by distillation and the residue was found by gas chromatography to contain 79.5 g of n-butyl alcohol for a 15% yield based on butyl–boron bond, assuming a 100% yield of butyl alcohol from the two butoxy groups. Hence, the 15% yield is a minimum figure. The aqueous layer after extraction was acidified and the butylboronic acid was suction filtered and allowed to air dry. It had a weight of 40.5 g [mp 83–85° and, with pure material of mp 92° (Callery Chemical Co.), mmp 90–92°] for a 79.5% yield or 20.5% oxidation of the butyl–boron bond. On this basis the total butyl alcohol yield was 73%.

The above run was repeated at 0° for 11 hr and the butyl alcohol weight was 83.0 g for a 24.5% minimum yield assuming a 100% yield of butyl alcohol from the two butoxy groups. The total butyl alcohol yield was 74.9%.

Oxidation of Diethyl n-Butylboronate with Oxidized Triethylborane.—A solution of 10.0 g of triethylborane (0.10 mole) in 480 g of n-heptane was air oxidized as above at 0° for 82 min. The peroxide content at this point had reached 0.457 mole/mole of B. The air was shut off and nitrogen was passed through until

there was no further oxygen in the exit gas (<0.1% oxygen). A solution of 47.4 g of diethyl n-butylboronate (0.30 mole) in 50 g of n-heptane was added at 0° with stirring. The reaction mixture was slowly heated to 50° during 1 hr (peroxide content now 0.390 mole/mole of B) and then kept at 50° for 13 hr. The peroxide content had dropped to 0.254 mole of peroxide/mole of B for a total drop of 45% and 42% of this drop occurred during the first hour. The drop in peroxide content corresponds to about a 20 mole % yield of n-butyl alcohol from the diethyl n-butylboronate. After saponification of the oxidation reaction product, a yield of 2.2 g of butyl alcohol was found which corresponds to a 30 mole % yield based on the boronate ester.

Preparation and Reactions of Some Alkylthiomethyllithium Compounds

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The highly reactive complex comprised of n-butyllithium and N,N,N′,N′-tetramethylethylenediamine readily metalates dimethyl sulfide to give high yields of methylthiomethyllithium. The thiomethyllithium compound has been shown to be of value as an intermediate in the synthesis of carbon functionally substituted sulfides by its reactions to give $C_6H_5CH(OH)CH_2SCH_3$, n-$C_3H_7CH(OH)CH_2SCH_3$, $(CH_3)_3SiCH_2SCH_3$, $(C_6H_5)_2PCH_2SCH_3$, $P(CH_2SCH_3)_3$, and $CH_3SC_{11}H_{23}$. The reaction of the metalating complex with dialkyl sulfides containing β hydrogens resulted primarily in the formation of olefins.

As part of an extensive study of the reactions of organometallic compounds with weak organic acids, Gilman and co-workers, several years ago, investigated the reaction of n-butyllithium with methyl phenyl sulfide and ethyl phenyl sulfide in diethyl ether.[1] They established that, in contrast to methyl phenyl sulfide which underwent lateral metalation, ethyl phenyl sulfide was metalated on the aromatic ring to give o-lithiophenyl ethyl sulfide. Very recently, Corey and Seebach reported[2] a greatly improved procedure for the preparation of phenylthiomethyllithium which utilized n-butyllithium complexed with diazabicyclo-[2.2.2]octane as the metalating agent.

Surprisingly, no systematic attempt appears to have been made to extend the metalation of sulfur compounds to include the less reactive dialkyl sulfides. In view of the current interest in and widespread utilization of other sulfur-stabilized carbanions such as $R_2S^+CH_2^-$, $CH_3S(O)CH_2M$, and $R_2S^+(O)CH_2^-$, we have independently developed a method for the preparation of some alkylthiomethyllithium compounds[3] which parallels to some extent the method reported by Corey and Seebach for the preparation of phenylthiomethyllithium. Our method is particularly useful for the preparation of the parent compound, methylthiomethyllithium, CH_3SCH_2Li (I).

