geraniol in a ratio of 2:74:3:21 (93% combined yield). A similar tendency was also observed in the case of perillyl alcohol. Thus, the aluminum method under the comparable conditions as described above gave rise to a monocyclopropanation product **5** exclusively (64%) with recovery of unreacted perillyl alcohol (17%), although the zinc method yielded a mixture of **5**, **6**, **7**, and perillyl alcohol in a ratio of 3:49:8:40 (81% combined yield).

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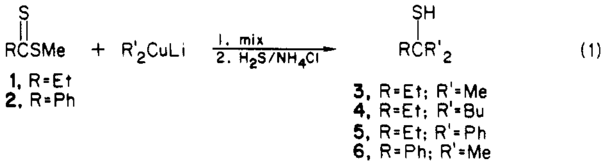
Reaction of Organocuprates with Dithio Esters: Double-Barrelled Carbophilic Addition and a New Synthetic Route to Tertiary Thiols[1a]

Summary: Organocuprates prepared from lithium reagents or Grignard reagents react with dithio esters to give high yields of tertiary thiols; in the absence of Cu(I), only thiophilic addition products are observed.

Sir: Thiocarbonyl compounds such as thioketones[2,3] and dithio esters[4] generally react with organometallic nucleophiles such as Grignard and lithium reagents via *thiophilic* addition,[5] e.g., these reagents convert thiobenzophenone[2] to alkyl or aryl benzhydryl sulfides and dithio esters to dithianes.[4] In contrast, we have discovered that organocuprates react with thiobenzophenone via *carbophilic* addition and with dithio esters via "double-barrelled" carbophilic addition (eq 1) to give excellent yields of tertiary thiols.



$$\mathrm{R\overset{\displaystyle S}{\overset{\|}{C}}SMe} + \mathrm{R'_2CuLi} \xrightarrow[\text{2. } H_2S/NH_4Cl]{\text{1. mix}} \mathrm{R\overset{\displaystyle SH}{\overset{|}{C}}R'_2} \qquad (1)$$

1, R=Et
2, R=Ph

3, R=Et; R'=Me
4, R=Et; R'=Bu
5, R=Et; R'=Ph
6, R=Ph; R'=Me

We have investigated this new reaction as a function of substrate (R = Et, Ph), cuprate (R' = Me, Bu, Ph), organometallic precursor (R'Li, R'MgBr), copper(I) precursor (CuX, X = CN, Br, I, CF_3SO_3), solvent (ether, THF), and temperature (−78 °C, 0 °C) with the results summarized in Tables I and II. In all cases 2.0 mmol of Li or Mg reagent were used per 1.0 mmol of substrate; in the stoichiometric reactions 1.0 mmol of Cu(I) was used vs. 0.10 mmol in the catalytic reactions. The magnesiocuprates were prepared from CuO_3SCF_3 (Cu(I) triflate) in ether.

With methyl dithiopropionate (**1**) as the substrate and Me_2CuLi as the reagent, the yield of 2-methyl-2-butanethiol (**3**) is virtually quantitative (96–100%), and the best yields of 5-ethyl-5-nonanethiol (**4**) and 1,1-diphenyl-1-propanethiol (**5**) (using Bu_2CuLi and Ph_2CuLi, respectively, as reagents) are not far behind (93% and 97%, respectively). The best yield of α,α-dimethylbenzyl mercaptan (**6**) from methyl dithiobenzoate (**2**) and Me_2CuLi (88%) is not as good as the corresponding yield from **1** and Me_2CuLi, but it is very good nevertheless. Moreover, a 99% yield of **6** is obtained by treating **2** with 2 equiv of MeCu(SMe)Li. The yields from large-scale reactions are the same provided the same concentrations are used (see supplementary material).

Only traces (<0.1%) of thiophilic addition products (dithioacetals) are observed in any of the reaction mixtures. With **2** we also observe small amounts (up to 2%) of methyl 1-phenyl-1-ethyl sulfide, the product of an initial carbophilic attack followed by thiophilic attack on an intermediate thioketone (vide infra). The only situation in which we observe a significant amount of "carbophilic–thiophilic" product occurs when **1** and Bu_2CuLi from CuI are mixed at −78 °C in THF. Under these conditions the yield of butyl 3-heptyl sulfide is ~15%. Mixing the reactants at 0 °C in THF, or at either −78 °C or 0 °C in ether, results in just the "double-barrelled" carbophilic addition product, **4**.

