THE JOURNAL OF Organic Chemistry

VOLUME 52, NUMBER 10

MAY 15, 1987

Organocuprates Containing Dimethyl Sulfoxide Anion as a Nontransferable Ligand

Carl R. Johnson* and Daljit S. Dhanoa

Department of Chemistry, Wayne State University, Detroit, Michigan 48202

Received October 14, 1986

Mixed homocuprates [$(MeSOCH_2CuR)Li$] and [$(MeSOCH_2CuR)Li(LiCN)$] in which the anion of dimethyl sulfoxide acts as a nontransferable ligand are readily prepared from $MeSOCH_2Li$, alkyl- or aryllithium reagents, and Cu(I) salts. These novel cuprates are useful in the conversions of acid chlorides to ketones, conjugate additions to α,β-unsaturated ketones, S_N2' reactions with allylic or propargylic acetates and epoxides, and coupling reactions with primary iodides and tosylates. All of these reactions proceed with selective transfer of the ligand R. From the points of view of cost, availability, and lack of interference with product isolation, the Me_2SO anion is an ideal nontransferable ligand.

Organocuprates are widely utilized reagents for the production of carbon–carbon bonds.[1-4] The popularity of these reagents in synthesis is attributable to their high regio-, stereo-, and chemoselective reactivity. In the use of classical homocuprates (R_2CuLi) often one of the R ligands is sacrificed. This drawback becomes serious when the R group to be transferred is a valuable one. This problem has led to the development of mixed organocuprates (R_rR_tCuLi) in which only one of the copper ligands (R_t) is transferred, the retained ligand R_r being expendable.[5] Several types of nontransferable ligands have been developed. The first report was by Corey[6] on the use of n-$PrC{\equiv}C^-$ as a nontransferable ligand. Other such ligands that have found use in mixed organocuprates are $(MeOC(Me)_2C{\equiv}C^-$,[7] t-$BuC{\equiv}C^-$,[8] $Me_2NCH_2C{\equiv}C^-$,[9] PhS^-,[10] t-BuO^-,[10] Ph_2P^-,[11] $(c\text{-}C_6H_{11})_2N^-$,[11] and (2-thienyl)$^-$.[12]

In a preliminary report we have described a new class of mixed homocuprates containing sulfonyl-stablized carbanions (e.g., $MeSO_2CH_2^-$) as nontransferable ligands.[13] The stimulus for this earlier and the present work is our hypothesis that the order of transferability of ligands from copper was related to the pK_a of the conjugate acid of the ligand. (The hypothesis has its origins in the well-known lack of tranfer of alkynyl ligands and the more facile transfer of higher alkyl ligands compared to methyl, phenyl, and vinyl). If this concept is valid heteroatom-stabilized carbanions should be less readily transferred in cuprate reactions than simple alkyl and aryl anions. From the points of view of cost, availability and ease of product isolation the anion derived from dimethyl sulfoxide (Me_2SO) seemed to be an ideal candidate. There follows a description of the preparation and reactions of mixed homocuprates [$(MeSOCH_2CuR)Li$] (1) and [[$MeSOCH_2Cu(CN)R]Li_2$] (2), termed, for discussion purposes, Me_2SO cuprates and Me_2SO cyanocuprates.

Results and Discussion

Me_2SO cuprates were readily prepared in situ by the sequential treatment of Me_2SO with n-BuLi followed by CuI to give [(methylsulfinyl)methyl]copper and then 1 equiv of organolithium (RLi) at −78 °C. The resulting