Results

Methylthiomethyllithium is readily obtained from the reaction of dimethyl sulfide with the potent metalating complex[4] comprised of equimolar quantities of n-butyllithium and N,N,N′,N′-tetramethylethylenediamine (TMEDA). The reaction is quite rapid at
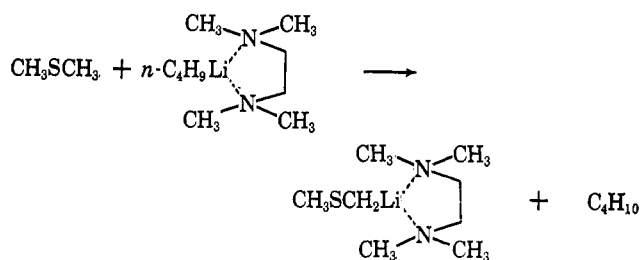
room temperature (essentially complete within 4 hr) and in hexane solvent, thereby obviating the necessity for using organometallic-sensitive ethers.[5]

Compound I has been characterized by H^1 nmr spectral analysis and by chemical derivatization with several reagents.

An H^1 nmr spectrum obtained on a benzene solution of I had signals centered at τ 7.92 (relative to benzene) for the methyl protons and 9.26 for the methylene protons. This corresponds to an internal chemical shift of 1.34 ppm which is somewhat smaller than that found for the related trimethylsilylmethyllithium compound.[6] The TMEDA portion of the complex was

(1) (a) H. Gilman and F. J. Webb, *J. Am. Chem. Soc.*, **71**, 4062 (1949). (b) For a comprehensive review of metalation reactions, see H. Gilman and J. W. Morton, Jr., *Org. Reactions*, **8**, 258 (1954).

(2) E. J. Corey and D. Seebach, *J. Org. Chem.*, **31**, 4097 (1966).

(3) The literature contains two reports describing attempted preparations of alkylthioalkylmetal compounds by nonmetalation routes: F. G. Bordwell and B. M. Pitt [*J. Am. Chem. Soc.*, **77**, 572 (1955)] were unsuccessful in their efforts to prepare CH₃SCH₂MgCl from chloromethyl methyl sulfide, and W. E. Parham, M. A. Kalnins, and D. R. Theissen [*J. Org. Chem.*, **27**, 2698 (1962)] met with limited success (*ca.* 5% yields) in the preparation of α-lithioalkyl hexyl sulfide by additions of organolithium compounds to n-hexyl vinyl sulfide.

(4) (a) G. G. Eberhardt and W. A. Butte, *ibid.*, **29**, 2928 (1964); (b) A. W. Langer, Jr., *Trans. N. Y. Acad. Sci., Ser. II*, **27**, 741 (1965); (c) D. J. Peterson, *J. Organometal. Chem.*, in press.

(5) See, for example, C. D. Broaddus, *J. Org. Chem.*, **30**, 4131 (1965), and references cited therein.

(6) G. E. Hartwell and T. L. Brown, *J. Am. Chem. Soc.*, **88**, 4625 (1966); J. W. Connolly and G. Urry, *norg. Chem.*, **2**, 645 (1963).

characterized by signals centered at τ 7.76 (N-methyl) and 7.52 (N-methylene).

Chemical proof for the existence of I was obtained by reaction of dimethyl sulfide–n-butyllithium–TMEDA metalation mixtures with benzaldehyde to give the known 2-hydroxy-2-phenethyl methyl sulfide[7] (II), with butyraldehyde to give 2-hydroxy-n-pentyl methyl sulfide (III), and with decyl bromide to give methyl undecyl sulfide (IV) (see Table I).