When **1** and R'_2CuLi (R' = Me, Bu, Ph) are mixed at −78 °C, samples withdrawn with a cold syringe and quenched with deoxygenated ammonium chloride solution contain neither starting material nor product by GLC. If the reaction mixture is then allowed to warm to 0 °C, a good yield of product appears. Apparently, an intermediate nonvolatile complex is formed first and yields product only upon warming. In some cases better yields are obtained by initiating the reactions at 0 °C rather than −78 °C (the optimal conditions are summarized in footnotes to Table I). Saturating the reaction mixtures with H_2S (−78 °C) before quenching with ammonium chloride solution gives slightly better yields from **1** and Me_2CuLi and has a negligible effect on yields from **1** and Bu_2CuLi. In contrast, H_2S treatment has a vital effect on yields from **1** and Ph_2CuLi, as it suppresses the formation of 1,1-diphenyl-1-propene (from elimination of H_2S from **5**). It also has a dramatic effect on the yields of **6** from **2** and Me_2CuLi—they are more than doubled in some cases.

We have verified that in the absence of Cu(I), **1** and **2** are converted to dithioacetals by MeLi, BuLi, and PhLi, and BuMgBr. (With MeMgBr and PhMgBr thioenolization of **1** occurs, yielding ketene dithioacetals upon quenching with benzyl bromide.) No products of carbophilic attack are observed in these reactions. Thus, the inclusion of Cu(I) has a profound effect upon the course of the reaction. For the thiophilic attack on thiobenzophenone, Beak and co-workers preferred a direct nucleophilic addition mechanism, since they found the yields of thiophilic products to be inversely proportional to the ability of a series of organometallics to transfer an electron.[2] On the other hand, Ohno et al.[3] proposed electron transfer followed by radical combination for the reaction of PhLi with di-*tert*-butyl thioketone, which affords both C-phenylated and S-phenylated products. An electron-

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[1] (a) Part 9 of a series on New Copper Chemistry, for part 8, see: Bertz, S. H.; Dabbagh, G. *Inorg. Chem.* **1985**, *24*, 3488; for part 7, see: Bertz, S. H.; Dabbagh, G.; Cook, J. M.; Honkan, V. *J. Org. Chem.* **1984**, *49*, 1739. (b) AT&T Bell Laboratories Summer Research Program for Minorities and Women, 1983 participant.

[2] Beak, P.; Yamamoto, J.; Upton, C. J. *J. Org. Chem.* **1975**, *40*, 3052.

[3] Under appropriate conditions, carbophilic addition is observed with aliphatic thioketones, see: Ohno, A.; Nakamura, K.; Shizume, Y.; Oka, S. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 1003.

[4] The only documented examples of carbophilic attack on dithioesters involve allyl, benzyl, and propargyl Grignard reagents, see: Masson, S.; Saquet, M.; Thuillier, A. *Tetrahedron Lett.* **1976**, 4179; *Tetrahedron* **1977**, *33*, 2949. R. D. Miller and co-workers have observed carbophilic attack on some trithiocarbonates. (R. D. Miller, personal communication).

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Table I. Yields of Thiols from Dithio Esters and Diorganocuprates

			% yield[a] in ether (THF) cuprate precursor			
substrate	cuprate	product	CuCN	$CuBr\cdot SMe_2$	CuI	$(CuO_3SCF_3)_2C_6H_6$
1[b]	Me_2CuLi	3[c]	96 (47)	98 (87)	100 (86)	98 (84)
1	Bu_2CuLi	4[d]	93 (88)	92[e] (39)	87[e] (26)	91 (94)
1	Ph_2CuLi	5[f]	91 (44)	85[e] (67)	44 (66)	97[e] (39)
2[g]	Me_2CuLi	6[h]	66 (50)	88 (70)	84 (72)	88 (56)

[a] Yields were determined by GLC calibrated with authentic products and internal standards. Unless noted otherwise (see *e*) the reactants (1.0 mmol) were mixed at 0 °C and stirred at 0 °C for 1 h. All reactions were ~0.1 M. [b] Methyl dithiopropionate. [c] 2-Methyl-2-butanethiol. [d] 5-Ethyl-5-nonanethiol. [e] The reactants were mixed at −78 °C and then stirred at 0 °C for 1 h. [f] 1,1-Diphenyl-1-propanethiol. [g] Methyl dithiobenzoate. [h] α,α-Dimethylbenzyl mercaptan.

