its conjugate base with diphenyl disulfide to provide a 68% yield of **16** (which should be attainable in one step by treatment of methyl cyclohexene-1-carboxylate with aluminum thiophenoxide) and elimination of thiophenol by the agency of cuprous triflate. The conjugated ketene thioacetal, **17**, adds *n*-butyllithium,[20] and the resulting allylic anion becomes protonated almost exclusively on the thioacetal carbon atom (as expected from the results of the conversion of **8** to **9**) to provide pure **18**, which is an alkylated analogue of **9** and the thioacetal of 3-*n*-butyl-cyclohexene-1-carboxaldehyde, in 84% yield from **16** (57% overall yield from cyclohexanecarboxylic acid).

Similar conversion of isovaleric acid to sulfur-substituted diene **25** (Scheme II) was frustrated by the resistance of its derived ketene thioacetal (**22**) to removal of the tertiary allylic proton[21] required for the production of the sulfur-stabilized allylic anion **21**. However, this anion could be produced cleanly from the ketene thioacetal **20**, derived from the corresponding conjugated ester **19**, by reductive lithiation at −70 °C, using lithium naphthalenide (Li naph).[22] Protonation of the anion **21** with methanol at −70 °C resulted in a 71% yield of the thioacetal (**23**) of 3-methyl-2-butenal. During chromatographic separation on silica gel of naphthalene from **23**, the latter partially rearranged to *trans*-**24**. Treatment of the mixture of **23** and **24** with cuprous triflate[19] in the presence of diisopropylethylamine caused elimination of thiophenol and the production of 76% (46% from the unsaturated ester) of the purely trans diene **25**,[24] a sulfur-bearing isoprene unit which should be of use in the construction of terpenes by the Diels-Alder reaction.

Only a few of the many uses that may be envisioned for the now easily prepared sulfur-separated ketene thioacetals such as **8** and **20** have been demonstrated in this and the accompanying communication.[10] The value of the transformations revealed here is enhanced by a report which appeared while our work was being prepared for publication; Mendoza and Matteson have discovered a connective method for producing ketene bis(phenylthio)acetals from ketones utilizing anions derived from bis(phenylthio)methaneboronic esters.[25] Finally, this work demonstrates the power of reductive lithiation for the production of anions that are not accessible by the conventional deprotonation procedure.

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The Conversion of Carboxylic Acids and Esters into Acyl Anion Equivalents via Reduction Lithiation of Their Ketene Phenylthioacetal Derivatives

Summary: Treatment of ketene bis(phenylthio)acetals with lithium naphthalenide produces sulfur-stabilized vinyllithiums which can react with a variety of electrophiles.

Sir: We have recently reported that readily available[1] cyclopropanone bis(phenylthio)ketals are rapidly reduced to sulfur-stabilized cyclopropyl anions at −70 °C by the use of lithium naphthalenide,[2] and Screttas has shown that pentanal bis(phenylthio)acetal behaves similarly with this reagent.[3] We now report that ketene bis(phenylthio)-acetals (**1**), which are readily available in high yield by the reaction of carboxylic acids or esters with aluminum thiophenoxide,[4,5] are reductively lithiated with comparable ease by lithium naphthalenide (Li naph). The resulting lithio derivatives (**2**) are potential acyl anion equivalents since they react with a variety of electrophiles (E) to yield substituted vinyl sulfides (**3**; Table I),[6] a type of functionality which is hydrolyzable to a ketone.[7]

Sulfur-stabilized vinyllithiums such as **5** are usually produced by deprotonation of enol thioethers of aldehydes[8-11] (**4**), but, except for those cases in which the

(1) T. Cohen and W. M. Daniewski, *Tetrahedron Lett.*, 2991 (1978).

(2) T. Cohen, W. M. Daniewski, and R. B. Weisenfeld, *Tetrahedron Lett.*, 4665 (1978).

(3) C. G. Screttas and M. Micha-Screttas, *J. Org. Chem.*, 44, 713 (1979). The preparation of simple alkyllithiums from phenyl thioethers by this procedure is also demonstrated in this paper as well as in C. G. Screttas and M. Micha-Screttas, *ibid.*, 43, 1064 (1978), and C. G. Screttas, Abstract 56, Seventh International Conference on Organometallic Chemistry, Venice, Italy, Sept. 1975.

(4) T. Cohen, R. E. Gapinski, and R. R. Hutchins, *J. Org. Chem.*, accompanying paper.