TABLE I
REACTIONS OF METHYLTHIOMETHYLLITHIUM

| Reactant	Product	Yield, %
C_6H_5CHO	$CH_3SCH_2CH(OH)C_6H_5$ (II)	84
n-C_3H_7CHO	$CH_3SCH_2CH(OH)C_3H_7$-n (III)	51
n-$C_{10}H_{21}Br$	$CH_3SC_{11}H_{23}$-n (IV)	~32
$(C_6H_5)_2PCl$	$CH_3SCH_2P(C_6H_5)_2$ (V)	50
$(CH_3O)_3P$	$P(CH_2SCH_3)_3$ (VI)	~10
$(C_6H_5O)_3P$	$P(CH_2SCH_3)_3$ (VI)	54
$(CH_3)_3SiCl$	$CH_3SCH_2Si(CH_3)_3$ (VII)	59

The synthetic versatility of I was further demonstrated by the successful synthesis of diphenyl(methylthiomethyl)phosphine (V), tris(methylthiomethyl)phosphine (VI), and (methylthiomethyl)trimethylsilane (VII) from reactions of I with chlorodiphenylphosphine, trimethyl- and triphenylphosphite, and chlorotrimethylsilane, respectively (see Table I).

The isolation of II in 84% yield demonstrates that I is the predominant product resulting from the reaction of dimethyl sulfide with the metalating complex. However, the identification of lithium methyl mercaptide as a minor product of the reaction provides evidence that some displacement accompanies the desired metalation reaction. The mercaptide, which coprecipitates from the reaction mixture with varying quantities of I, was identified by reaction with methyl iodide and decyl bromide to give trimethylsulfonium iodide and decyl methyl sulfide, respectively.

A more serious complicating side reaction occurred in reactions of the metalating complex with two model alkyl (>CH₃) methyl sulfides. Thus, in addition to the formation of the desired decylthiomethyllithium (18%), 1-decene was isolated in 38% yield from the reaction of decyl methyl sulfide with the n-BuLi–TMEDA complex. A similar reaction with 2-methylbutyl methyl sulfide afforded $ca.$ 42% of 2-methyl-1-butene.

Discussion

The preparation of methylthiomethyllithium by the metalation of dimethyl sulfide with the n-butyllithium–TMEDA complex represents the third and final member of a series of second-row element substituted carbanions so obtained. Thus, phosphinomethyllithium[4c] and silylmethyllithium[8] compounds have been similarly realized from reactions of the corresponding methylphosphorus and methylsilicon compounds. These three second-row elements, phosphorus, silicon, and sulfur, have the common feature of possessing d orbitals which appear to be capable of stabilizing adjacent

$$ZCH_2^-M^+ \longleftrightarrow [Z^-=CH_2]M^+$$
$$Z = R_3Si, R_2P, RS$$
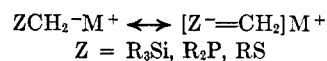
centers of high electrical demand, $i.e.$, d-orbital resonance stabilization.[9]

The relative rates of metalations of the three heteroatom-substituted methanes, $-SCH_3 >$ $>PCH_3 >$ $\gg SiCH_3$, are in the order expected from a consideration of the exchange data for similar compounds reported by Shatenshtein and co-workers[10] and Price and Sowa.[11] Thus, Shatenshtein reports that methyl sulfides exchange at rates of $ca.$ 5×10^3 as fast as the corresponding methylphosphines, while Price finds that methyl sulfides undergo extensive exchange under conditions where the corresponding methylsilanes are inert.

Although the magnitude and nature of sulfur stabilization of carbanions is debatable,[12] it is to be expected from a consideration of fundamental principles that divalent sulfur-substituted carbanions would be more reactive than their higher valence state counterparts, $i.e.$, carbanions such as $CH_3SOCH_2^-$ and $(CH_3)_2S^+CH_2^-$, enjoy considerable added stabilization, relative to I, because of favorable electrostatic factors and, probably, an increased d-orbital participation. The latter can be considered as resulting from a contraction of the relatively diffuse d orbitals by the increased effective electronegativity of the sulfur atom, relative to divalent sulfur, thereby creating a more effective overlap of the π orbitals.[13]

It should be noted that, in addition to possessing a chemical reactivity inherently greater than that of tri- and tetravalent sulfur substituted carbanions, I, as an intermediate in the synthesis of carbon functionally substituted organosulfur compounds, has the unique advantage of affording derivatives in the sulfide oxidation state. These derivatives can be converted readily to the corresponding sulfoxides, sulfones, and sulfonium compounds by established procedures. In contrast, considerable difficulty would be encountered in the conversion of the higher oxidation state derivatives to the sulfide state.

