Dipole-Stabilized Carbanions from Thioesters. Evidence for Stabilization by the Carbonyl Group

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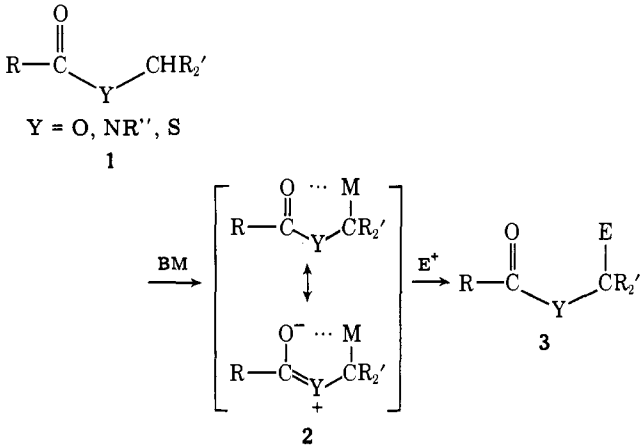
Abstract: Reactions are reported which establish that metalation can occur α to the sulfur of methyl and ethyl thioesters to give synthetically useful species. The methyl thiobenzoates **4a, 4b, 4c,** and methyl thiopivalate (**4d**) react with lithium 2,2,6,6-tetramethylpiperidide (LiTMP) in tetrahydrofuran at ambient temperature to give the corresponding dibenzoylmethanes, **5a, 5b, 5c,** and dipivaloylmethane (**5d**), respectively, in yields of 60–80%. Ethyl thiobenzoate (**6**) on reaction with LiTMP gives 23% methyldibenzoylmethane (**7**) at ambient temperature and 22% 2-thiobenzoylpropiophenone (**8**) at −98 °C. A double labeling experiment with **6** and **6**-d_{10} gives **8** and **16** consistent with the intermediacy of the dipole-stabilized species **12** and inconsistent with formation of the homoenolate **15**. Accordingly, the conversions of **4a–d** and **6** to the β-diketones are considered to proceed as shown in Scheme I. The isomerization of the vinylogous thioester **23** to 3-thia-*tert*-butylindanone (**24**) in 43% yield is suggested to involve the metalated intermediate **25**. Stable α-lithioalkyl thioesters, represented by **31**, are produced by metalation of methyl 2,4,6-triethylthiobenzoate (**27b**) and ethyl 2,4,6-triethylthiobenzoate (**28**) with butyllithiums at −78 and −98 °C. Reactions of the dipole-stabilized carbanions from **27b** and **28** with alkyl halides and with carbonyl compounds provide the expected adducts **32**. Conversions of some of these adducts to a primary thiol, a secondary thiol, a 2,3-disubstituted thiirane, and an olefin illustrate the synthetic potential of **31**. Evidence that the carbonyl group of the thioester provides significant thermodynamic stabilization for the formal carbanion **36** is provided by the observation that methyl 2,4,6-triisopropylthiobenzoate is completely metalated by thiomethylmethyllithium.

Carbanions which bear an α heteroatom warrant special attention as useful nucleophiles. Information about their formation, stability, and synthetic use is of continuing interest.

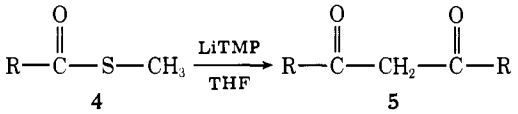
We have presented evidence that metalations can occur adjacent to oxygen, nitrogen, and sulfur when the heteroatom is conjugated to a carbonyl group and have suggested that such species should be considered formally dipole-stabilized carbanions.[1-3] Electrophilic substitution of these species is potentially very useful. A sequence in which the carbonyl group is initially added and subsequently removed from the heteroatom would provide the α-lithio alcohol, α-lithio amine, and α-lithio thiol synthons, respectively. The key steps of such a sequence are illustrated for the conversion of **1** to **3** via the intermediate **2**.



Preparations of the α-heteroatom organolithium reagents represented by **2** or reasonable analogues are known in a number of systems. Direct removal of a proton from a methyl group bonded to the oxygen of an ester,[1] to the nitrogen of an amide,[2] a thioamide,[4] or an imide,[5] or to the sulfur of a thioester,[2] a thiothiazoline,[6] a thiooxazoline,[7] a thioimidate,[8] a dithiocarbonate,[9] a dithiocarbamate,[6b] or an iminodithiocarbonate[10] have been reported. The lithiothiomethyl species **2**, Y = S, R_2' = H_2, produced by those metalations not only undergo the reactions expected for an organometallic but also have proven uniquely useful in the synthesis of optically active thiiranes and olefins from aldehydes and ketones,[7b,8,9] in the one-carbon homologation of primary halides to primary iodides,[11] and in the homologative conversion of a trialkylboron to primary alcohol.[12] The potentially more useful α-metalated ethyl derivatives of **2**, R_2 = H, CH_3, presently appear to be available only from the ester, amide, and thioester functions.[1,2,4-10] We now wish to report the results of our investigation of the formation, stability, and electrophilic substitutions of formally dipole-stabilized carbanions from methyl and ethyl thioesters.

Results and Discussion

Thioesters. Intermolecular Self-Trapping. The conversion of methyl thiobenzoate (**4a**) to dibenzoylmethane (**5a**) on reaction with lithium 2,2,6,6-tetramethylpiperidide (LiTMP) in tetrahydrofuran provided the first suggestion that a methyl thioester could be metalated adjacent to sulfur.[13] As shown in Table I, conversion of three methyl thiobenzoates, **4a–c**, and of methyl thiopivalate (**4d**) to the corresponding β-diketones, **5a–d**, proceeds in 60–82% yield. The use of the relatively nonnucleophilic LiTMP is important;[14,15] if lithium dicyclohexylamide is the base the yield of **5a** is 13% while no **5a** can be isolated from the reaction of **4a** with lithium diisopropylamide.



a, R = C_6H_5 c, R = p-ClC_6H_4
b, R = p-$CH_3OC_6H_4$ d, R = $(CH_3)_3C$

Reaction of ethyl thiobenzoate (**6**) gives methyldibenzoylmethane (**7**) in 23% yield, as well as 2-mercaptopropiophenone and thiobenzoic acid. The latter two products were identified by methylation of the acidic products of the reaction to 2-methylmercaptopropiophenone and methyl thiobenzoate in 10 and 6% yields, respectively, based on **6**. If the reaction of **6** is carried out at −98 °C, the only isolated product is 2-thiobenzoylpropiophenone (**8**) in 22% yield. Reaction of benzyl thiobenzoate (**9**) with LiTMP at ambient temperature provides deoxybenzoin (**10**) in 65% yield. Attempts to isolate thiobenzoin (**11**), the other expected product, were unsuccessful, al-

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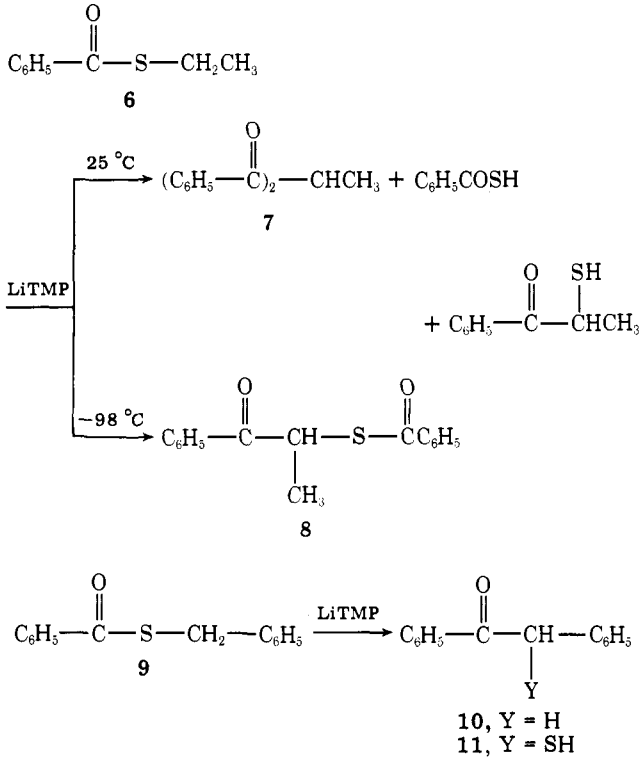
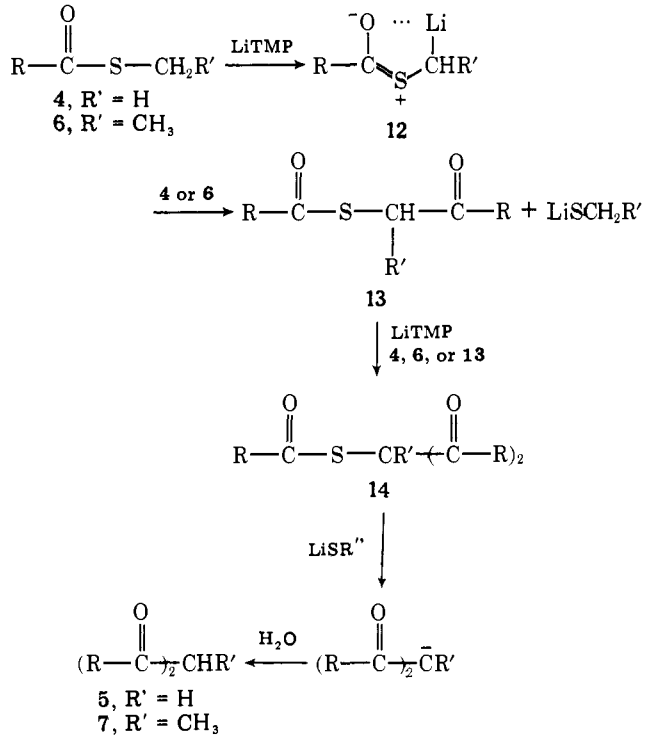
Table I. Formation of β-Diketones from Thioesters with Lithium 2,2,6,6-Tetramethylpiperidide

reactant	product	yield, %
4a	**5a**	78[a]
4b	**5b**	82
4c	**5c**	63
4d	**5d**	60 (79)[b]