(1) Posner, G. H. *An Introduction to Synthesis using Organocopper Reagents*; Wiley: New York, 1980.
(2) Normant, J. F.; Alexakis, A. In *Current Trends in Organic Synthesis*; Nozaki, H., Ed.; Pergamon Press: New York, 1983; pp 291–302.
(3) Lipshutz, B. H.; Wilhelm, R. S.; Kozlowski, J. A. *Tetrahedron* **1984**, *40*, 5005.
(4) Taylor, R. J. K. *Synthesis* **1985**, 364.
(5) Other methods for the efficient utilization of a transferable group (R_t) include the use of RCu·BF (Yammamoto, Y.; Maruyama, J. *J. Am. Chem. Soc.* **1978**, *100*, 3240); RCu·n-Bu_3P (Suzuki, M.; Yanagisawa, A.; Noyori, R. *J. Am. Chem. Soc.* **1985**, *107*, 3348); and RCu·(1,5-cyclooctadiene) (Leyendecker, F.; Jesser, F. *Tetrahedron Lett.* **1980**, *21*, 1311).
(6) Corey, E. J.; Beames, D. J. *J. Am. Chem. Soc.* **1972**, *94*, 7210.
(7) Corey, E. J.; Floyd, D. M.; Lipshutz, B. H. *J. Org. Chem.* **1978**, *43*, 3418.
(8) House, H. O; Umen, M. J. *J. Org. Chem.* **1973**, *38*, 3893.
(9) Ledlie, D. B.; Miller, G. *J. Org. Chem.* **1979**, *44*, 1006.
(10) Posner, G. H.; Whitten, C. E.; Sterling, J. *J. Am. Chem. Soc.* **1973**, *95*, 7788.
(11) Bertz, S. H.; Dabbagh, G.; Villacorta, G. M. *J. Am. Chem. Soc.* **1982**, *104*, 5824.
(12) (a) Lipshutz, B. H.; Kozlowski, J. A.; Parker, D. A.; Nguyen, S. L.; McCarthy, K. E. *J. Organomet. Chem.* **1985**, *285*, 437. (b) Malmberg, H.; Nilsson, M.; Ullenius, C. *Tetrahedron Lett.* **1982**, *23*, 3823.
(13) Johnson, C. R.; dhanoa, D. S. *J. Chem. Soc., Chem. Commun*, **1982**, 358.

0022-3263/87/1952-1885$01.50/0

Table I. Reactions of "Me_2SO Cuprates" with Acid Chlorides

$$Li(CH_3SOCH_2CuR) + R'COCl \xrightarrow[-78\ °C,\ ca.\ 1\ h]{THF} R'COR$$

cuprate, R =	acid chloride, R′ =	isolated yield ketone (%)
Me	Ph	92
n-Bu	Ph	90
t-Bu	Ph	92
Me	(*E*)-PhCH=CH	95
n-Bu	(*E*)-PhCH=CH	94
t-Bu	(*E*)-PhCH=CH	85
sec-Bu	(*E*)-PhCH=CH	82
i-Pr	(*E*)-PhCH=CH	72
Ph	(*E*)-PhCH=CH	92
Me	(*E*)-MeCH=CH	90
n-Bu	(*E*)-MeCH=CH	92
t-Bu	(*E*)-MeCH=CH	78
Me	(*E*)-Me_2C=CHCH=CH	90

mixture was allowed to warm to −20 to 0 °C for a short period to ensure completion of formation of the mixed cuprate (eq 1).[14] The cuprate solution was recooled to −78 °C before use.

$$CH_3SCH_3 \xrightarrow[2)\ CuI]{1)\ n\text{-BuLi}} CH_3SCH_2Cu \xrightarrow{RLi} Li(CH_3SCH_2CuR) \quad (1)$$

1

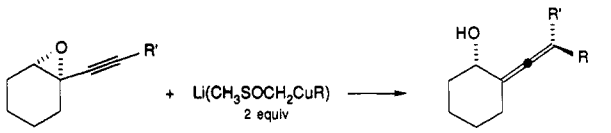
Me_2SO cuprates react with a wide variety of substrates typically reactive with cuprates in addition and substitution reactions. The byproduct, Me_2SO, does not pose any problem in product isolation as it is completely removed by water during aqueous workup.

Reagent 1 (R = *n*-Bu) underwent smooth conjugate additions to 2-cyclohexenone and *trans*-benzalacetophenone to produce the corresponding β-substituted ketones in yields of 96% and 83%, respectively. These yields are comparable or better than those reported by using other mixed organocuprates.[6-13]

Reactions of cuprates 1 with benzoyl chloride at −78 °C resulted in clean displacement of chloride to afford the corresponding ketones in excellent yields. Without competition from 1,4-addition, *trans*-cinnamoyl chloride and *trans*-crotonyl chloride underwent conversion to the corresponding unsaturated ketones upon treatment with Me_2SO cuprates (Table I).