Experimental Section

General Methods.—All reactions involving organophosphines and organometallic compounds were conducted under an atmosphere of oxygen-free argon. The air-sensitive compounds were transferred by syringe techniques.

Nmr spectral determinations were made on Varian HA-100 (proton) and HR-60 (phosphorus) spectrometers operating at 100 and 24.3 Mc, respectively. The mass spectral data were obtained on Atlas CH-4 and SM1 spectrometers.

Preparation of Methylthiomethyllithium.—To 0.05 mole of the n-butyllithium–TMEDA complex, prepared by the dropwise addition of 5.8 g (0.05 mole) of TMEDA to 36 ml of 1.4 M (0.05 mole) n-butyllithium in hexane (temperature maintained below 20° by means of water bath), was added 3.0 g (0.05 mole) of dimethyl sulfide. Subsequent to $ca.$ 0.25 hr of stirring, a white precipitate composed of lithium methyl mercaptide and methylthiomethyllithium was observed to have formed. The reaction mixture was stirred for a minimum of 4 hr before utilization of I.

(7) G. A. Russell, E. Sabourin, and G. J. Mikol, $J. Org. Chem.$, **31**, 2854 (1966).

(8) D. J. Peterson, $J. Organometal. Chem.$, in press.

(9) C. C. Price and co-workers prefer to regard the stabilization of some sulfur-substituted carbanions as resulting from 3_{p}-$2_{p\pi}$ overlap rather than a $3d$-$2_{p\pi}$ bond: C. C. Price, M. Hori, T. Parasaran, and M. Polk, $J. Am. Chem. Soc.$, **85**, 2278 (1963).

(10) E. A. Yakovleva, E. N. Tsvetkov, D. I. Lobanov, M. I. Kabachnik, and A. I. Shatenshtein, $Tetrahedron Letters$, 4161 (1966), and references cited therein.

(11) C. C. Price and J. R. Sowa, Abstracts of the 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1965.

(12) G. Cilento, $Chem. Rev.$, **60**, 147 (1960).

(13) D. P. Craig and E. A. Magnusson, $J. Chem. Soc.$, 4895 (1956).

Identification of Lithium Methyl Mercaptide. Derivatization with Methyl Iodide.—The white precipitate obtained from the reaction of 0.1 mole of dimethyl sulfide with 0.1 mole of the metalating complex was washed with benzene to remove any I, dissolved in 30 ml of tetrahydrofuran, and treated with 5 ml of methyl iodide. The mixture was stirred overnight, and the 4.2 g of insoluble material that had formed was removed by filtration. A H^1 nmr spectral analysis revealed the material to be a combination of [(CH₃)₃N⁺CH₂]₂2I⁻, tetrahydrofuran, and trimethylsulfonium iodide, as evidenced by signals centered at τ 5.5 (CH₂N⁺≡) and 6.22 [(CH₃)₃N⁺], 5.82 (CH₂O) and 7.68 (CH₂-CH₂O), and 6.62 [(CH₃)₃S⁺], respectively, in D₂O. The chemical shifts for the two "onium" salts corresponded to those observed for authentic samples obtained from reactions of dimethyl sulfide and TMEDA with excesses of methyl iodide.

Reactions of Methylthiomethyllithium. A. With Decyl Bromide.—A mixture of I and lithium methyl mercaptide, obtained from the reaction of 0.05 mole of dimethyl sulfide with 0.05 mole of the metalating complex, was added slowly to 12.2 g (0.06 mole) of decyl bromide dissolved in 50 ml of tetrahydrofuran. The coupling reactions were mildly exothermic.

Subsequent to a total of 2 hr of stirring at room temperature, the reaction mixture was washed successively with 100 ml of 2 M ammonium chloride and dilute sulfuric acid. The organic layer was dried over sodium sulfate and concentrated. A glpc analysis of the concentrate revealed it to be a mixture of decyl bromide, decyl methyl sulfide, and methyl undecyl sulfide. The approximate area ratio of the two sulfur compounds was 1:9, respectively.