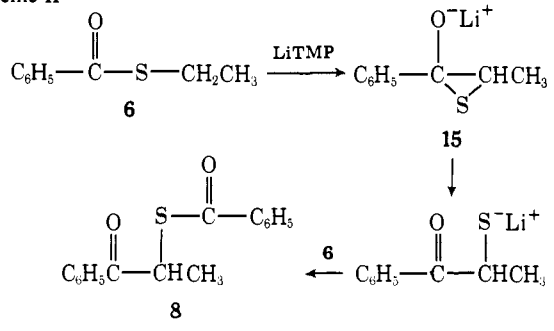
[a] The yield is 13% with lithium dicyclohexylamide, and <1% with lithium diisopropylamide or with lithium 2,2,6,6-tetramethylpiperidide in the presence of dicyclohexyl-18-crown-6. [b] Yield by GLC.



Scheme I



Scheme II



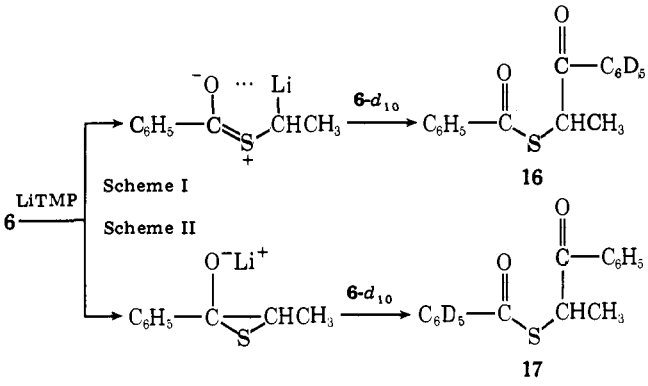
though signals attributable to this material could be observed in the NMR spectrum of the crude product.

The initial step in the conversion of the thioesters **4** to the β-diketones **5** is considered to be formation of the formally dipole-stabilized carbanion **12.** As shown in Scheme I, that intermediate may undergo benzoylation by the reactant thioester to form **13** which is benzoylated again to provide **14.** Reaction of **14** with mercaptide anion gives the β-diketoenolate which is converted to the β-diketone **5** on aqueous workup. Analogy for the carbon–sulfur bond cleavage of **14** is found in the report that α-thiolalkyl ketones are smoothly reduced to ketones by thiolate anions.[16]

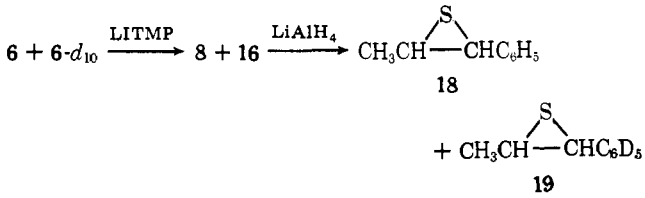
The intermediacy of **13** is consistent with the fact that phenacyl thiobenzoate (**13**, R = C_6H_5; R' = H) gives **5a** in 84% yield on treatment with LiTMP and with the isolation of **8** (**13**, R = C_6H_5; R' = CH_3) from the reaction of **6** at −98 °C. The possibility that **8** is a precursor to 2-mercaptopropiophenone is supported by the NMR observation of the latter, along with **6**, when **8** is treated with 1 equiv of lithioethyl mercaptide. The formation of thiobenzoic acid from **6** may result from hydrolysis of the acyl disulfide which can be envisioned to arise on reaction of **14** with mercaptide. Deoxybenzoin is considered to be formed from **9** by desulfurization of **13** (R = R' = C_6H_5). In that case, the phenyl group of **13** (R = R' = C_6H_5) may be considered to inhibit the conversion to **14** or to accelerate the reduction to **10.** Complexation of the lithium ion to the carbonyl group illustrated in **12** is included because if the reaction of **4a** is attempted with LiTMP in the presence of dicyclohexyl-18-crown-6 or if bromomagnesium 2,2,6,6-tetramethylpiperidide is the base, less than 1% **5a** is formed. A similar cation effect, also attributed to complexation, has been suggested in the formation of dipole-stabilized carbanions from amides.[17] It should be noted that the steps proposed in Scheme I could occur in a different sequence; desulfurization at the stage of **13** followed by reaction of the enolate thus produced with thioester to give the β-diketone has not been ruled out. However, that sequence would not appear to rationalize the formation of **10** as well as the sequence shown.

Although the intermediacy of **12** is indicated by the mechanism of Scheme I, another process can be written for the initial step which does not involve a dipole-stabilized carbanion. As shown in Scheme II for the conversion of **6** to **8,** proton removal, concerted with the formation of **15** followed by ring opening and benzoylation to give **8,** could also then lead to the observed products. Such a direct formation of **15** finds analogy in the formation of homoenolate ions.[18] It is also possible that **15** could be formed from **12.**

The distinction between Schemes I and II can be made by a double labeling experiment. If the reaction of **6** at −98 °C is carried out in the presence of **6**-d_{10}, and the expected large kinetic isotope effect discriminates effectively against metalation of the latter,[18] the products should be **8** and **16** if the mechanism of Scheme I is followed or **8** and **17** if the mechanism proceeds as suggested in Scheme II. In practice the distinction between **16** and **17** could not be made directly;[20] conversion of the product thioesters to 2-methyl-3-phenyl-

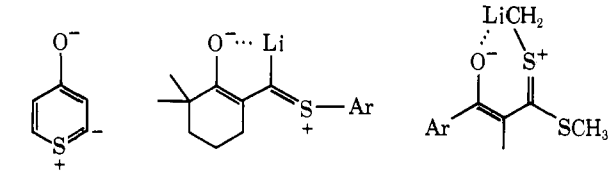


thiirane (**18**) and benzyl alcohol with lithium aluminum hydride was required prior to mass spectra analysis.[21] The products of the reaction of an equimolar mixture of **6** and **6**-d_{10} with LiTMP at −98 °C, followed by the conversion of **8** to the thiirane, were shown by mass spectrometry to be a 42:58 mixture of **18** and **19**. Moreover, the mass spectrum of the



benzyl alcohol also produced showed there to be less than 5% benzyl alcohol-d_5 present. The reaction products then are at least 95% **8** and **16** and the reaction does not follow the path of Scheme II nor does **12** rearrange to **15**. Accordingly the mechanism for the formation of the β-diketones **5** and **7** from the thioesters **4** and **6** is considered to involve intermolecular trapping of the formally dipole-stabilized carbanion **12** as shown in Scheme I.

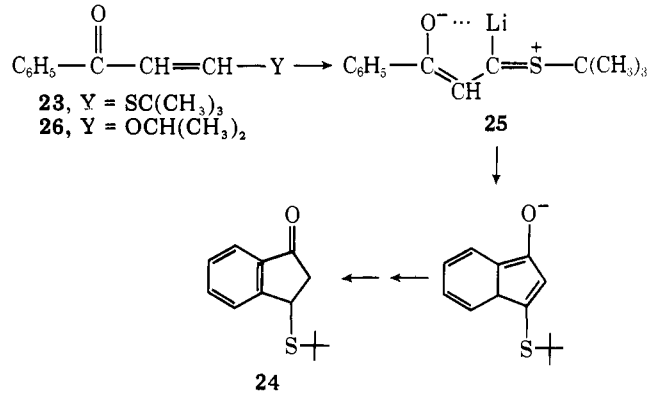
A Vinylogous Thioester. Intramolecular Trapping. Formal carbanion formation by abstraction of a proton adjacent to sulfur of some vinylogous thioesters has been observed. Examples include the species **20**,[22] **21**,[23] and **22**,[24] which are



represented for the present as dipole-stabilized species. The latter two are particularly useful synthetically.[23,24]

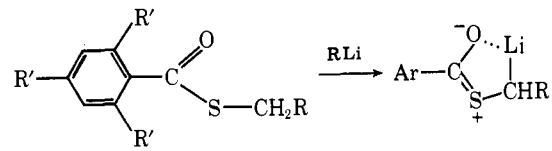
We have observed that the vinylogous sulfide **23** undergoes cyclization to the indanone **24** on reaction with LiTMP in 41% yield. The structure of the product was established by its analytical and spectral properties and by reduction to indan. Recovery of starting material showed that the *Z* isomer of **23** remained from an initial *Z* and *E* mixture. The mechanism we suggest for this conversion involves cyclization of the formally dipole-stabilized intermediate *E*-**25** followed by a 1,5-sigmatropic hydride shift. An alternative process which could be envisioned to be initiated by ortho metalation of the ring has not been ruled out unambiguously,[19,25] However, **26** does not give a product corresponding to **24** on treatment with LiTMP under similar conditions,[26]

Thioesters. Trapping by Subsequently Added Electrophiles. The intermediacy of the formally dipole-stabilized carbanion **12** from the thioesters **4** and **6** as shown in Scheme I establishes that such species can be formed, do not rapidly rearrange intramolecularly, and can be trapped intermolecularly. However, the self-trapping which gives the β-diketones **5** and **7** is clearly