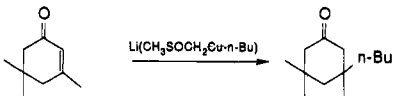
One of the most effective and extensively studied reactions for the regio- and stereoselective alkylation of allylic compounds is the coupling of lithium organocuprates with allylic acetates—a reaction that proceeds via antiselective S_N2' displacement of the acetate group.[15-17] Treatment of 3-acetoxy-3,7-dimethyl-1,6-octadiene (linalyl acetate) with cuprate 1 (R = Me or *t*-bu) in THF produced

Table II. Preparation of 2-Ethenylidenecyclohexanol



substrate, R′ =	cuprate, R =	conditions	solvent	product yield (%)
H	Me	−78 °C, 1 h; 0 °C, 0.5 h	EtOEt	78
H	*n*-Bu	−78 °C, 10 min; 0 °C, 0.5 h	EtOEt	85
H	*t*-Bu	−78 °C, 1 h; 0 °C, 0.25 h	THF	95
H	Ph	−78 °C, 1 h; 0 °C, 1 h	THF	80
Me	*t*-Bu	0 °C, 1 h	THF	90
Ph	Me	−20 °C, 1 h; 0 °C, 1 h	EtOEt	93
Ph	*n*-Bu	−78 °C, 1 h; 0 °C, 0.5 h	EtOEt	94
Ph	*t*-Bu	−78 °C, 4 h; 0 °C, 1 h	THF	92

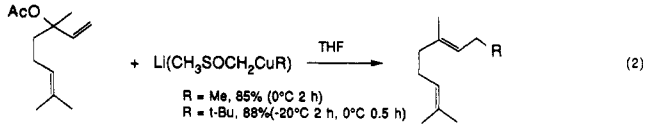
Table III. Effect of $BF_3 \cdot Et_2O$ on the Reactivity of $Li(CH_3SOCH_2Cu\text{-}n\text{-}Bu)$



equiv of cuprate	solvent[a]	reactn condns[c]	ratio of BF_3/cuprate	yield (%)
1.03	EtOEt	−78 °C, 1 h; −25 °C, 3 h 0 °C, 0.5 h; rt, 0.25 h	no BF_3	22
2.3	EtOEt	−78 °C, 3 h; −20 °C, 2 h 0 °C, 0.5 h	no BF_3	78
2.5	EtOEt	−78 °C, 0.2 h	1/1	100[b]
2.7	THF	−78 °C, 1 h	no BF_3	0
2.3	THF	−78 °C, 1 h, −30 °C, 3 h 0 °C, 1 h	no BF_3	22
2.7	THF	−78 °C, 1 h, −30 °C, 3 h 0 °C, 1 h	no BF_3	34
2.5	THF	−78 °C, 1 h	2/1	89

[a] All reactions were run at concentrations of 0.2 M. [b] Determined by VPC. [c] rt = room temperature.

(6*E*)-2,6-dimethyl-2,6-nonadiene or (6*E*)-2,6,9,9-tetramethyl-2,6-decadiene (eq 2) without contamination with



(2)

the *Z* isomers to any detectable extent by ^1H NMR analysis. Cuprate 1 (R = Me) failed to react with (2*E*)-1-acetoxy-3,7-dimethyl-2,6-octadiene (geranyl acetate) in THF, indicating a propensity of these cuprates to react selectively with unhindered allylic acetates.

The ring opening of epoxides by lithium diorganocuprates has been shown to be a highly effective.[18,19] The regio- and stereochemical course of such reactions with vinyl epoxides is well-documented.[20-22] In general, vinyl epoxides undergo anti-S_N2' attack by lithium organo-

(14) ($MeSOCH_2CuR$)Li is used to represent the stochiometric and not the structural composition of Me_2SO cuprates. For recent studies on the structure of organocuprates in solution, see: Lipshutz, B. H.; Kozlowski, J. A.; Breneman, C. M. *J. Am. Chem. Soc.* **1985**, *107*, 3197.