Distillation of the concentrate at reduced pressure (0.5 mm) gave the following fractions: (1) 1.51 g, bp 30°; (2) 1.34 g, bp 77–90°; (3) 3.24 g, bp 90–97°; and (4) 1.19 g, bp 97°. Gas phase chromatographic analysis revealed fraction 1 to be 84% 1-decene and 16% undecene; fraction 2 to be 59% decyl bromide, 15% decyl methyl sulfide, and 21% methyl undecyl sulfide; fraction 3 to be 12% decyl bromide, 14% decyl methyl sulfide, and 71% methyl undecyl sulfide; and fraction 4 to be 5% decyl methyl sulfide and 95% methyl undecyl sulfide. These fractions correspond to ca. 0.7 g (7%) of decyl methyl sulfide and ca. 3.9 g (32%) of methyl undecyl sulfide.

B. With Chlorodiphenylphosphine.—To a solution of 44 g (0.2 mole) of chlorodiphenylphosphine in 100 ml of tetrahydrofuran was added dropwise, over 1 hr, 0.2 mole of I. The reaction mixture was stirred for an additional 2 hr; it was then carefully hydrolyzed with 100 ml of 2.5 M ammonium chloride. The organic layer was dried, concentrated, and distilled under reduced pressure to give 24.4 g (50%) of V, bp 160–165° (0.5 mm). The V gave rise to a P³¹ nmr signal at +21 ppm in CHCl₃ and H^1 nmr signals centered at τ 2.8 (aromatic), 7.08 (methylene, doublet, J = 3 cps), and 8.02 (methyl, singlet) in the correct area ratios.

Treatment of 1 ml of V with an excess of methyl iodide in 20 ml of acetone gave 2.45 g of diphenylmethyl(methylthiomethyl)-phosphonium iodide, mp 160–162° (sealed capillary). A crystallization from an acetone–methanol mixed solvent gave the analytical sample, mp 161.5–163.5°. An nmr spectral analysis of the phosphonium salt in CDCl₃ gave the following data: H^1 signals centered at τ 2.18 (aromatic), 5.27 (methylene, doublet, J = 8 cps), 7.07 (≡⁺PCH₃, doublet, J = 13 cps), and 7.71 (SCH₃, singlet).

Anal. Calcd for C₁₅H₁₈IPS: C, 46.39; H, 4.64; I, 32.73. Found: C, 46.0; H, 4.4; I, 30.6.

C. With Chlorodiphenylphosphine and Subsequent Sulfurization.—To a solution of 15 g (0.07 mole) of chlorodiphenylphosphine in 15 ml of tetrahydrofuran was added dropwise 0.05 mole of I. The coupling reaction was quite exothermic. After the mixture was stirred for ca. 1 hr, 1.9 g (0.06 g-atom) of sulfur was introduced in four parts over a 0.5-hr period. Subsequent to an additional 0.5 hr of stirring, the reaction was poured into chilled, aqueous ammonium chloride (0.2 mole in 150 ml of H₂O). The organic layer was separated and combined with an ether extract of the aqueous layer. Concentration of the combined organic fractions yielded a viscous oil. A P³¹ nmr spectrum of the oil (in CHCl₃) exhibited a single signal at −41.6 ppm.

The oil was chromatographed on alumina. Hexane eluted only a small amount of sulfur. Benzene as solvent gave 6.98 g (50%) of diphenyl(methylthiomethyl)phosphine sulfide which on standing crystallized, mp 43–45°. An analytical sample, mp 82–84°, was obtained by crystallization of the compound from ethanol. An H^1 nmr spectral analysis of the compound in CDCl₃ confirmed the structure assignment: aromatic protons centered at τ 2.4,

methylene protons at 6.61 (doublet, J = 8 cps), and methyl protons at 7.95 (singlet) in the correct area ratios.