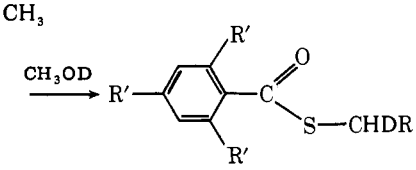


of limited synthetic value. Consideration of Scheme I suggests that if the reaction of **12** with thioester could be suppressed, that intermediate might be stable and trappable by subsequently added electrophiles. In fact, we have found that steric hindrance of nucleophilic addition to the carbonyl successfully accomplishes that end.[2]

Reaction of the methyl 2,4,6-trialkylthiobenzoates, **27a-d**, or ethyl 2,4,6-triethylthiobenzoate (**28**) with 1.3-3.1 equiv of *n*-butyllithium or *sec*-butyllithium-tetramethylethylenediamine (TMEDA) at −78 or −98 °C for 2 h followed by quenching with methanol-*d* gives the deuterated esters **29a**, **29b**, **29c**, **29d**, and **30** in the yield indicated in Table II. The site



27a, R' = CH$_3$; R = H
27b, R' = C$_2$H$_5$; R = H
27c, R' = CH(CH$_3$)$_2$; R = H
27d, R' = C(CH$_3$)$_3$; R = H
28, R' = C$_2$H$_5$; R = CH$_3$



29a, R' = CH$_3$; R = H
29b, R' = C$_2$H$_5$; R = H
29c, R' = CH(CH$_3$)$_2$; R = H
29d, R' = C(CH$_3$)$_3$; R = H
30, R' = C$_2$H$_5$; R = CH$_3$

and extent of deuterium incorporation were determined by NMR spectroscopy and mass spectrometry, respectively. Comparison of the acylium ions of the respective starting materials gives the deuterium incorporation in the ring and at the benzyl position and shows that greater than 98% of the deuterium incorporation has taken place at the thiomethyl group.[27] The apparent dideuteration of the methyl observed for **27d** is probably an artifact resulting from proton transfers which occur during quenching after some of the carbanion has been monodeuterated. Clearly metalation of **27a-d** occurs overwhelmingly adjacent to sulfur and stable organolithium reagents **31** can be prepared.

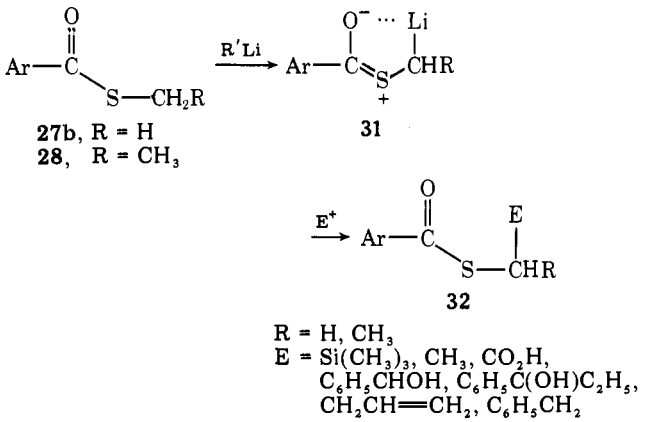
The reactions of **31** from methyl 2,4,6-triethylthiobenzoate (**27b**) and from ethyl 2,4,6-triethylthiobenzoate (**28**) with a variety of electrophiles to give the products **32** shown in Scheme III and Table III illustrate more general trapping of these organolithium reagents. The product yields in the table are for isolated pure materials. The sequence with the ethyl thioester **28** is especially significant because attempts to generate similar α-thio species in related systems have not been successful.[6b,7,8]

Table II. Deuteration of Lithiomethyl Thioesters and an α-Lithioethyl Thioester by Methanol-d^a

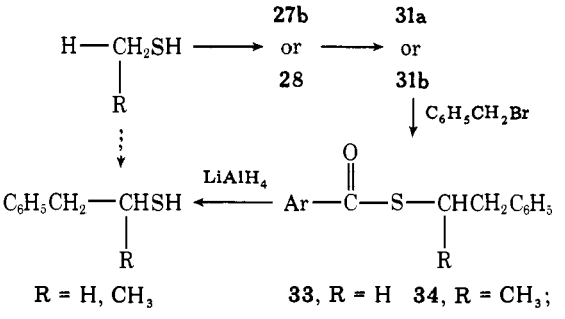
thioester	base	temp, °C	d_0, %	d_1, %	d_2, %	d_{acyl}, %[b]	yield, %
27a	*n*-C_4H_9Li	−78	0.5	98.2	1.3	0.5	86
27b	*n*-C_4H_9Li	−78[c]	0.7	99.3	0	0.4	87
27c	*n*-C_4H_9Li	−78	0.3	99.7	0	0	85
27c	*sec*-C_4H_9Li/TMEDA	−78[c]	0	95.2	4.8	0	90
27d	*sec*-C_4H_9Li/TMEDA	−78	12.2	75.3	12.5	0	87
28	*n*-C_4H_9Li	−98	81.6	18.4	0	0	90
28	*sec*-C_4H_9Li/TMEDA	−98	1.3	97.7	1.0	1.6	89

[a] Determined by mass spectrometry. The error is ±1%. [b] The total amount of deuterium incorporation in the ring and benzyl positions. [c] CD_3OD was used.

Scheme III



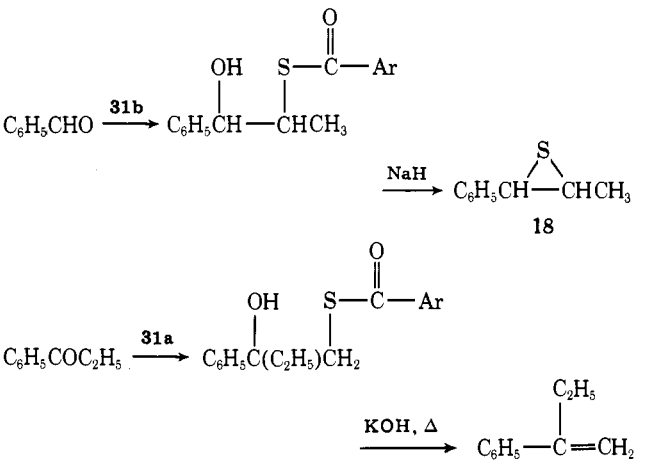
Scheme III provides the key steps for utilization of the lithiomethanethiol and α-lithioethanethiol synthons. For example, the thioesters produced from trapping **31** with benzyl bromide, **33** and **34**, can be reduced with lithium aluminum hydride to the primary and secondary thiols 2-phenylethanethiol in 77% yield and to 3-phenylpropane-2-thiol in 91% yield, respectively. Since the thioester precursors **27b** and **28** are synthesized from methanethiol and ethanethiol, respectively, these constitute overall electrophilic substitutions at a proton adjacent to a thiol sulfur.



Reaction of the β-hydroxy thioester **32**, R = CH_3; E = C_6H_5CHOH, with sodium hydride provides an epimeric mixture of 2-methyl-3-phenylthiiranes (**18**) in 78% yield. In this case the α-lithioethanethiol synthon has been used to deliver that function to a carbonyl carbon prior to a subsequent benzoyl migration and ring closure.[6b,7,8,21] This approach to the synthesis of 2,3-disubstituted thiiranes complements that for 2-substituted thiiranes reported by Hirai,[8] Johnson,[6b] and Meyers.[7] This formation of **18** also provided authentic material for comparison with the thiirane formed by lithium aluminum hydride reduction of **8** and **16** in the double labeling experiment (vide supra). A thiirane is also presumed to be involved in the reaction of the β-hydroxy thioester **32**, R = CH_3; E = $C_6H_5C(OH)C_2H_5$, to α-ethylstyrene with potassium hydroxide in 58% yield.[6b,7,8] The formation and trapping of **31**

Table III. Products **32** from the Reactions of the α-Lithiothioalkyl Thioesters **31** from Methyl 2,4,6-Triethylthiobenzoate and from Ethyl 2,4,6-Triethylthiobenzoate with Electrophiles

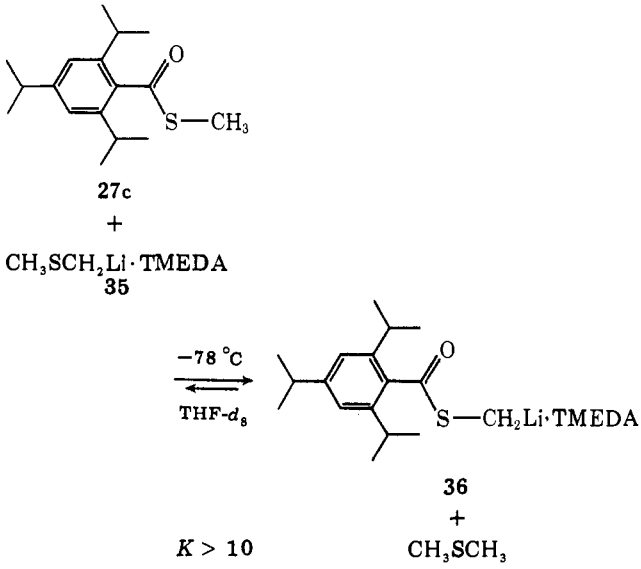
reactant ArCOSC-H_2R	base	temp, °C	electrophile	yield, % ArCOS-CH(E)R
27b	*n*-C_4H_9Li	−78	$(CH_3)_3SiCl$	45
27b	*n*-C_4H_9Li	−78	CH_3I	86
27b	*n*-C_4H_9Li	−78	CO_2	51
27b	*n*-C_4H_9Li	−78	C_6H_5CHO	80
27b	*n*-C_4H_9Li	−78	CH_2=CH-CH_2Br	82
27b	*n*-C_4H_9Li	−78	C_6H_5CO-C_2H_5	74
27b	*n*-C_4H_9Li	−78	$C_6H_5CH_2Br$	78
28	*sec*-C_4H_9Li/TMEDA	−98	C_6H_5CHO	91
28	*sec*-C_4H_9Li/TMEDA	−98	$C_6H_5CH_2Br$	72



firmly established the existence of α-metalated thioesters and provides useful reagents which should be further developed.