(5) Connective methods for the production of this type of thioacetal are also available: D. Seebach, M. Kolb, and B.-T. Gröbel, *Chem. Ber.*, 106, 2277 (1973); B.-T. Gröbel, R. Bürstinghaus, and D. Seebach, *Synthesis*, 121 (1976); A. Mendoza and D. S. Matteson, *J. Org. Chem.*, 44, 1352 (1979).

(6) New compounds were characterized by ^{1}H NMR, IR, and mass spectroscopy and by their exact masses as determined by high-resolution mass spectroscopy.

(7) B.-T. Gröbel and D. Seebach, *Synthesis*, 357 (1977).

(8) K. Oshima, K. Shimoji, H. Takahashi, H. Yamamoto, and H. Nozaki, *J. Am. Chem. Soc.*, 95, 2694 (1973).

(9) R. Muthukrishnan and M. Schlosser, *Helv. Chim. Acta*, 59, 13 (1976).

(20) D. Seebach, M. Kolb, and B.-T. Gröbel, *Angew. Chem., Int. Ed. Engl.*, 12, 69 (1973); D. Seebach, R. Bürstinghaus, B.-T. Gröbel, and M. Kolb, *Justus Liebigs Ann. Chem.*, 830 (1977); B. Cazes and S. Julia, *Tetrahedron Lett.*, 4065 (1978).

(21) The following bases were used in the presence of TMEDA: *sec*-butyllithium in the presence and absence of lithium diisopropylamide in THF and *tert*-butyllithium in hexanes. In the former cases, substrate was recovered; in the latter, lithium thiophenoxy exchange appears to have occurred.
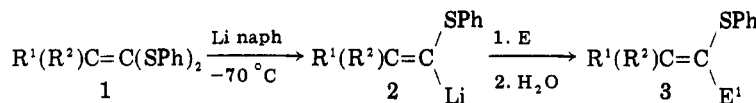
(22) We[10,23a] and Screttas[23b] have used this readily prepared reagent previously for the production of sulfur-stabilized anions. However, this is the first report of the formation by this means of an anion further stabilized by allylic resonance.

(23) (a) T. Cohen, W. M. Daniewski, and R. B. Weisenfeld, *Tetrahedron Lett.*, 4465 (1978); (b) C. G. Screttas and M. Micha-Screttas, *J. Org. Chem.*, 44, 713 (1979).

(24) E. Guittet and S. Julia, *Tetrahedron Lett.*, 1155 (1978); T. J. Jacobs and A. Mihailovski, *ibid.*, 2607 (1967); C. Huynh, V. Ratovelomanana, and S. Julia, *Bull. Soc. Chim. Fr.*, 710 (1977).

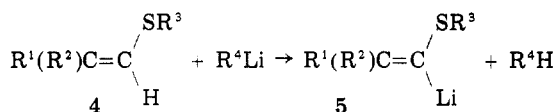(25) A. Mendoza and D. S. Matteson, *J. Org. Chem.*, 44, 1352 (1979).

Table I

$$R^1(R^2)C=C(SPh)_2 \xrightarrow[-70\ ^\circ C]{\text{Li naph}} R^1(R^2)C=C\begin{smallmatrix}SPh\\ \\Li\end{smallmatrix} \xrightarrow[2.\ H_2O]{1.\ E} R^1(R^2)C=C\begin{smallmatrix}SPh\\ \\E^1\end{smallmatrix}$$

$$\quad\quad\quad 1 \quad\quad\quad\quad\quad\quad\quad\quad\quad 2 \quad\quad\quad\quad\quad\quad\quad\quad\quad 3$$

R^1	R^2	E	E^1	yield, %[a]
cyclohexyl	H	$n\text{-}C_6H_{13}CHO$	$n\text{-}C_6H_{13}CHOH$	68[b]
Me	Me	$n\text{-}C_6H_{13}CHO$	$n\text{-}C_6H_{13}CHOH$	77
Me	Me	cyclohexanone	$(CH_2)_5COH$	56
Me	Me	CO_2	CO_2H	49[c]
$CH_2CH_2CH_2CH_2CH_2$		$(Me)_3SiCl$	$Si(Me)_3$	91[d]
$CH_2CH_2CH_2CH_2CH_2$		PhCHO	PhCHOH	70
$CH_2CH_2CH_2CH_2CH_2$		$n\text{-}C_6H_{13}CHO$	$n\text{-}C_6H_{13}CHOH$	70
$CH_2CH_2CH_2CH_2CH_2$		cyclohexanone	$(CH_2)_5COH$	74
$CH_2CH_2CH_2CH_2CH_2$		$(Me)_2NCHO$	CHO	19[e]
$CH_2CH_2CH_2CH_2CH_2$		CO_2	CO_2H	74[f]