Anal. Calcd for C₁₄H₁₅PS₂: C, 60.43; H, 5.4; P, 11.15; S, 23.02; mol wt, 278.0353. Found: C, 60.7; H, 5.7; P, 10.85; S, 24.4; mol wt, 278.0344 (by a peak-matching technique).

Continued elution of the column with chloroform and methanol gave varying amounts of glassy materials that resisted characterization.

D. With Benzaldehyde.—To 6.36 g (0.06 mole) of benzaldehyde, dissolved in 30 ml of tetrahydrofuran and cooled by Dry Ice, 0.05 mole of I was added rapidly. Subsequent to the addition, the reaction mixture was allowed to warm to room temperature and stirring was continued for 1 hr. Aqueous ammonium chloride was added, and the organic layer which formed was separated, dried over sodium sulfate, concentrated, and distilled under vacuum to give 7.1 g (84%) of II, bp 100–102° (1 mm) [lit.[7] bp 92–95° (1 mm)]. Methylation of II gave the known[7] sulfonium iodide, mp 134–136°.

E. With Chlorotrimethylsilane.—To a solution of 10.8 g (0.1 mole) of chlorotrimethylsilane in 20 ml of tetrahydrofuran was added slowly 0.1 mole of I, resulting in a mildly exothermic reaction. After the addition, the reaction mixture was heated at reflux for 0.5 hr, cooled, and hydrolyzed with 200 ml of 2 M ammonium chloride. Work-up in the usual manner and distillation gave the following fractions: (1) 1.3 g, bp 50–130°; and (2) 6.67 g (49.6%) of VII, bp 135°. Fraction 1 was shown to contain ca. 90% (1.15 g) VII by gas chromatographic analysis. The total yield of VII was 59%.

An H^1 nmr spectral analysis of the compound confirmed the structure assignment: three singlets centered at τ (relative to internal CHCl₃) 7.95 (SCH₃), 8.35 (>SiCH₂S), and 9.97 [Si-(CH₃)₃] in the correct area ratios. A mass spectral analysis (70 ev) was also consistent with the structure assignment with intense parent peak at 134, intense M − 15 (methyl) peak, and a base peak at m/e 73.

A solution of 2.68 g (0.02 mole) of VII in 20 ml of acetone was treated with 5.7 g (0.04 mole) of methyl iodide to give 4.95 g of dimethyl(trimethylsilylmethyl)sulfonium iodide,[14] mp 100–104°. A crystallization from acetone gave an analytical sample, mp 105–107° (the melt was cloudy, apparently as a result of decomposition and formation of two liquid phases). An H^1 nmr spectrum of the sulfonium iodide in CDCl₃ was found to be in fair agreement with the reported spectrum in deuterioacetonitrile:[14] singlets centered at τ 6.94 [(CH₃)₂S⁺], and 7.08 [>SiCH₂S< relative to (CH₃)₃Si group which was assigned as 0 ppm[14]] in the correct area ratios.

Anal. Calcd for C₇H₁₇ISSi: C, 26.1; H, 6.15; I, 46.0; S, 11.6. Found: C, 25.6; H, 6.3; I, 44.3; S, 11.5.

F. With Butyrylaldehyde.—To a solution of 15.9 g (0.22 mole) of butyryladehyde in 100 ml of tetrahydrofuran, cooled to −30°, was added dropwise 0.2 mole of I. Subsequent to the complete addition, the reaction mixture was stirred at −60° for 1 hr, then allowed to warm to room temperature and stirred for 1 hr.

Hydrolysis with dilute, aqueous ammonium chloride and work-up in the usual manner gave 13.7 g (51%) of III, bp 45–49° (0.5 mm), n^{25}D 1.4716.

An H^1 nmr spectral analysis of the compound in CDCl₃ confirmed the structure assignment: signals centered at τ 6.3 (methine, unresolved complex multiplet), 7.42 (SCH₂, ABX pattern, J_{AB} = 13.5 cps, J_{AX} = 3.5 cps, J_{BX} = 8.5 cps), 7.9 (CH₃S, singlet), 8.52 (HOCCH₂CH₂, multiplet), and 9.04 (CCH₃, triplet) in the correct area ratios. The OH proton was masked by the methylene protons centered at τ 7.42.