Dipole Stabilization of a Lithiomethyl Thioester. The mechanism of stabilization of a negative charge on a carbon adjacent to sulfur has been discussed in terms of delocalization by d-orbital expansion or some other electron acceptance of sulfur, or by polarization.[28-30] Although the operation of dipole stabilization for the metalated thioesters **12**, **25**, and **31** has been presumed in this work, the fact that methyl thioethers readily undergo metalation[31] raises the question as to whether the carbonyl group plays a role in the formation or stability of these species. We are now able to report that the presence of a carbonyl bonded to the lithiothiomethyl group does provide substantial stabilization relative to that of a lithiomethyl thioether.

The reaction of methyl 2,4,6-triisopropylthiobenzoate (**27c**) with thiomethylmethyllithium-TMEDA (**35**) at −78 °C in tetrahydrofuran-d_8 can be followed by ^1H NMR spectrosco-



py.[32] The signals of the lithiomethylene protons of **35** and the thiomethyl protons of **27c** at δ 0.48 and 2.47 ppm, respectively, are observed to decrease at the same rate over a period of 11 days and are replaced by a signal due to dimethyl sulfide at δ 2.07 ppm and a signal attributed to the metalated thioester **36** at δ 0.20 ppm. Addition of methanol-*d* and isolation of the monodeuterated thioester **29c** confirm that assignment.[33] Since no **35** could be observed prior to quenching, we estimate that the equilibrium favors **36** by at least an order of magnitude.

This equilibration experiment clearly establishes that the carbonyl group plays a role in providing thermodynamic stabilization of a lithiomethyl thioester group relative to a lithiomethyl thioether function. This result can be taken as evidence for the operation of dipole stabilization of a carbanion.[34] Whether this dipole stabilization is a direct effect, i.e., an inductive stabilization due to the adjacency of unlike charges, or an indirect effect, i.e., a contraction of d orbitals, an increased polarization, a reinforcement of a conjugation mechanism, or a complexation effect, cannot be answered at present. However, regardless of the source of the stabilization the generation and reaction of α-lithioalkyl thioesters would seem to be of both synthetic and mechanistic interest.

Experimental Section[35]

Materials. All solvents and starting materials from commercial sources were used without further purification except for tetrahydrofuran (THF), which was dried by distillation from sodium benzophenone ketyl, and tetramethylethylenediamine (TMEDA), which was dried by distillation from lithium aluminum hydride. All reactions involving the use of *n*-butyllithium, *sec*-butyllithium/TMEDA, or lithium 2,2,6,6-tetramethylpiperidide (LiTMP) were performed under a nitrogen atmosphere using equipment which had been oven dried. The activities of *n*-butyllithium (Ventron) and *sec*-butyllithium (Ventron) were determined by titration with *sec*-butyl alcohol in xylene using 1,10-phenanthroline as indicator.[36] Methyl thiobenzoate (**4a**), methyl *p*-methoxythiobenzoate[38] (**4b**), methyl *p*-chlorothiobenzoate[38] (**4c**), ethyl thiobenzoate (**6**), benzyl thiobenzoate[39] (**9**), and phenacyl thiobenzoate[40] (**13**, R = C_6H_5; R′ = H) were prepared by established methods or from excess mercaptan and the corresponding acid chloride. The melting point or boiling point, IR, and NMR spectra were consistent with the established structure.

Methyl thiopivalate (4d) was prepared from excess methyl mercaptan and pivaloyl chloride in diethyl ether containing pyridine in 71% yield: bp 142 °C; NMR ($CDCl_3$) δ 1.24 (s, 9, $C(CH_3)_3$), 2.24 (s, 3, SCH_3); IR (neat) 2980, 2960, 1690 (C=O), 1480, 1370, 1040, 980, 940 cm^{-1}; mass spectrum (70 eV) *m/e* (rel intensity) 132 (18), 89 (15), 85 (82), 57 (100), 56 (27), 47 (20), 41 (100), 39 (39), 29 (81).

Anal. Calcd for $C_6H_{12}OS$: C, 54.50; H, 9.15; S, 24.25. Found: C, 54.61; H, 9.23; S, 24.13.

Ethyl Thiobenzoate-d_{10} (6-d_{10}). Hydrogen sulfide was bubbled into a methanol solution of 6.6 g (100 mmol) of potassium hydroxide until the solution was no longer alkaline. The solution was cooled to 0 °C and 7.0 g (50 mmol) of freshly distilled benzoyl chloride-d_5 was added. The reaction mixture was allowed to stir for 2 h prior to the addition of 5.0 g (46 mmol) of ethyl bromide-d_5 and then stirred overnight. The solvent was removed in vacuo and the crude product dissolved in ether. Treatment with aqueous base and water gave an organic phase which was dried ($MgSO_4$), concentrated, and distilled. The colorless product was obtained in 91% yield: bp 82 °C (0.9 mm); IR (neat) 2290, 2230, 2140, 2070, 1665 (C=O), 1560, 1370, 1325, 1295, 1160, 1050, 1040, 1020, 960, 915, 860, 820 cm^{-1}; mass spectrum (10 eV) *m/e* (rel intensity 178 (2), 177 (3), 176 (30), 111 (8), 110 (100), 109 (4).

Anal. Calcd for $C_9D_{10}OS$: C, 61.34; S, 18.19. Found: C, 61.39; S, 18.41.

2-Thiomethylpropiophenone. The reaction mixture of 5.00 g (0.104 mol) of 50% oil dispersion of sodium hydride after petroleum ether washings and 13.96 g (0.104 mol) of propiophenone in THF was heated to reflux until hydrogen evolution ceased. The solution was cooled to room temperature prior to the addition of 240 g (2.55 mol) of methyl disulfide and the mixture stirred at reflux overnight. The THF was removed in vacuo and ether was added; the ethereal solution was washed five times with water and dried ($MgSO_4$). The ether and excess methyl disulfide were removed in vacuo leaving a dark orange solution which was vacuum distilled to give 14.7 g (79%) of a colorless liquid: bp 112-114 °C (1.8 mm); NMR ($CDCl_3$) δ 1.53 (d, 3, J = 7 Hz, CH_3CH), 1.93 (s, 3, SCH_3), 4.36 (q, 1, J = 7 Hz, CH_3CH), 7.38-7.70 (m, 3, ArH), 7.97-8.24 (m, 2, *o*-ArH); IR (neat) 3070, 2980, 2930, 1680 (C=O), 1600, 1583, 1450, 1338, 1238, 955 cm^{-1}; mass spectrum (70 eV) *m/e* (rel intensity) 180 (17), 134 (44), 105 (100), 77 (55), 75 (86), 51 (21).

Anal. Calcd for $C_{10}H_{12}OS$: C, 66.63; H, 6.71; S, 17.79. Found: C, 66.34; H, 6.72; S, 17.80.

2-Thiobenzoylpropiophenone (8). An ethereal solution of 5.00 g (23.5 mmol) of α-bromopropiophenone was added to an ethereal solution of 3.24 g (23.5 mmol) of thiobenzoic acid and 2.40 g (23.5 mmol) of triethylamine under a nitrogen atmosphere. After 4 h, the reaction mixture was washed with aqueous acid, aqueous base, and water and dried ($MgSO_4$). The ether was removed in vacuo to give 5.6 g (88%) of a colorless solid, mp 40-42 °C. The product was recrystallized from methanol: mp 42-43 °C; NMR ($CDCl_3$) δ 1.65 (d, 3, J = 7 Hz, $CHCH_3$), 5.57 (q, 1, J = 7 Hz, $CHCH_3$), 7.30-7.70 (m, 6, ArH), 7.90-8.25 (m, 4, *o*-ArH); IR (KBr) 1690 (C=O), 1660 (SC=O), 1595, 1580, 1450, 1330, 1300, 1220, 1175, 980, 960, 920, 795, 775, 705, 690, 650 cm^{-1}; mass spectrum (10 eV) *m/e* (rel intensity) 271 (1), 270 (5), 165 (3), 132 (5), 106 (8), 105 (100), 77 (3), 58 (2).

Anal. Calcd for $C_{16}H_{14}O_2S$: C, 71.08; H, 5.22; S, 11.86. Found: C, 70.88; H, 5.08; S, 11.96.

2-Thiobenzoylpropiophenone-d_5 was prepared from α-bromopropiophenone, thiobenzoic acid-d_5, and triethylamine as above for **8**: mp 42-43 °C; NMR ($CDCl_3$) δ 1.65 (d, 3, J = 7 Hz, $CHCH_3$), 5.57 (q, 1, J = 7 Hz, $CHCH_3$), 7.20-7.65 (m, 3, ArH), 7.82-8.18 (m, 2, *o*-ArH); IR (KBr) 1690 (C=O), 1660 (SC=O), 1600, 1450, 1375, 1330, 1300, 1215, 1170, 960, 920, 705 cm^{-1}; mass spectrum (10 eV) *m/e* (rel intensity) 276 (2), 275 (13), 170 (2), 165 (3), 136 (4), 132 (6), 111 (7), 110 (100), 106 (7), 105 (94), 82 (2), 77 (2), 71 (3), 43 (2).