(15) For a review on nucleophilic and organometallic displacement reactions of allylic substrates, see: Magid, R. M. *Tetrahedron* **1980**, *36*, 1901.

(16) (a) Corey, E. J.; Boaz, N. W. *Tetrahedron Lett.* **1984**, *25*, 3063. (b) Goering, H. L.; Kanter, S. S. *J. Org. Chem.* **1984**, *49*, 422 and previous papers in this series. (c) Schmuff, N. R.; Trost, B. M. *J. Org. Chem.* **1983**, *48*, 1404. (d) Fleming, I.; Terrett, N. K. *Tetrahedron Lett.* **1983**, *24*, 4151. (e) Still, W. C. *J. Am. Chem. Soc.* **1979**, *101*, 2493. (f) Mychajlowskij, W.; Chan, T. H. *Tetrahedron Lett.* **1976**, 4439. (g) Anderson, R. J.; Henrick, C. A.; Siddall, J. B.; Zurfluh, R. *J. Am. Chem. Soc.* **1972**, *94*, 5379. (h) Anderson, R. J.; Henrick, C. A.; Siddall, J. B. *J. Am. Chem. Soc.* **1970**, *92*, 735. (i) Rona, P.; Tokes, L.; Trenble, J.; Crabbe', P. *J. Chem. Soc. D.* **1969**, 43.

(17) Levisalles, J.; Rudler-Chanvin, M. Rudler, H. *J. Organomet. Chem.* 1977, *136*, 103.

(18) Johnson, C. R.; Herr, R. W.; Wieland, D. M. *J. Org. Chem.* **1973**, *38*, 4263.

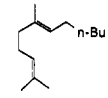
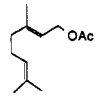
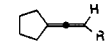
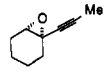
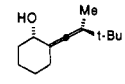
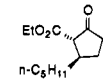
(19) (a) Herr, R. W.; Widland, D. M.; Johnson, C. R. *J. Am. Chem. Soc.* **1970**, *92*, 3813. (b) Herr, R. W.; Johnson, C. R. *J. Am. Chem. Soc.* **1970**, *92*, 4979. (c) Wieland, D. M.; Johnson, C. R. *J. Am. Chem. Soc.* **1971**, *93*, 3047. (d) Anderson, R. J. *J. Am. Chem. Soc.* **1970**, *92*, 4978. (e) Lipshutz, B. H.; Wilhelm, R. S.; Kozlowski, J. A.; Parker, D. *J. Org. Chem.* **1984**, *49*, 3928.

(20) (a) Marino, J. P.; Floyd, D. M. *Tetrahedron Lett.* **1979**, 675. (b) Marino, J. P.; Hatanaka, N. *J. Org. Chem.* **1979**, *44*, 4467. (c) Marino, J. P.; Abe, H. *Synthesis* **1980**, *11*, 872. (d) Marino, J. P.; Abe, H. *J. Am. Chem. Soc.* **1981**, *103*, 2907. (f) Marino, J. P.; Kelly, M. G. *J. Org. Chem.* **1981**, *46*, 4389.

(21) Ziegler, F. E.; Cady, M. A. *J. Org. Chem.* **1981**, *46*, 122.

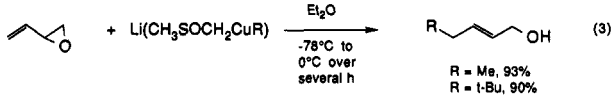
(22) Cahiez, C.; Alexakis, A.; Normant, J. F. *Synthesis* **1978**, 528.