Anal. Calcd for C₆H₁₄OS: C, 53.73; H, 10.45; S, 23.88; mol wt, 134. Found: C, 53.9; H, 10.5; S, 23.4; mol wt (mass spectral), 134.

A solution of 1.76 g (0.013 mole) of III in 10 ml of acetone was treated with 3.75 g (0.026 mole) of methyl iodide to give a quantitative yield of (2-hydroxypentyl)dimethylsulfonium iodide, mp 64–66°. An analytical sample was obtained by dissolving the sulfonium iodide in ethanol and adding ether until a small amount of insoluble oil formed. Rapid stirring at room temperature resulted in crystallization of 2.13 g (58%) of sulfonium iodide, mp 66–68°.

Anal. Calcd for C₇H₁₇IOS: C, 30.43; H, 6.16; I, 46.0; S, 11.56. Found: C, 30.2; H, 6.4; I, 45.1; S, 11.7.

An H^1 nmr spectrum of the compound confirmed the structure assignment.

(14) N. E. Miller, *Inorg. Chem.*, **4**, 1458 (1965); no melting point was reported.

G. With Trimethyl Phosphite.—To 6.2 g (0.05 mole) of trimethyl phosphite dissolved in 100 ml of tetrahydrofuran was added 0.2 mole of I over 0.25 hr. The resulting reaction was mildly exothermic. Subsequent to the complete addition, the reaction mixture was heated at gentle reflux for 1 hr. A Gilman Color Test I[15] was negative at this time.

The reaction mixture was then hydrolyzed with 200 ml of 1.5 M ammonium chloride. The organic layer was separated, dried over sodium sulfate, concentrated, and distilled to give 1.4 ml of a mixture boiling over the range 95–120° (0.1 mm). The mixture was shown by gas phase chromatography to contain *ca.* 60% of VI. The phosphine, for the purpose of analysis, was converted to the corresponding phosphine sulfide. An analytical sample of the sulfide was obtained by gas phase chromatography.

Anal. Calcd for $C_6H_{15}PS_4$: C, 29.26; H, 6.1; S, 52.02. Found: C, 29.0; H, 6.2; S, 51.3.

The structure assignment of tris(methylthiomethyl)phosphine sulfide was positively confirmed by spectral analysis: H^1 nmr signals centered at τ 6.93 (methylene, doublet, J = 6.8 cps), and 7.66 (methyl, singlet) in the correct area ratios and a mass spectrum of the material had an intense parent peak at m/e 245.9792 (by a peak matching technique) which corresponds closely to a calculated m/e of 245.9794.

H. With Triphenyl Phosphite.—To 31 g (0.1 mole) of triphenyl phosphite dissolved in 100 ml of tetrahydrofuran was added, over 0.5 hr, 0.3 mole of I. Subsequent to the complete addition, the reaction was heated at gentle reflux for 2 hr and then stirred over night at room temperature. Work-up of the reaction mixture as described above gave 11.2 g (52%) of VI, bp 120–126° (0.3 mm). The purity of this material was shown to be >98% by gas phase chromatographic analysis. An H^1 nmr spectrum of VI exhibited signals at τ 7.27 (>PCH_2, doublet, J = 4 cps) and 7.8 (SCH_3, singlet) in the correct area ratios. Also, the material gave tris(methylthiomethyl)phosphine sulfide (see above experiment) on treatment with sulfur.

Reaction of n-Decyl Methyl Sulfide with n-Butyllithium–TMEDA.—To a solution of 0.05 mole of the n-butyllithium–TMEDA complex there was added, at room temperature, 9.4 g (0.05 mole) of n-decyl methyl sulfide. During a total reaction time of 4 hr, a white precipitate formed.