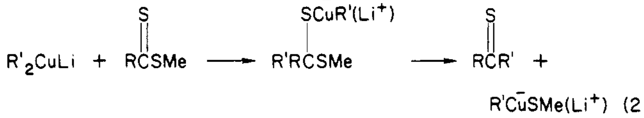
Table II. Yields of Thiols from Dithio Esters and Magnesium Organocuprates

			% yield[a]	
substrate	Grignard	product	stoich.	catalytic
1	MeMgBr	3	85	96
1	BuMgBr	4	16	80
1	PhMgBr	5	77	83
2	MeMgBr	6	71	23

[a] See note *a* of Table I.

transfer mechanism has been proposed for the reaction of organocuprates with α,β-unsaturated ketones,[6] and we note that Cu(I) changes the selectivity of Li and Mg reagents toward dithio esters (from thiophilic to carbophilic attack) just as it changes the selectivity of these reagents toward α-enones (from 1,2- to 1,4-addition). We chose 1 for study because its reduction potential (−1.43 to −1.78V, SCE)[7] is in the range of α-enone reduction potentials (−1.4 to −2.3V) noted by House for the successful conjugate addition of organocuprates.[6] The reduction potential of 2 (−1.11 to −1.34V, SCE)[7] is above that noted for conjugate addition. Clearly, the reduction potential of the substrate is not the only factor determining reactivity. We believe complexation between dithio ester and Cu(I) to be important in this reaction, so that electron transfer, if it does occur, is an "inner sphere" process. Alternatively, complexation of S by Cu could activate the C=S bond to direct nucleophilic attack at C. Thiocarbonyl S–Cu(I) bonding has been well-characterized crystallographically.[8]

Whether it is due to electron transfer or direct nucleophilic attack, the first step involves the carbophilic addition of R′ to the dithio ester followed by the loss of methanethiolate from the tetrahedral intermediate to generate the thioketone and a (methylthio)cuprate (eq 2). Reaction



$$R'_2CuLi + RC(=S)SMe \longrightarrow R'RC(S\overset{-}{Cu}R'(Li^+))SMe \longrightarrow RC(=S)R' + R'\overset{-}{Cu}SMe(Li^+) \quad (2)$$

of the thioketone with the (methylthio)cuprate then completes the process, except for the hydrolysis step. Posner and co-workers have shown than (phenylthio)- and (*tert*-butylthio)cuprates are highly reactive,[9] and we find the same is true of (methylthio)cuprates. Thus, 2.0 equiv of MeCu(SMe)Li converts 2 to 6 in virtually quantitative yield (vide supra). In addition, thiobenzophenone (7) is converted to 5 by either EtCu(SMe)Li (95%) or Et_2CuLi from any of the precursors studied. These experiments and the observation of "carbophilic–thiophilic" products (vide supra) establish the plausibility of (Cu-bound) thioketones as intermediates.

In summary, the reaction of organocuprates with dithio esters proceeds via a novel sequence of carbophilic additions. Furthermore, considering the high yields obtained and the fact that two C–C bonds are formed in a single step, this new reaction appears synthetically promising as well as mechanistically interesting.

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Supplementary Material Available: Experimental details for 5-ethyl-5-nonanethiol, a representative example (1 page). Ordering information is given on any current masthead page.

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Carbene and Silicon Routes toward a Simple Nitrile Ylide. Spectroscopic, Kinetic, and Chemical Characterization

Summary: The generation and characterization of methyl nitrile ylide photochemically by addition of singlet methylene to acetonitrile and chemically from a silylthioimidate and subsequent dipolar cycloaddition are carried out.

Sir: One of the more interesting members of the 1,3-dipole family is the nitrile ylides.[1–5] Although a variety of methods are available for the preparation of aryl-substituted nitrile ylides,[6–9] these techniques are not generally suitable for the synthesis of simple alkyl-substituted systems. In searching for alternate ways to form these dipoles, we have discovered two new and potentially general routes for nitrile ylide formation. Generation of an intermediate

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