Anal. Calcd for $C_{16}H_9D_5O_2S$: C, 69.79; S, 11.64. Found: C, 69.49; S, 11.87.

β-*tert*-Butylthiophenyl vinyl ketone (23) was prepared from 9.21 g (62.1 mmol) of benzoylacetaldehyde, 5.60 g (62.3 mmol) of *tert*-butyl mercaptan, and 0.010 g (10 mg) of *p*-toluenesulfonic acid in benzene at reflux for 3 h.[41] Vacuum distillation at 130-135 °C bath temperature and 0.3 Torr afforded 8.9 g (65%) of **23** as a mixture of *Z* and *E* isomers: NMR ($CDCl_3$) *Z* isomer, δ 1.42 (s, 9, CH_3), 7.10 (d, 1, =C*H*-, J = 10.0 Hz), 7.5-7.9 (m, 5, ArH), 7.58 (d, 1, =C*H*-, J = 10.0 Hz); *E* isomer, δ 1.45 (s, 9, CH_3), 7.08 (d, =C*H*-, J = 15.0 Hz), 7.5-7.9 (m, 5, ArH), 8.17 (d, =C*H*-, J = 15.0 Hz); IR (KBr) 1640 (C=O), 1600, 1580, 1545, 1525, 1460, 1370 cm^{-1}; mass spectrum (70 eV) *m/e* (rel intensity), 220 (8.7), 164 (34.6), 163 (100), 131 (3.2), 105 (18.8), 77 (29.3), 57 (74.4), 41 (25.5), 29 (20.4).

Anal. Calcd for $C_{13}H_{16}OS$: C, 70.89; H, 7.32; S, 14.55. Found: C, 70.97; H, 7.49; S, 14.63.

Methyl 2,4,6-Trimethylthiobenzoate (27a). Excess methyl mercaptan was condensed into an ethereal solution of 32.2 g (0.182 mol) of 2,4,6-trimethylbenzoyl chloride[42] and 20.0 g (0.198 mol) of triethylamine. The reaction mixture was allowed to stir overnight and

extractive workup gave 31.3 g (88%) of a solid which was purified by vacuum distillation: mp 46–47 °C; bp 130–131 °C (6.2 mm); NMR ($CDCl_3$) δ 2.22 (s, 9, $ArCH_3$), 2.40 (s, 3, SCH_3), 6.73 (s, 2, ArH); IR (KBr) 1670 (C=O), 1610, 1215, 1140, 965, 890, 855, 630 cm^{-1}; mass spectrum (10 eV) *m/e* (rel intensity) 194 (4), 148 (11), 147 (100), 120 (1), 119 (10).

Anal. Calcd for $C_{11}H_{14}OS$: C, 68.00; H, 7.26; S, 16.50. Found: C, 68.02; H, 7.05; S, 16.30.

Methyl 2,4,6-Triethylthiobenzoate (27b). Reaction of 49 g (0.57 mol) of potassium methylmercaptide in condensed methyl mercaptan at 0 °C with 77.7 g (0.350 mol) of 2,4,6-triethylbenzoyl chloride[43] afforded **27b**. The reaction mixture was stirred for 6 h under a nitrogen atmosphere at 0 °C, allowed to warm to room temperature, and dissolved in ether. The ethereal solution was washed with aqueous base and then water, dried ($MgSO_4$), and concentrated. The product was purified by vacuum distillation to give 65.2 g (80%) of a colorless liquid: bp 106–107 °C (0.03 mm); NMR ($CDCl_3$) δ 1.20 (t, 9, J = 7 Hz, $ArCH_2CH_3$), 2.43 (s, 3, SCH_3), 2.61 (q, 6, J = 7 Hz, $ArCH_2CH_3$), 6.90 (s, 2, ArH); IR (neat) 2980, 2945, 2890, 1685 (C=O), 1610, 1465, 1210, 1147, 921, 875 cm^{-1}; mass spectrum (10 eV) *m/e* (rel intensity) 236 (1), 191 (1), 190 (4), 189 (100), 161 (1).

Anal. Calcd for $C_{14}H_{20}OS$: C, 71.14; H, 8.53; S, 13.56. Found: C, 71.39; H, 8.47; S, 13.65.

Ethyl 2,4,6-Triethylthiobenzoate (28). A solution of 10.8 g (108 mmol) of potassium ethylmercaptide in ethyl mercaptan at 0 °C and 15.1 g (67.2 mmol) of 2,4,6-triethylbenzoyl chloride was stirred overnight and dissolved in ether. The ethereal solution was washed with aqueous base and then water, dried ($MgSO_4$), and concentrated. The product was purified by vacuum distillation to give 13.6 g (81%) of a colorless liquid: bp 105–106 °C (0.15 mm); NMR ($CDCl_3$) δ 1.20 (t, 9, J = 7 Hz, $ArCH_2CH_3$), 1.35 (t, 3, J = 7 Hz, SCH_2CH_3), 2.63 (q, 2, J = 7 Hz, *p*-$ArCH_2CH_3$), 2.65 (q, 4, J = 7 Hz, *o*-$ArCH_2CH_3$), 3.03 (q, 2, J = 7 Hz, SCH_2CH_3), 6.89 (s, 2, ArH); IR (neat) 2980, 2940, 2880, 1675 (C=O), 1610, 1460, 1375, 1265, 1210, 1145, 920, 870 cm^{-1}; mass spectrum (70 eV) *m/e* (rel intensity) 250 (2), 190 (14), 189 (100), 133 (5), 117 (5), 115 (5), 105 (12), 91 (7).

Anal. Calcd for $C_{15}H_{22}OS$: C, 71.95; H, 8.86; S, 12.80. Found: C, 71.98; H, 8.71; S, 12.85.

Methyl 2,4,6-Triisopropylthiobenzoate (27c). A solution of 12.9 g (0.150 mol) of potassium methylmercaptide in condensed methyl mercaptan and 26.7 g (0.100 mol) of 2,4,6-triisopropylbenzoyl chloride[44] was stirred for 12 h under a nitrogen atmosphere at 0 °C, allowed to warm to room temperature, and dissolved in ether. The ethereal solution was washed with aqueous base and then water, dried ($MgSO_4$), and concentrated. The product was purified by sublimation at 70 °C (0.01 mm) to give 24.8 g (89%) of a colorless solid: mp 97–97.5 °C; NMR ($CDCl_3$) δ 1.22 (d, 18, J = 7 Hz, $ArCH(CH_3)_2$), 2.45 (s, 3, SCH_3), 2.92 (m, 3, J = 7 Hz, $ArCH(CH_3)_2$), 6.98 (s, 2, ArH); IR (KBr) 2970, 2037, 2880, 1660 (C=O), 1610, 1465, 1210, 950, 900, 880 cm^{-1}; mass spectrum (70 eV) *m/e* (rel intensity) 232 (19), 231 (100), 213 (5), 129 (5), 91 (5), 43 (9).

Anal. Calcd for $C_{17}H_{26}OS$: C, 73.33; H, 9.41; S, 11.51. Found: C, 73.19; H, 9.32; S, 11.65.

Methyl 2,4,6-Tri-*tert*-butylthiobenzoate (27d). The procedure used by Newman[45] to prepare sterically hindered esters was adapted to the preparation of **27d** from 1.15 g (3.97 mmol) of 2,4,6-tri-*tert*-butylbenzoic acid[46] and methyl mercaptan. The product was purified by sublimation at 75 °C (0.01 mm) to give 610 mg (48%) of a colorless solid: mp 126–127 °C; NMR ($CDCl_3$) δ 1.29 (s, 9, *p*-$ArC(CH_3)_3$), 1.39 (s, 18, *o*-$ArC(CH_3)_3$), 2.35 (s, 3, SCH_3), 7.38 (s, 2, ArH); IR (KBr) 2982, 1665 (C=O), 1600, 1364, 1195, 933, 880, 757 cm^{-1}; mass spectrum (70 eV) *m/e* (rel intensity) 275 (3), 274 (22), 273 (100), 57 (60).

Anal. Calcd for $C_{20}H_{32}OS$: C, 74.94; H, 10.06; S, 10.00. Found: C, 74.87; H, 10.03; S, 9.96.

Thiomethylmethyllithium–TMEDA (35). The procedure of Peterson[31b] was modified to ensure that unreacted *n*-butyllithium did not contaminate the product. In a drybox under an atmosphere of argon, 40 mL (74 mmol) of a 1.85 M *n*-butyllithium in hexane solution was added slowly to 10.7 g (93 mmol) of TMEDA and 17.2 g (279 mmol) of dimethyl sulfide. The reaction mixture was allowed to stir for 24 h and filtered to remove lithium methylmercaptide, and the hexane was removed. The residue was evacuated at 0.01 mm for 24 h to remove excess dimethyl sulfide and TMEDA. The solid was dissolved in a minimum of pentane; the resulting solution was filtered and the pentane partially removed in vacuo until crystallization was observed. The crystals of **35** were collected, washed with pentane, and dried in vacuo. The sequence was repeated.