The reaction mixture was then carbonated by pouring onto a Dry Ice–ether slurry and worked up by standard procedures. The neutral fraction was dried over sodium sulfate, concentrated, and distilled under reduced pressure to give 2.63 g (37.5%) of 1-decene, bp 66–70° (*ca.* 15 mm), as evidenced by infrared and gas phase chromatographic analysis.

The acid fraction on concentration gave 1.96 g (17%) of decylthioacetic acid, mp 48–50°. A crystallization from hexane gave the analytical sample, mp 51–53°.

(15) H. Gilman and F. Shulze, *J. Am. Chem. Soc.*, **47**, 2002 (1925).

Anal. Calcd for $C_{12}H_{24}O_2S$: C, 62.07; H, 10.35; S, 13.79. Found: C, 62.0; H, 10.6; S, 14.5.

The experimental neutralization equivalent of the acid was found to be 226 (theoretical, 232).

An H^1 nmr spectral analysis of the compound confirmed the structure assignment: signals centered at τ 0.1 (acid), 6.76 (SCH_2CO_2), 7.34 (CH_2CH_2S, triplet, J = 6 cps), 8.7 [SCH_2-$(CH_2)_8$], and 9.1 (CH_2CH_3, triplet) in the correct area ratios.

Reaction of (2-Methylbutyl)methyl Sulfide with n-Butyllithium–TMEDA.—The reactants, in equimolar ratios (0.05 mole), were stirred at room temperature for 18 hr. The small quantity of precipitate that formed during this time was recovered by filtration. The filtrate was then carefully quenched with D_2O with any gas evolved being passed through a solution of bromine in carbon tetrachloride.

The organic phase was separated and distilled (again evolved gas scrubbed by passing through a Br_2–CCl_4 trap) to give 1.26 g (10.7%) of partially deuterated starting olefin. A small quantity of the olefin was purified by glpc and shown by mass spectral analysis to contain 99.0% d_0 and 0.9% d_1.

The solvents from the preceding distillation were shaken with the Br_2–CCl_4 solution to remove any 2-methyl-1-butene. Subsequent to the destruction of excess bromine with aqueous sodium sulfite, the organic phase was distilled to give 9.8 g (42%) of 1,2-dibromo-2-methylbutane, bp 67–69° (*ca.* 15 mm), $n^{25}D$ 1.5049. An H^1 nmr spectral analysis confirmed the structure assignment: signals centered at τ 6.2 (singlet, CH_2Br), 8.1 (quartet, J = 7 cps, CH_3CH_2), 8.2 (singlet, $BrCCH_3$), and 8.95 (triplet, J = 7 cps, CH_3CH_2).

Anal. Calcd for $C_5H_{10}Br_2$: C, 26.09; H, 4.35; Br, 69.56. Found: C, 25.4; H, 4.6; Br, 70.1.

Reaction of Butylmagnesium Bromide with Ketones

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Addition of an ether solution of n-butylmagnesium bromide to acetone in ether gave n-butane (I) and n-butyldimethylcarbinol (II). When acetone was added to the Grignard reagent, a large amount of n-octane was produced along with I and II. Addition of methanol or acetic acid to the Grignard reagent also caused the formation of n-octane. The carbinol II was easily produced at the higher temperature as well as at the higher concentration of the Grignard reagent. A factor determining the reactivity of a ketone toward the Grignard reagent is the steric effect of the alkyl group of the ketone.

In the course of our study on the anionic polymerization of α,β-unsaturated carbonyl compounds with an organometallic catalyst, we noticed that, the lower the concentration of n-butyllithium was, the more significant were the changes that appeared in the reaction mode of the lithium alkyl toward the unsaturated carbonyl compounds.[1] A similar situation seems also

(1) N. Kawabata and T. Tsuruta, *Makromol. Chem.*, **86**, 231 (1965).

to be true for a reaction mode of Grignard reagent in such a small concentration range.

By adding an ether solution of n-butylmagnesium bromide to acetone in ether, there was observed the formation of n-butane, n-butyldimethylcarbinol and, sometimes, a very small amount of n-octane. The formation of n-butane was not due to the destruction of the Grignard reagent with the small quantity of water present in ether and acetone, since the concentration