[a] After silica chromatography, except where noted and in the case of the carboxylic acids. [b] Mixture of *E* and *Z* isomers. [c] After recrystallization [mp 84.5–85.5 °C (lit.[18] mp 85–86 °C)]; the crude product (80% yield) was not obtained spectroscopically pure. [d] Obtained pure after removal of the naphthalene by sublimation. [e] Mp 60.0–61.5 °C; formylation by this method is known to be sensitive to steric hindrance: P. C. Traas, H. Boelens, and H. J. Takken, *Tetrahedron Lett.*, 2287 (1976). [f] This acid, mp 101.5–102.0 °C, was spectroscopically pure as obtained directly from the reaction, and its physical properties did not change upon recrystallization.

additional presence of an allylic heteroatom strongly influences the position of deprotonation,[10e,13] there are very few examples in which an alkyl group was present on the β-carbon atom, and in only one case (see below) was the resulting anion treated with a carbonyl compound.[8]

$$R^1(R^2)C=C\begin{smallmatrix}SR^3\\ \\H\end{smallmatrix} + R^4Li \rightarrow R^1(R^2)C=C\begin{smallmatrix}SR^3\\ \\Li\end{smallmatrix} + R^4H$$

$$\quad\quad 4 \quad\quad\quad\quad\quad\quad\quad\quad\quad\quad 5$$

Muthukrishnan and Schlosser[9] obtained generally poor yields of alkylation products 3 upon treatment of 4 (R^1 = H; R^2 = alkyl; R^3 = Ph) with *n*-butyllithium–potassium *tert*-butoxide; in the case in which R^2 = Me, evidence was obtained for production of both vinyl and allylic anions. Oshima et al.,[8] in the pioneering paper on the deprotonation of vinyl sulfides, reported the treatment of 4 (R^1 = H; R^2 = *n*-C_8H_{17}; R^3 = Me) with *sec*-butyllithium in tetrahydrofuran–hexamethylphosphoric triamide (9:1) at –78 °C and the reaction of the resulting lithio derivative with *n*-octyl bromide and with benzaldehyde to produce 82 and 51%, respectively, of products 3 (Me in place of Ph); reaction of the deprotonated substrate with an enolizable ketone was not reported.

Because of this omission and because no reports have appeared on the preparation of sulfur-stabilized vinyllithiums (5) by deprotonation of vinyl sulfides (4) in which both R^1 and R^2 are alkyl groups, we have applied the deprotonation procedure of Oshima et al.[8] to 4 (R^1 = R^2

= Me; R^3 = Ph),[14] prepared by copper(I)-induced elimination of thiophenol from the thioacetal of isobutyraldehyde,[14] and have treated the lithio derivative(s) with carbon dioxide and with cyclohexanone. In the former case, an 85% yield of a mixture of several carboxylic acids was obtained; analyses of the ^1H NMR spectrum of this mixture and the gas chromatogram of the derived methyl esters[15] revealed that no more than 25% and probably only ca. 5% of the mixture was the acid 3 (R^1 = R^2 = Me; E^1 = CO_2H). Reaction of the anionic intermediate(s) with cyclohexanone led to recovered starting materials, presumably due to extensive enolization in the rather polar medium;[16] no detectable quantity of the adduct 3 (R^1 = R^2 = Me; E^1 = $(CH_2)_5COH$) was produced. In contrast, reaction of the anion 2 (R^1 = R^2 = Me), generated by reductive lithiation, with carbon dioxide and with cyclohexanone gave acceptable yields of adducts (Table I), although these two yields are less satisfactory than most in the table.

The only synthesis that has been reported for 3 (E^1 = Me_3Si), except for the special case in which R^1 = R^2 = H^{10c}, involves a Peterson olefination,[17] but the procedure is unsuccessful for enolizable ketones and is somewhat longer than that reported here; a study of the anticipated synthetic utility of such intermediates is planned.