The complex **35** is extremely hygroscopic and very soluble in pentane and benzene, and does react with THF at ambient temperature. An NMR spectrum in benzene-d_6 shows only signals due to **35**. We estimate that possible impurities would have been detectable at the 5% level: NMR (C_6D_6) δ 0.94 (s, 2, SCH_2Li), 2.18 (s, 3, SCH_3), 2.33 (s, 12, NCH_3), 2.42 (s, 4, NCH_2CH_2N); (THF-d_8 at −78 °C) δ 0.48 (s, 2, SCH_2Li), 1.91 (s, 3, SCH_3), 2.23 (s, 12, NCH_3), 2.33 (s, 4, NCH_2CH_2N).

General Procedure for the Reaction of Thioesters with LiTMP at Ambient Temperature. A THF solution of LiTMP was prepared by the addition of 1.0 equiv of *n*-butyllithium in hexane to a solution of 1.1 equiv of 2,2,6,6-tetramethylpiperidine in THF. A 1.0-equiv sample of the thioester was dissolved in THF and added dropwise to the LiTMP solution. The reaction mixture was allowed to stir for 1 h at ambient temperature before being quenched with dilute acid. Diethyl ether was added and an extractive product isolation was carried out with washes of 10% HCl, 5% HCl, and water. The organic phase was dried ($MgSO_4$) and removal of the ether in vacuo gave the crude product which was purified by methods described below.

Reaction of 4d with LiTMP. A 272-mg (2.00 mmol) sample of **4d** was added to a THF solution of 2.00 mmol of LiTMP. The crude product was purified by preparative gas chromatography to give 23 mg (8%) of recovered **4d** and 73 mg (60% based on 3 mol of thioester) of dipivaloylmethane (**5d**). The IR, NMR, and GLC retention times of **5d** are identical with those of authentic material (Pierce Chemical Co.). Product analysis by GLC of a subsequent reaction indicated a 79% yield of **5d** and 10% recovered **4d**.

Reaction of 4b with LiTMP. A 195-mg (5.00 mmol) sample of **4b** was added to a THF solution of 5.00 mmol of LiTMP. The crude product was purified by column chromatography on 100 g of silica gel with 25% ether/hexane as eluent. A 130-mg (14%) sample of recovered **4b** was eluted first followed by 392 mg (82% based on 3 mol of thioester) of di(*p*-methoxybenxoyl)methane (**5b**): mp 115–116 °C (lit.[48] mp 116 °C); NMR ($CDCl_3$) δ 3.83 (s, 6, OCH_3), 4.48 (s, 0.23, CH_2), 6.68 (s, 0.76, C=CH), 6.83–7.08 (m, 4, ArH), 7.80–8.05 (m, 4, *o*-ArH); IR (KBr) 1605 (C=O), 1510, 1260, 1235, 1175 cm^{-1}.

Reaction of 4c with LiTMP. A 1.87-g (10.0 mmol) sample of **4c** was added to a THF solution of 10.0 mmol of LiTMP. The crude product was purified by column chromatography on 150 g of silica gel with ether/hexane as eluent. A 217-mg (12%) sample of recovered **4c** was eluted with 5% ether/hexane and 620 mg (63% based on 3 mol of thioester) of di(*p*-chlorobenzoyl)methane (**5c**) was eluted with 40% ether/hexane: mp 158–159 °C (lit.[48] mp 159 °C); NMR ($CDCl_3$) δ 6.70 (s, 1, C=CH), 7.30–7.53 (m, 4, ArH), 7.75–7.98 (m, 4, *o*-ArH); IR (KBr) 1595 (C=O), 1485, 1230, 1095, 1015, 850, 785 cm^{-1}.

Reaction of 4a with LiTMP. A 762-mg (5.00 mmol) sample of **4a** was added to a THF solution of 5.00 mmol of LiTMP. The crude product was purified by column chromatography on 70 g of silica gel with 2.5% ether/hexane as eluent. A 45-mg (6%) sample of recovered **4a** was eluted first followed by 296 mg (78% based on 3 mol of thioester) of dibenzoylmethane (**5a**). The melting point, IR, NMR, and TLC R_f values of **5a** are identical with those of authentic material (Aldrich).

Reaction of Phenyl Thiobenzoate (13) with LiTMP. A solution of 1.0 mmol of LiTMP in THF was treated with 2.0 mmol of **13** in THF. The reaction was quenched and worked up extractively after 45 min at ambient temperature to provide **5a** in 84% yield.

Reaction of 9 with LiTMP. A 1.58-g (7.00 mmol) sample of **9** was added to a THF solution of 7.00 mmol of LiTMP. An ethereal solution of the crude product was extracted three times with 10% NaOH and the organic phase washed with water and dried ($MgSO_4$). The ether was removed in vacuo and the concentrate analyzed by GLC to contain 447 mg (65% based on 2 mol of thioester) of deoxybenzoin (**10**). The product was collected and shown to have IR, NMR, and TLC R_f values identical with those of authentic material (Aldrich).

The basic extracts were combined, acidified, and extracted with ether. The ether extracts were combined, washed with water, dried ($MgSO_4$), and concentrated. NMR analysis of the concentrate showed it to be a mixture of thiobenzoic acid, benzyl mercaptan, and thiobenzoin (**11**); NMR ($CDCl_3$) δ 2.52 (d, 1, J = 8 Hz, SH), 5.62 (d, 1, J = 8 Hz, CH), 7.05–7.52 (m, ArH), 7.82–8.17(m, *o*-ArH). Upon shaking with D_2O, the doublet at δ 2.52 disappeared and the doublet at δ 5.62 collapsed into a singlet.

Reaction of 6 with LiTMP. A 1.67-g (10.0 mmol) sample of **6** was

added to a THF solution of 10.0 mmol of LiTMP. The ethereal solution of the crude product was extracted three times with 10% NaOH. The organic phase was washed with water, dried ($MgSO_4$), and concentrated; the concentrate was placed on preparative TLC plates and eluted with a 10% ether/hexane mixture. The first band collected was 198 mg (12%) of unreacted **6** after which 184 mg (23% based on 3 mol of thioester) of methyldibenzoylmethane (**7**) was eluted: mp 83-84 °C (lit.[49] 82.5-84 °C); NMR ($CDCl_3$) δ 1.58 (d, 3, J = 7 Hz, $CHCH_3$), 5.27 (q, 1, J = 7 Hz, $CHCH_3$), 7.18-7.68 (m, 6, ArH), 7.80-8.08 (m, 4, o-ArH); IR (KBr) 1695, 1670, 1600, 1455, 1350, 1235, 1210, 975 cm^{-1}.

The basic extracts were combined, acidified, and extracted with ether. The ether was removed in vacuo and the concentrate dissolved in 5 mL of THF to which was added a solution of 2 mL of dimethyl sulfate dissolved in 5 mL of 10% NaOH. The reaction mixture was stirred for 24 h in a sealed flask and then extracted three times with ether. The ether extracts were combined, washed with water, dried ($MgSO_4$), and concentrated. The concentrate was purified by GLC to give 87 mg (10%) of 2-methylmercaptopropiophenone and 45 mg (6%) of methyl thiobenzoate. The materials collected had IR, NMR, and mass spectral properties and GLC retention times identical with those of independently prepared materials.

Reaction of 6 with LiTMP at −98 °C. A THF solution of LiTMP was prepared by the addition of 6.1 mmol of n-butyllithium in hexane to 960 mg (6.8 mmol) of 2,2,6,6-tetramethylpiperidine in 50 mL of THF. The solution was cooled to −98 °C in a methanol/liquid nitrogen slush and 1.01 g (6.1 mmol) of **6** in 10 mL of THF was added over a 5-min period. After the addition was complete, the reaction was immediately quenched with aqueous acid. The solvent was removed in vacuo and ether was added. The organic phase was washed with acid, dried ($MgSO_4$), and concentrated. The product was purified by preparative thin layer chromatography to give 177 mg (22%) of **8**; mp 42-43 °C; identical by IR, NMR, MS, and analysis with independently prepared material.

Reaction of 8 with Lithium Ethylmercaptide. A THF solution of lithium ethylmercaptide was prepared by the addition of 3.7 mmol of n-butyllithium in hexane to 260 mg (4.2 mmol) of ethyl mercaptan in 50 mL of THF under a nitrogen atmosphere. A 1.00-g (3.7 mmol) sample of **8** in 10 mL of THF was added and the mixture was allowed to stir for 1 h at ambient temperature prior to quenching with aqueous acid. The solvent was removed in vacuo and ether was added. The organic phase was washed with acid, dried ($MgSO_4$), and concentrated. Analysis by NMR showed the concentrate to be a mixture of **6**, **8**, and 2-thiomethylpropiophenone.

Reaction of an Equimolar Mixture of 6 and 6-d_{10} with LiTMP at −98 °C. A THF solution of LiTMP was prepared by the addition of 7.4 mmol of n-butyllithium in hexane to 1.25 g (8.9 mmol) of 2,2,6,6-tetramethylpiperidine in 50 mL of THF. The solution was cooled to −98 °C in a methanol/liquid nitrogen slush and a mixture of 489 mg (2.94 mmol) of **6** and 509 mg (2.89 mmol) of **6**-d_{10} in 10 mL of THF was added over a 5-min period. After the addition was complete, the reaction was immediately quenched with aqueous acid. The solvent was removed in vacuo, ether added, and the organic phase washed with acid, dried ($MgSO_4$), and concentrated to give a mixture of **6** and **8**. This mixture was separated by preparative thin layer chromatography to give 630 mg (63%) of recovered **6** [mass spectrum (8.0 eV) m/e (rel intensity) 176 (56), 171 (1), 166 (43)] and 80 mg (10%) of **8** [mass spectrum (10 eV) m/e (rel intensity) 275 (58.8), 270 (41.2)].

