_3 (Alpha) with thiophenol in refluxing benzene for 48 h gives a nearly quantitative yield of triphenyl thioborate as white crystals which can be handled rapidly in air and stored in a desiccator.

(5) The presence of galvinoxyl does not influence this result: G. W. Kabalka, H. C. Brown, A. Suzuki, S. Honma, A. Arase, and M. Itoh, *J. Am. Chem. Soc.*, **92**, 710 (1970).

(6) A. J. Mura, Jr., D. A. Bennett, and T. Cohen, *Tetrahedron Lett.*, 4433 (1975).

(7) T. B. Stevens, Ph.D. Thesis, Vanderbilt University, 1968.

(8) T. Cohen, G. Herman, J. R. Falck, and A. J. Mura, Jr., *J. Org. Chem.*, **40**, 812 (1975); T. Cohen, D. Kuhn, and J. R. Falck, *J. Am. Chem. Soc.*, **97**, 4749 (1975).

(9) The same sequence is also successful starting from methacrolein. A subsequent publication will elaborate on eliminations from such tris(phenylthio) compounds by means of cuprous triflate.

(10) Corey has shown that the lithio derivative of 1,3-bis(methylthio)propene behaves as a synthetic equivalent of the hypothetical β anion of acrolein: E. J. Corey, B. W. Erickson, and R. Noyori, *J. Am. Chem. Soc.*, **93**, 1724 (1971); E. J. Corey and R. Noyori, *Tetrahedron Lett.*, 311 (1970). See also K. Oshima, H. Yamamoto, and H. Nozaki, *Bull. Chem. Soc. Jpn.*, **48**, 1567 (1975); R. G. Carlson and W. S. Mardis, *J. Org. Chem.*, **40**, 817 (1975).

(11) Hydrolysis of this compound was also successful (quantitatively, according to ^1H NMR) using the cupric chloride method[12] but in this case it was necessary to separate the product from diphenyl disulfide.

(12) T. Mukaiyama, K. Narasaka, and M. Furusato, *J. Am. Chem. Soc.*, **94**, 8641 (1972).

(13) Unpublished work of Richard Gapinski indicates that this method is also successful with a third 1,3-bis(phenylthio)propene which was prepared by a different procedure.

(14) A similar solution can be prepared more easily by adding water to a solution formed by heating cupric triflate and copper metal in acetonitrile: C. L. Jenkins and J. K. Kochi, *J. Am. Chem. Soc.*, **94**, 843 (1972).

(15) The only other method of which we are aware for preparing β-acyl vinyl anion equivalents directly from enones requires four separate operations in some cases and five in others: K. Kondo and D. Tunemoto, *Tetrahedron Lett.*, 1007 (1975).

(16) B. M. Trost and J. L. Stanton, *J. Am. Chem. Soc.*, **97**, 4018 (1975).

(17) A. W. Mellon Predoctoral Fellow.

Theodore Cohen,* David A. Bennett
Albert J. Mura, Jr.[17]
Department of Chemistry, University of Pittsburgh
Pittsburgh, Pennsylvania 15260

Received March 16, 1976

Nitrogen Acids. 1. Carboxamides and Sulfonamides

Summary: Measurement of the equilibrium acidities in Me_2SO of carbon, nitrogen, and oxygen acids has revealed the expected order, i.e., $GOH \gg GNH_2 \gg GCH_3$, when G is Ph, CH_3SO_2, or F_3CSO_2, but when G is CH_3CO or PhCO the carbon and nitrogen acids have comparable acidities.

Sir: Carboxamides are too weakly acidic to allow equilibrium acidities to be measured in water by ordinary methods. In fact, to our knowledge, no report of an *absolute* acidity measurement for a simple carboxamide has been recorded in the literature in the 48 years since Branch and Clayton reported the equilibrium constant of acetamide in water to be 8.3×10^{-16}.[1,2] Measurements on carboxamides in strongly basic aqueous media by acidity function techniques are made difficult, if not impossible, by hydrolysis, and p*K* data are scarce for this important class of weak nitrogen acids.[2] We wish to report that absolute equilibrium acidity measurements in dimethyl sulfoxide solution can be made accurately and conveniently for carboxamides, as well as for sulfonamides, by the competitive indicator method developed for carbon acids.[4] These nitrogen acids differ from oxygen acids in this respect, the latter having a strong tendency to undergo hydrogen bonding ("homoconjugation") with their conjugate bases (e.g., $RO^-\cdot\cdot HOR$), which makes measurements more difficult.[4,5] The p*K*'s in Me_2SO for a few carboxamides and sulfonamides are compared in Table I with those of their carbon and oxygen analogues.

Examination of Table I shows that the p*K* for dissociation of the N–H bond in acetamide is much higher in Me_2SO than in water (25.5 vs. 15.1). This is consistent with results obtained with other acids in which the negative charge in the anion is concentrated on oxygen where it can be stabilized by strong H bonding in water, but not in Me_2SO.[4] Judging from preliminary results with *N,N*-dimethylacetamide, the p*K* for dissociation of the C–H bond in acetamide is above 32 in Me_2SO, which places the acidity more than 7 units higher than the p*K* in water estimated from deuterium exchange rates.[6]

The order of acidities of carbon, nitrogen, and oxygen acids is seen from Table I to be $GCH_3 \ll GNH_2 \ll GOH$, when G