A representative procedure follows: A solution of 1.00 mmol of the ketene thioacetal in 3 mL of THF was added to a solution containing 4 mL of THF and 4.4 mL (2.2 mmol) of a 0.51 M stock solution of lithium naphthalenide (prepared by stirring an equimolar mixture of lithium chips and naphthalene in THF at 25 °C for 6 h), and the solution was stirred for 15 min at –70 °C under an argon atmosphere. A solution of 3 to 4 equiv of the aldehyde or ketone in 3 mL of THF was added, and the solution was allowed to stir for 5 min at –70 °C and for 3 h at ambient temperature. After dilution of the reaction mixture with water, standard extraction procedures, and chromatography on silica gel (5% ethyl acetate–hexanes), the product was

(10) (a) I. Vlattas, L. D. Vecchia, and A. O. Lee, *J. Am. Chem. Soc.*, 98, 2008 (1976); (b) R. C. Cookson and P. J. Parsons, *J. Chem. Soc., Chem. Commun.*, 990 (1976); (c) M. Braun, *Tetrahedron Lett.*, 3695 (1978); B. Harirchian and P. Magnus, *J. Chem. Soc., Chem. Commun.*, 522 (1977); (d) R. H. Everhardus, H. G. Eeuwhorst, and L. Brandsma, *ibid.*, 801 (1977); R. R. Schmidt and B. Schmid, *Tetrahedron Lett.*, 3583 (1977); R. H. Everhardus, R. Gräfing, and L. Brandsma, *Recl. Trav. Chim. Pays-Bas*, 97, 69 (1978); (e) J. J. Fitt and H. W. Gschwend, *J. Org. Chem.*, 44, 303 (1979).

(11) There are a few cases of production of 5 by exchange of bromine[10a] or tin[12a] attached to an olefinic linkage by the lithium of an alkyllithium, but these methods suffer from lack of general availability of the precursors of the anions. Such anions have also been produced by attack of phenyl- or methyllithium on thioketenes,[12b] but the latter are only preparable if the functional group is highly hindered.

(12) (a) B.-T. Gröbel and D. Seebach, *Chem. Ber.*, 110, 867 (1977); (b) E. Schaumann and W. Walter, *ibid.*, 107, 3562 (1974).

(13) 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); 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); T. Cohen, D. A. Bennett, and A. J. Mura, Jr., *ibid.*, 41, 2506 (1976); M. Wada, H. Nakamura, T. Taguchi, and H. Takei, *Chem. Lett.*, 345 (1977).

(14) T. Cohen, G. Herman, J. R. Falck, and A. J. Mura, Jr., *J. Org. Chem.*, 40, 812 (1975). A detailed procedure for performing such eliminations will soon appear: T. Cohen, R. J. Ruffner, D. W. Shull, E. R. Fogel, and J. R. Falck, *Org. Synth.*, in press. The cuprous trifluoromethanesulfonate used in the elimination can now be obtained from Strem Chemical Co., P.O. Box 108, Newburyport, MA 01950.

(15) The esters were prepared by treatment of the sodium salt with methyl iodide in refluxing methanol.

(16) E. Juaristi and E. L. Eliel, *Tetrahedron Lett.*, 543 (1977).

(17) B.-T. Gröbel and D. Seebach, *Chem. Ber.*, 110, 852 (1977).

obtained as an oil. In the case of carbonation, dry carbon dioxide was passed through the solution at $-70\ °C$ and, after the reaction mixture had warmed to ambient temperature, the acidic product was isolated by extraction; no chromatography was performed. The preparation of **3** (R^1 = R^2 = Me; E^1 = CO_2H) compares favorably with a previous synthesis in which a 21% overall yield in three steps starting from 3-methyl-2-butenoic acid was obtained.[18]

In summary, for many applications, the preparation of sulfur-stabilized vinyl anions by reductive lithiation, proceeding as it does from a different and generally more accessible oxidation state (that of a carboxylic acid rather than an aldehyde), may be a useful complement to the deprotonation method; for certain applications, as demonstrated above, the method disclosed here is clearly superior to any presently known technology. However, as presently constituted, reductive lithiation may be inferior to deprotonation in cases in which simple alkylation of the anion is planned; the thiophenoxide anion, which is necessarily present, would possibly destroy 1 equiv of the alkylating agent, and the separation of the product from the naphthalene byproduct may require a careful chromatography. We are giving some attention to surmounting such problems. Finally, this work emphasizes anew the great potential value of reductive lithiation for the production of sulfur-stabilized anions.[2-4] Further examples will be revealed in subsequent publications.

(18) W. E. Parham and D. W. Boykin, *J. Org. Chem.*, **42**, 260 (1977).

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Conversion of Monoalkyl Olefins to 1,1-Dialkyl Olefins by Reaction with Bis(cyclopentadienyl)titanium Dichloride–Trialkylaluminum

Summary: Reaction of certain monoalkyl olefins with a reagent generated by mixing bis(cyclopentadienyl)titanium dichloride and a trialkylaluminum compound provides a single-step procedure for preparing 1,1-dialkyl olefins.