Reaction of the 8 and 8-d_5 Mixture with Lithium Aluminum Hydride and Mass Spectrometric Analysis of the Isotopically Labeled 2-Methyl-3-phenylthiirane. A solution of 80 mg (0.30 mmol) of the isotopic mixture of **8** and **8**-d_5 was added slowly to a suspension of 100 mg (2.6 mmol) of lithium aluminum hydride in 15 mL of ether. The reaction mixture was heated to reflux and allowed to stir overnight under a nitrogen atmosphere before the excess hydride was destroyed by the cautious addition of 10% NaOH. The mixture was made acidic with dilute mineral acid and extracted with ether. The extracts were combined, washed with water, dried ($MgSO_4$), and concentrated. The product mixture was molecularly distilled and analyzed by oscillographic trace mass spectrometry: mass spectrum (8.2 eV) m/e (rel intensity) 155 (57.5), 150 (42.5), 108 (100).

Reaction of 23 with LiTMP. A THF solution of LiTMP was prepared by the addition of 0.5 mmol of methyllithium to 0.5 mmol of 2,2,6,6-tetramethylpiperidine in THF. To this solution 0.110 g (0.5 mmol) of **23** was added at ambient temperature followed after 5 min by 5 mL of 1 M HCl. The solution was extracted with diethyl ether, and the organic extract was washed with water, dried (Na_2SO_4) and removed in vacuo to give a red oil. Column chromatography on silica gel with benzene as the eluent provided 45 mg (41%) of crystalline material. Sublimation provided an analytical sample of **24**: mp 104-105 °C; NMR ($CDCl_3$) δ 1.46 (s, 9, CH_3), 2.81 (d of d, 1, J = 3.5, 19.0 Hz, CHH), 3.33 (d of d, 1, J = 7.0, 19 Hz, CHH), 4.52 (d of d, 1, J = 7 Hz, CHS), 7.5 (m, 4, ArH); IR (KBr) 1710, 1600, 1470, 1370 cm^{-1}; mass spectrum (70 eV) m/e (rel intensity) 220 (25), 164 (56), 163 (22), 131 (100), 57 (40).

Anal. Calcd for $C_{12}H_{16}OS$: C, 70.87; H, 7.32; S, 14.55. Found: C, 70.73; H, 7.27; S, 14.49.

A preparative run with 1.32 g of **23** provided 0.46 g (35%) of **24** after two sublimations.

Raney Nickel Reduction of 24. To 0.50 g of **24** in absolute ethanol was added 7 g of RaNi in absolute ethanol. The mixture was heated to reflux for 45 min and 55 mg (21%) of crude indan obtained by evaporation of the solvent. This material was shown to be identical with the indan formed by reduction of 1-indanone with RaNi by GLC retention time, NMR, and mass spectral criteria.

General Procedure for the Reaction of 2,4,6-Trialkylthiobenzoates with Butyllithiums at −78 or −98 °C, Followed by Reaction with Deuterated Methanol. The thioester was dissolved in THF and cooled to −78 °C in a dry ice/acetone bath or to −98 °C in a methanol/liquid nitrogen slush prior to the slow addition of n-butyllithium in hexane or sec-butyllithium in cyclohexane. The resulting yellow-orange solution of the anion was allowed to stir at −78 or −98 °C for 1 h and then allowed to warm to room temperature for an additional 30 min with stirring. The solvent was removed in vacuo and the product dissolved in ether. The ethereal solution was washed with water, dried ($MgSO_4$), and concentrated. The crude product was purified by methods described below. The position of deuterium incorporation and percent incorporated were determined by oscillographic trace mass spectrometric comparison with all-protio material. The details are available.[50]

General Procedure for the Reaction of 27b with n-Butyllithium at −78 °C, Followed by Reaction with an Electrophile. Methyl 2,4,6-triethylthiobenzoate was dissolved in THF and cooled to −78 °C in a dry ice/acetone bath prior to the slow addition of n-butyllithium in hexane. The yellow-orange solution was allowed to stir for 2 h before the electrophile was added. After quenching, the reaction mixture was allowed to stir at −78 °C for 1 h and then allowed to warm to room temperature for an additional 30 min of stirring. The solvent was removed in vacuo and the product dissolved in ether. The ethereal solution was washed with water, dried ($MgSO_4$), and concentrated. The crude product was purified as described.

Reaction with Chlorotrimethylsilane to Give 32 (R = H; E = $Si(CH_3)_3$). A 402-mg (1.70 mmol) sample of **27b** was dissolved in 25 mL of THF and treated with 1.35 equiv (2.30 mmol) of n-butyllithium. The anion solution was quenched with 2 mL of chlorotrimethylsilane. The product was purified by GLC to give 236 mg (45%) of isolated material; GLC analysis of the crude product mixture indicated a yield of 90%; NMR ($CDCl_3$) δ 0.17 (s, 9, $Si(CH_3)_3$), 1.25 (t, 9, J = 7 Hz, $ArCH_2CH_3$), 2.33 (s, 2, SCH_2Si), 2.65 (q, 6, J = 7 Hz, $ArCH_2CH_3$), 6.95 (s, 2, ArH); IR (neat) 2960, 2900, 2870, 1670 (C=O), 1610, 1460, 1250, 1220, 1145, 930, 840 cm^{-1}; mass spectrum (70 eV) m/e (rel intensity) 308 (1), 190 (17), 189 (100), 105 (9), 73 (6).

Anal. Calcd for $C_{17}H_{28}OSSi$: C, 66.17; H, 9.15; S, 10.39. Found: C, 66.03; H, 9.31; S, 10.31.

Reaction with Methyl Iodide to Give 32 (R = H; E = CH_3). A 2.019-g (8.54 mmol) sample of **27b** was dissolved in 50 mL of THF and treated with 1.35 equiv (11.5 mmol) of n-butyllithium. The anion solution was quenched with 5 mL of methyl iodide. The product was purified by distillation to give 1.83 g (86%) of a light yellow liquid: bp 107-108 °C (0.03 mm); NMR ($CDCl_3$) δ 1.20 (t, 9, J = 7 Hz, $ArCH_2CH_3$), 1.35 (t, 3, J = 7 Hz, SCH_2CH_3), 2.63 (q, 2, J = 7 Hz, p-$ArCH_2CH_3$), 2.65 (q, 4, J = 7 Hz, o-$ArCH_2CH_3$), 3.03 (q, 2, J = 7 Hz, SCH_2CH_3), 6.89 (s, 2, ArH); IR (neat) 2980, 2940, 2880, 1675 (C=O), 1610, 1460, 1375, 1265, 1210, 1145, 920, 870 cm^{-1}; mass spectrum (70 eV) m/e (rel intensity) 250 (2), 190 (14), 189 (100), 133 (5), 117 (5), 115 (5), 105 (12), 91 (7).

Anal. Calcd for $C_{15}H_{22}OS$: C, 71.95; H, 8.86; S, 12.80. Found: C, 71.89; H, 8.83; S, 12.73.

Reaction with Carbon Dioxide to Give 32 (R = H; E = CO_2H). A 2.024-g (8.56 mmol) sample of **27b** was dissolved in 50 mL of THF

and treated with 1.5 equiv (13 mmol) of *n*-butyllithium. The anion solution was quenched with carbon dioxide which was bubbled through the solution for 30 min. An ethereal solution of the product mixture was extracted with aqueous base and the basic extracts were combined, acidified, and extracted with ether. The ether extracts were combined, washed with water, dried ($MgSO_4$), and concentrated. The product was recrystallized from pentane to give 1.22 g (51%) of a colorless solid: mp 84-86 °C; NMR ($CDCl_3$) δ 1.24 (t, 6, J = 7 Hz, *o*-$ArCH_2CH_3$), 1.27 (t, 3, J = 7 Hz, *p*-$ArCH_2CH_3$), 2.62 (q, 6, J = 7 Hz, $ARCH_2CH_3$), 3.84 (s, 2, SCH_2), 6.86 (s, 2, ArH), 9.75 (s, 1, CO_2H); IR (KBr) 2980, 2940, 2880, 1715 (OC=O), 1695 (SC=O), 1610, 1470, 1425, 1300, 1210, 1160, 920, 870 cm^{-1}; mass spectrum (90 eV) *m/e* (rel intensity) 280 (1), 206 (1), 205 (1), 204 (3), 191 (2), 190 (14), 189 (100), 188 (3), 161 (3), 160 (3), 145 (3), 133 (27), 131 (5).

Anal. Calcd for $C_{15}H_{20}O_3S$: C, 64.26; H, 7.19; S, 11.44. Found: C, 64.51; H, 7.28; S, 11.50.

Reaction with Benzaldehyde to Give 32 (R = H; E = C_6H_5CHOH). A 1.513-g (6.40 mmol) sample of **27b** was dissolved in 50 mL of THF and treated with 1.12 equiv (7.17 mmol) of *n*-butyllithium. The anion solution was quenched with 1.5 equiv (9.4 mmol) of benzaldehyde. The crude product was chromatographed on silica gel with 20% ether/hexane as eluent and 1.75 g (80%) of a viscous liquid was isolated: NMR ($CDCl_3$) δ 1.19 (t, 6, J = 7 Hz, *o*-$ArCH_2CH_3$), 1.22 (t, 3, J = 7 Hz, *p*-$ArCH_2CH_3$), 2.57 (q, 4, J = 7 Hz, *o*-$ArCH_2CH_3$), 2.59 (q, 2, J = 7 Hz, *p*-$ArCH_2CH_3$), 3.30-3.53 (m, 2, SCH_2CH), 4.77-5.08 (m, 1, SCH_2CH), 5.17 (s, , OH), 6.89 (s, 2, ArH), 7.14-7.53 (m, 5, ArH); IR (neat) 3600-3150 (OH), 2980, 2940, 2880, 1675 (C=O), 1610, 1460, 1210, 1160, 920, 870 cm^{-1}; mass spectrum (10 eV) *m/e* (rel intensity) 342 (1), 191 (1), 190 (14), 189 (100), 188 (1), 107 (4).