Table IV. Reactions of "Me_2SO Cyanocuprates", $Li_2[CH_3SOCH_2Cu(CN)R]$

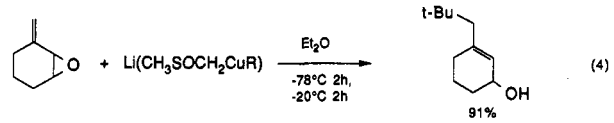
substrate	cuprate, R =	equiv	conditions (in Et_2O)	product	yield (%)
PhCOCl	*sec*-Bu	1.2	−78 °C, 0.5 h	PhCO-s-Bu	95
n-$C_8H_{17}I$	*n*-Bu	1.1	−78 °C, 1 h[a]	n-$C_{12}H_{26}$	90
	Me	2.4	0 °C, 8 h		63[b]
	n-Bu	1.02	−78 °C, 1 h; −25 °C, 4 h		67[b]
	n-Bu	2.2	−78 °C, 3 h; 0 °C, 1 h		95[b]
	*n*-Bu	1.1	−78 °C, 5 min; 0 °C, 1 h		45
	*n*-Bu	1.1	−78 °C, 0.5 h; 0 °C, 2 h		30
	*n*-Bu	1.1	−78 °C, 1 h; 0 °C, 1 h		92
	*t*-Bu	1.1	−78 °C, 1 h; 0 °C, 0.5 h		97
	t-Bu	2.5	−78 °C, 0.5 h; −20 °sC, 0.5 h		99
	*n*-Bu	1.1	−78 °C, 5 min; −20 °C, 2 h; 0 °C, 2 h		41

[a] In THF. [b] VPC yield.

cuprates. Examples of reactions of vinyl epoxides with cuprates 1 are shown in eq 3 and 4.

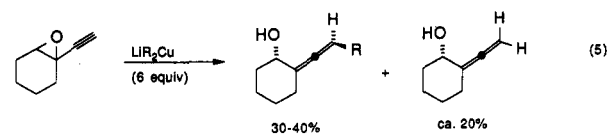


(3)



(4)

Although numerous methods for the preparation of allenes have been recorded, general methods for the synthesis of α-hydroxyallenes are scarce[23] despite their presence in a number of natural substances and potential use in replacing allylic and acetylenic alcohols in pharmaceuticals. Among the reports[22,24] on the production of α-hydroxyallenes using ring opening of α-acetylenic epoxides by cuprates, only one describes reactions involving cyclic substrates.[24a] In this earlier study (eq 5) a large excess of cuprate was employed; a significant amount of reduction byproduct was observed. The high propensity of Me_2SO



(5)

cuprates to attack vinyl epoxides and allylic acetates in an S_N2' manner prompted our investigation of the reactions of cuprates 1 with alkynyl epoxides. The desired hydroxyallenes were produced in excellent yields (Table II). The stereochemical assignments have been made on the basis of literature evidence for the preferential anti-S_N2' stereochemical pathway for the reaction of organocopper reagents with proparglyic substrates to give allenes.[24,25]

Me_2SO cuprates undergo coupling reactions with primary tosylates and iodides cleanly and in high yields. Treatment of *n*-octyl tosylate in diethyl ether with 1 (R = Me) at 0 °C gave *n*-nonane in 95% yield. The coupling reaction of *n*-BuI with 1 (R = *n*-Bu) gave *n*-octane (98%).

Recent reports[26,27] on the improved reactivity of organocuprates in the presence of boron trifluoride etherate suggested an examination of the effect of this promoter on the reactivity of Me_2SO cuprates. For this study the addition of 1 (R = *n*-Bu) to the sluggish substrate 3,5,5-trimethyl-2-cyclohexen-1-one (isophorone) was chosen. The results, summarized in Table III, indicate that BF_3 is an effective catalyst and that diethyl ether, as anticipated, is a more effective reaction medium than THF. The necessity for use of excess cuprate in these systems limits the utility of the procedure.

Organocuprates prepared from cuprous cyanide often display different and typically higher reactivity than their counterparts derived from cuprous halides. We have examined the preparation and reactions of Me_2SO cyanocuprates. These new cuprates were prepared by mixing [(methylsulfinyl)methyl]lithium with cuprous cyanide in diethyl ether or THF followed by the slow addition of RLi. Reagents $[[MeSOCH_2Cu(CN)R]Li_2]$ (2) thus prepared participate in the typical reactions of organocuprates in good to excellent yields with exclusive transfer of the R ligand. The efficiency and economy of these cuprates is illustrated by their high-yield reactions with the various

(23) (a) Keck, G. E.; Webb, R. R. II *Tetrahedron Lett.* **1982**, *23*, 3051. (b) Pappalardo, P.; Ehlinger; Magnus, P. *Tetrahedron Lett.* **1982**, *23*, 3051. (c) Clinet, J.-C.; Linstrumell, G. *Synthesis* **1981**, 875.