Sir: We wish to report that the reaction of certain monoalkyl olefins with a reagent generated by mixing bis(cyclopentadienyl)titanium dichloride and a trialkylaluminum compound provides a single-step procedure for preparing the corresponding 1,1-dialkyl olefins (eq 1).[2,3]
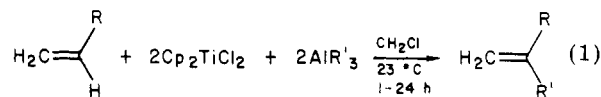
This reaction proceeds most cleanly using a twofold molar excess of both titanium and aluminum components. Smaller excesses result in lower yields of alkylated olefin and increased yields of byproducts (CH_3CH_2R, CH_3CHR^1R, $CH_3CR^1_2R$, and higher molecular weight compounds). Use of methylene chloride as solvent gives more rapid reaction than toluene. Table I summarizes results obtained at room temperature using 1:2:2 molar ratios of olefin/Cp_2TiCl_2/AlR^1_3. Reactions were followed by GLC, and the indicated times are those giving the maximum yield of alkylated product.

In a representative reaction, $AlMe_3$ (24 mL of a 3 M solution in hexanes, 72 mmol) was added under argon to a vigorously stirred solution of Cp_2TiCl_2 (18 g, 72 mmol), 1-decene (6.8 mL, 36 mmol), and ethyl acetate (3.5 mL, 36 mmol) in CH_2Cl_2 (125 mL).[4,5] After 14 h at room temperature, the reaction mixture was carefully poured onto a 3 M aqueous HCl–ice slush. The organic layer was separated and solvent was removed by rotary evaporation in the presence of neutral alumina (15 g). Rapid elution of the product mixture with 300 mL of pentanes from a 2 × 30-cm column of neutral alumina and evaporation of solvent afforded a clear oil (4.06 g) composed of 2-methyl-1-decene (92%), n-decane (5%), and 1-decene (3%).

The reaction appears to be sensitive to steric effects: the larger the alkyl group of the trialkylaluminum compound, the lower the yield of alkylated olefin; bis(ethyltetramethylcyclopentadienyl)titanium dichloride[6] gives a slower reaction and lower yields than Cp_2TiCl_2; branched primary olefins give lower yields than unbranched; internal olefins are unreactive. Lewis bases slow the reaction and, frequently, lower the product yield: ethers (1:1 molar ratio of diethyl ether/olefin) suppress the reaction almost

(1) Supported by the National Science Foundation, 7711282 CHE, and by Hercules Inc.

(2) Alkylation of unfunctionalized olefins is a recognized side reaction in Ziegler–Natta polymerization but has not been exploited in organic synthesis. Dyachkovskii, F. S. in "Coordination Polymerization"; Chien, J. C. W., Ed.; Academic Press: New York, 1975; pp 199–222, and references cited therein.

(3) Variously substituted olefins have been prepared via alkyl metalation of acetylenes with organoaluminum–transition metal reagents: Negishi, E.; Van Horn, D. E. *J. Am. Chem. Soc.* **1977**, *99*, 3170–3171. Van Horn, D. E.; Negishi, E. *Ibid.* **1978**, *100*, 2252–2254. Negishi, E.; Okukado, N.; King, A. O.; Van Horn, D. E.; Spiegel, B. I. *Ibid.* **1978**, 2254–2256. Mixtures of organoaluminum and -titanium compounds have been used to alkylate terminal acetylenes and olefins activated by proximate hydroxyl groups: Youngblood, A. V.; Nichols, S. A.; Coleman, R. A.; Thompson, D. W. *J. Organomet. Chem.* **1978**, *146*, 221–228, and references cited therein. Organoaluminum reagents add to substituted benzonorbornadienes and acetylenes: Eisch, J. J.; Burlinson, N. E. *J. Am. Chem. Soc.* **1976**, *98*, 753–761. Eisch, J. J.; Damasevitz, G. A. *J. Org. Chem.* **1976**, *41*, 2214–2215.

(4) Reactions were carried out using unexceptional inert atmosphere techniques: Brown, H. C. "Organic Syntheses via Boranes"; Wiley: New York, 1975; Chapter 9. Methylene chloride (reagent grade) was purged with argon before use. Solutions of trialkylaluminum compounds were obtained from Ethyl Corporation.

(5) **Caution.** Although solutions of trialkylaluminum compounds are claimed to be nonpyrophoric, they will ignite spontaneously if exposed to oxygen while dispersed on a high-surface support. Concentrated or neat trialkylaluminum compounds are strongly pyrophoric.

(6) Feitler, D.; Whitesides, G. M. *Inorg. Chem.* **1976**, *15*, 466–469.