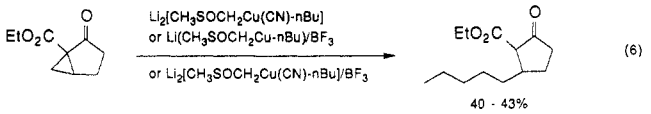
(24) (a) Ortiz de Montellano, P. R. *J. Chem. Soc., Chem. Commun.* **1973**, 709. (b) Vermeer, P.; Meijer, J.; Graaf, C.; Schreurs, H. *Recl. Trav. Chim. Pays-Bas* **1974**, *93*, 46. (c) Kleijn, H.; Meijer, J.; Overbeck, G. C.; Vermeer, P. *Recl. Trav. Chim. Pays-Bas* **1982**, *101*, 97. (d) Doutheau, A.; Saba, A.; Gore, J. *Tetrahedron Lett.* **1982**, *23*, 2461. (e) Oehlschlager, A. C.; Czyzewska, E. *Tetrahedron Lett.* **1983**, *24*, 5587.

(25) Elsevier, C. J.; Meijer, J.; Westmijze, H.; Vermeer, P.; Vaan Dijck, L. A. *J. Chem. Soc., Chem. Commun.* **1982**, 84.

(26) For Lewis acid mediated reactions of organocuprates, see: Yamamoto, Y.; Yamamoto, S.; Yatagai, H.; Ishihara, Y.; Maruyama, K. *J. Org. Chem.* **1982**, *47*, 119. Ibuka, T.; Tabushi, E. *J. Chem. Soc., Chem. Commun.* **1982**, 703. Smith, A. B., III.; Jerris, P. J. *J. Am. Chem. Soc.* **1981**, *103*, 194.

(27) (a) Ghrib, A.; Alexakis, A.; Normant, J. F. *Tetrahedron Lett.* **1984**, *25*, 3075, 3079, and 3083. (b) Ito, Y.; Imai, H.; Matsura, T.; Saegusa, T. *Tetrahedron Lett.* **1984**, *25*, 3091. (c) Lipshutz, B. H.; Parker, D. A.; Kozlowski, J. A.; Nguyen, S. L. *Tetrahedron Lett.* **1984**, *25*, 5959.

substrates given in Table IV. The Me_2SO cyanocuprates prepared from CuCN seem to be more reactive than the corresponding Me_2SO cuprates prepared from CuI. In additions (absence of BF_3) to 3,5,5-trimethyl-2-cyclohexen-1-one, the adduct, 3-butyl-3,5,5-trimethylcyclohexanone, was obtained in 20% and 78% yields, respectively, with 1 and 2.3 equiv of $(MeSOCH_2Cu\text{-}n\text{-}Bu)Li$ whereas the corresponding yields using $[[MeSOCH_2Cu(CN)n\text{-}Bu]Li_2]$ were 67% and 95%. The reaction of the electrophilic cyclopropane 1-(ethoxycarbonyl)bicyclo[3.1.0]hexan-2-one with various *n*-butyl/Me_2SO cuprates was examined; 2-(ethoxycarbonyl)-3-pentylcyclopentanone was obtained in yields of 40-43% (eq 6).



(6)

In summary, Me_2SO anion is an effective nontransferable ligand in organocuprate chemistry. The ready availability, cost, and water solubility of Me_2SO are attractive features.

Experimental Section

n-Butyllithium was obtained from Lithcoa as a solution in hexane. Methyllithium in ether, *sec*-butyllithium in cyclohexane, and *tert*-butyllithium in pentane were obtained from Aldrich Chemical Company. Cuprous iodide was obtained from Fisher Scientific Co. and purified.[28] Cuprous cyanide was purchased from Alfa Products Co.

General Procedures for the Preparation and Reactions of "Me_2SO Cuprates" $[(MeSOCH_2CuR)Li]$ (1) and "Me_2SO Cyanocuprates" $[[MeSOCH_2Cu(CN)R]Li_2]$ (2). All reactions were run on a 1.5 to 4.0 mmol scale in 0.2 to 0.25 M solutions of **1** or **2**. The lithio anion of dimethyl sulfoxide (Me_2SO) was generated as a white slurry in diethyl ether or a solution in tetrahydrofuran (THF) by treatment of Me_2SO with *n*-BuLi (1 equiv) at 0 °C for 15 min. (A crystal of triphenylmethane was occasionally added as an indicator and *n*-BuLi was added until a slight pink coloration persisted.) The mixture containing CH_3SOCH_2Li was tranferred to a slurry of CuI or CuCN (1 equiv of 0.5 to 1 M in diethyl ether or THF) at −78 °C via cannla or syringe. To ensure complete transference of CH_3SOCH_2Li, the flask was rinsed with solvent (1 to 2 mL) and the washing transferred. The mixture was warmed to 0 °C and stirred for 5 to 15 min. (In the case of CuI in THF, a yellow green solution was obtained at this point. In the case of CuI in diethyl ether an off-yellow slurry was obtained. With CuCN in either solvent a light green casted slurry was formed.) The resulting mixture was cooled to −78 °C and 1 equiv of organolithium reagent was added. The mixture was allowed to warm to 0 °C for cuprates with R = Me, *n*-Bu and Ph and to −20 °C for cuprates with R = *i*-Pr, *sec*-Bu, and *t*-Bu to ensure complete formation of the reagent. (The cuprates thus formed by the addition of RLi generally exhibited increased solubility but in many cases insoluble material remained. The exact state of solubility and color of the reaction mixture at this point did not seem to have much effect on the final results of the reactions with various substrates.) The mixture was cooled to −78 °C and an ether or THF solution of the substrate was added to the cuprate mixture with a syringe. The reaction mixture was maintained at the desired temperature for an appropriate period. The progress of the reaction was monitored by thin layer chromatography. Upon completion, a saturated, aqueous solution of ammonium chloride containing 10% ammonium hydroxide was poured into the reaction flask. The mixture was stirred for 10 to 15 min and suction filtered through Celite. The filter cake was washed with ether or dichloromethane and the aqueous phase was extracted with the same solvent. The combined organic phases were dried over anhydrous magnesium sulfate, filtered, and concentrated on a rotary evaporator. The products were purified by flash chromatography (silica gel with hexane–EtOAc mixtures).

General Procedure for BF_3-Mediated Reactions of "Me_2SO Cuprates". The "Me_2SO cuprates" (**1** or **2**) were generated as described above. To the stirred solution of the reagent at −78 °C was added a 1 M solution of the substrate followed by the addition of boron trifluoride diethyl etherate (1 or 2 equiv) using a syringe. The reaction mixture was worked up as described above. The products were analyzed by VPC (15% Carbowax 20M on Chromosorb W, 45/60 mesh, 0.25 in. × 12 ft column) and/or were purified by flash chromatography.

Acknowledgment. This work was supported by a grant from the National Science Foundation.

Registry No. **1** (R = Me), 107454-37-5; **1** (R = Bu), 107454-38-6; **1** (R = *t*-Bu), 107473-11-0; **1** (R = *sec*-Bu), 107454-39-7; **1** (R = *i*-Pr), 107454-40-0; **1** (R = Ph), 107454-41-1; **2** (R = *sec*-Bu), 107454-42-2; **2** (R = Bu), 107454-43-3; **2** (R = Me), 107454-44-4; **2** (R = *t*-Bu), 107454-45-5; CuI, 7681-65-4; CuCN, 544-92-3; Me_2SO, 67-68-5; PhCOCl, 98-88-4; (*E*)-PhCH=COCl, 17082-09-6; (*E*)-MeCH=CHCOCl, 625-35-4; (*E*)-Me_2C=CHCH=COCl, 107442-27-3; PhCOMe, 98-86-2; PhCOBu, 1009-14-9; PhCOBu-*t*, 938-16-9; (*E*)-PhCH=CHCOMe, 1896-62-4; (*E*)-PhCH=CHCOBu, 41903-83-7; (*E*)-PhCH=CHCOBu-*t*, 29569-91-3; (*E*)-PhCH=CHCOBu-*sec*, 84319-68-6; (*E*)-PhCH=CHCOPr-*i*, 10596-48-2; (*E*)-PhCH=CHCOPh, 614-47-1; (*E*)-MeCH=CHCOMe, 3102-33-8; (*E*)-MeCH=CHCOBu, 22286-99-3; (*E*)-MeCH=CHCOBu-*σ*, 20971-19-1; (*E*)-Me_2C=CHCH=CHCOMe, 16647-04-4; BF_3, 7637-07-2; $n\text{-}C_8H_{17}I$, 629-27-6; $(CH_3)_2C$=CH-$(CH_2)_2C(CH_3)(OAc)CH$=CH_2, 115-95-7; (*E*)-$(CH_3)_2C$=CH-$(CH_2)_2C(CH_3)$=$CHCH_2OAc$, 105-87-3; PhCOBu-*sec*, 938-87-4; $n\text{-}C_{12}H_{26}$, 112-40-3; (*E*)-$(CH_3)_2C$=CH$(CH_2)_2C(CH_3)$=CH-$(CH_2)_4CH_3$, 62947-42-6; $(CH_3)_2C$=CH$(CH_2)_2C(CH_3)$(CH=C-$H_2)(CH_2)_3CH_3$, 69747-29-1; (*E*)-$(CH_3)_2C$=CH$(CH_2)_2C(CH_3)$=$CHCH_2CH_3$, 1690-45-5; (*E*)-$(CH_3)_2C$=CH$(CH_2)_2C(CH_3)$=$CHCH_2C(CH_3)_3$, 107442-39-7; (*E*)-CH_3CH_2CH=$CHCH_2OH$, 1576-96-1; (*E*)-$(CH_3)_3CCH_2CH$=$CHCH_2OH$, 107442-40-0; 1-ethynyl-7-oxabicyclo[4.1.0]heptane, 932-03-6; 1-propynyl-7-oxabicyclo[4.1.0]heptane, 59627-41-7; 1-(2-phenylethenyl)-7-oxabicyclo[4.1.0]heptane, 87955-56-4; (*R**,*R**)-2-propenylidene-1-cyclohexanol, 107442-28-4; (*R**,*R**)-2-hexenylidene-1-cyclohexanol, 107442-29-5; (*R**,*R**)-2-(3,3-dimethylbutenylidene)-1-cyclohexanol, 107442-30-8; (*R**,*R**)-2-(2-phenylethenylidene)-1-cyclohexanol, 107442-31-9; (*R**,*R**)-2-(2,3,3-trimethylbutenylidene)-1-cyclohexanol, 107442-32-0; (*R**,*S**)-2-(2-phenylpropenylidene)-1-cyclohexanol, 107442-33-1; (*R**,*S**)-2-(2-phenylhexenylidene)-1-cyclohexanol, 107442-34-2; (*R**,*S**)-2-(2-phenyl-3,3-dimethylbutenylidene-1-cyclohexanol, 107442-35-3; 3,5,5-trimethyl-2-cyclohexen-1-one, 78-59-1; 3-butyl-3,5,5-trimethylcyclohexanone, 41601-84-7; 1-acetoxy-1-ethynylcyclopentane, 36193-52-9; 2-(ethoxycarbonyl)-6-oxabicyclo[3.1.0]hexan-2-one, 89540-18-1; 3,3,5,5-tetramethylcyclohexanone, 14376-79-5; hexenylidenecyclopentane, 107442-36-4; (3,3-dimethylbutenylidene)cyclopentane, 107442-37-5; *trans*-1-carboethoxy-5-pentyl-2-cyclopentanone, 107442-38-6; ethenyloxirane, 930-22-3; 2-methylene-7-oxabicyclo[4.1.0]heptane, 104190-00-3; 3-(2,2-dimethylpropyl)-1-hydroxy-2-cyclohexene, 107442-41-1; 2-ethenylidenecyclohexanol, 50994-80-4; 1-(ethoxycarbonyl)-5-pentyl-2-cyclopentanone, 107442-42-2.

Supplementary Material Available: Details of substrate preparation and product characterization (7 pages). Ordering information is given on any current masthead page.

(28) Kauffman, G. B.; Teter, L. A. *Inorg. Synth.* **1963**, *7*, 9.