Anal. Calcd for $C_{21}H_{26}O_2S$: C, 73.64; H, 7.65; S, 9.36. Found: C, 73.55; H, 7.88; S, 9.14.

Reaction with Allyl Bromide to Give 32 (R = H; E = $CH_2CH{=}CH_2$). A 1.512-g (6.41 mmol) sample of **27b** was dissolved in 60 mL of THF and treated with 1.2 equiv (7.7 mmol) of *n*-butyllithium. The anion solution was quenched with 2 mL of allyl bromide. The product was purified by molecular distillation to give 1.45 g (82%) of a colorless liquid: NMR ($CDCl_3$) δ 1.21 (t, 9, J = 7 Hz, $ArCH_2CH_3$), 2.25-3.35 (m, 10, $ArCH_2CH_3$ and $SCH_2CH_2CH{=}CH_2$), 4.95-5.38 (m, 2, $CH{=}CH_2$), 5.60-6.28 (m, 1, $CH_2CH{=}CH_2$), 6.95 (s, 2, ArH); IR (neat) 2980, 2940, 2880, 1675 (C=O), 1610, 1460, 1210, 1140, 915, 870 cm^{-1}; mass spectrum (10 eV) *m/e* (rel intensity) 276 (1), 191 (1), 190 (13), 189 (100).

Anal. Calcd for $C_{17}H_{24}OS$: C, 73.86; H, 8.75; S, 11.60. Found: C, 73.69; H, 8.56; S, 11.63.

Reaction with Propiophenone to Give 32 (R = H; E = $C_6H_5C(OH)C_2H_5$). A 2.034-g (8.60 mmol) sample of **27b** was dissolved in THF and treated with 1.1 equiv (9.5 mmol) of *n*-butyllithium. The anion solution was quenched with 1.30 g (9.7 mmol) of propiophenone. The product was recrystallized from hexane to give 2.35 g (74%) of a colorless solid: mp 89-90 °C; NMR ($CDCl_3$) δ 0.80 (t, 3, J = 7 Hz, CH_2CH_3), 1.00-1.20 (m, 9, $ArCH_2CH_3$), 1.93 (q, 2, J = 7 Hz, CH_2CH_3), 2.25-2.70 (m, 7, $ArCH_2CH_3$ and OH), 3.55 (s, 2, SCH_2), 6.78 (s, 2, Ar*H*), 7.05-7.18 (m, 5, Ar*H*); IR (KBr) 3700-3300 (OH), 2980, 2940, 2880, 1640 (C=O), 1610, 1460, 1210, 1150, 1140, 985, 930, 880, 765, 700 cm^{-1}; mass spectrum (20 eV) *m/e* (rel intensity) 371 (3), 370 (12), 355 (3), 323 (3), 236 (8), 221 (11), 220 (7), 207 (13) 206 (85), 202 (3), 194 (12), 192 (7), 191 (17), 190 (100), 189 (100), 188 (49), 187 (7), 186 (6), 172 (5), 164 (38), 162 (10), 161 (4), 160 (25), 136 (4), 135 (34), 134 (6), 133 (11), 132 (100), 131 (12), 118 (4), 117 (6), 105 (11), 64 (3), 56 (4).

Anal. Calcd for $C_{23}H_{30}O_2S$: C, 74.55; H, 8.16; S, 8.65. Found: C, 74.79; H, 8.09; S, 8.65.

Reaction with Benzyl Bromide to Give 33. A 5.16-g (21.8 mmol) sample of **27b** was dissolved in 150 mL of THF and treated with 1.2 equiv (26 mmol) of *n*-butyllithium. The anion solution was purified by vacuum distillation to give 5.53 g (78%) of product: bp 167-168 °C (0.05 mm); NMR ($CDCl_3$) δ 1.18 (t, 6, J = 7 Hz, *o*-$ArCH_2CH_3$), 1.21 (t, 3, J = 7 Hz, *p*-$ArCH_2CH_3$), 2.57 (q, 4, J = 7 Hz, *o*-$ArCH_2CH_3$), 2.60 (q, 2, J = 7 Hz, *p*-$ArCH_2CH_3$), 2.86-3.10 (m, 2, SCH_2CH_2Ph), 3.21-3.44 (m, 2, SCH_2CH_2Ph), 6.89 (s, 2, ArH), 7.24 (s, 5, ArH); IR (neat) 3100, 3070, 3040, 2980, 2940, 2880, 1680 (C=O), 1610, 1500, 1460, 1210, 1145, 920, 875, 700 cm^{-1}; mass spectrum (70 eV) *m/e* (rel intensity) 190 (13), 189 (100), 133 (4), 131 (3), 117 (3), 105 (11), 91 (6) 77 (3).

Anal. Calcd for $C_{21}H_{26}OS$: C, 77.25; H, 8.03; S, 9.82. Found: C, 77.51; H, 8.04; S, 9.80.

General Procedure for the Reaction of 28 with *sec*-Butyllithium/TMEDA at −98 °C, Followed by Reaction with an Electrophile. Ethyl 2,4,6-triethylthiobenzoate (**28**) and TMEDA were dissolved in THF and cooled to −98 °C in a methanol/liquid nitrogen slush prior to the slow addition of *sec*-butyllithium in cyclohexane. The red-orange solution was allowed to stir for 2 h before the electrophile was added. After quenching, the reaction mixture was allowed to stir at −98 °C for 1 h and then allowed to warm to room temperature for an additional 30 min of stirring. The solvent was removed in vacuo and the product dissolved in ether. The ethereal solution was washed with aqueous acid and water, dried ($MgSO_4$), and concentrated. The crude product was purified as described.

Reaction with Benzaldehyde to Give 32 (R = CH_3; E = C_6H_5CHOH). A 7.00-g (28.0 mmol) sample of **28** and 3.60 (31.0 mmol) of TMEDA were dissolved in 200 mL of THF and treated with 1.03 equiv (28.8 mmol) of *sec*-butyllithium. The anion solution was quenched with 3.0 g (28 mmol) of benzaldehyde. The crude product was chromatographed on silica gel with 20% ether/hexane as eluent to give 9.1 g (91%) of the very viscous product: NMR ($CDCl_3$) δ 1.00-1.40 (m, 9, $ArCH_2CH_3$), 2.27-2.85 (m, 7, $ArCH_2CH_3$ and OH), 3.90-4.30 (m, 1, SC*H*), 4.65-5.02 (m, 1, PhC*H*), 6.85 (s, 2, ArH), 7.10-7.55 (m, 5, ArH); IR (neat) 3700-3200 (OH), 2980, 2940, 2880, 1665 (C=O), 1610, 1455, 1375, 1205, 1140, 1030, 925, 875, 760, 705 cm^{-1}; mass spectrum (70 eV) *m/e* (rel intensity) 221 (3), 190 (14), 189 (100), 133 (2), 117 (2), 107 (2), 91 (3), 79 (3), 77 (2).

Anal. Calcd for $C_{22}H_{28}O_2S$: C, 74.12; H, 7.92; S, 8.99. Found: C, 73.91; H, 7.93; S, 9.09.

Reaction with Benzyl Bromide to Give 34. A 7.05-g (24.1 mmol) sample of **28** and 3.09 g (26.6 mmol) of TMEDA were dissolved in 150 mL of THF and treated with 1.0 equiv (24 mmol) of *sec*-butyllithium. The anion solution was quenched with 4.3 g (25 mmol) of benzyl bromide. The material was purified by vacuum distillation to give 5.7 g (72%) of product: bp 170-172 °C (0.05 mm); NMR ($CDCl_3$) δ 1.02-1.54 (m, 12, $ArCH_2CH_3$ and $SCHCH_3$), 2.33-2.70 (q, 6, J = 7 Hz, $ArCH_2CH_3$), 2.72-3.15 (m, 2, $PhCH_2$), 3.77-4.23 (m, 1, $SCHCH_3$), 6.87 (s, 2, ArH), 7.05-7.30 (m, 5, ArH); IR (neat) 2975, 2940, 2880, 1675 (C=O), 1605, 1495, 1455, 1375, 1205, 1145, 920, 870, 750, 705 cm^{-1}; mass spectrum (70 eV) *m/e* (rel intensity) 190 (13), 189 (100), 133 (2), 131 (2), 117 (3), 115 (2), 105 (9), 91 (9), 77 (2).

Anal. Calcd for $C_{21}H_{26}OS$: C, 77.25; H, 8.03; S, 9.82. Found: C, 77.50; H, 8.14; S, 9.94.

Reduction of 33 with Lithium Aluminum Hydride. A solution of 4.30 g (13.2 mmol) of **33** was added to 1.31 g (33 mmol) of lithium aluminum hydride. The product mixture was chromatographed on silica gel with hexane to give 1.40 g (77%) of 2-phenylethanethiol which was eluted first as a colorless liquid, bp 99-100 °C (15 mm) (lit.[51] bp 105°C (23 mm)). The IR, NMR, MS, and analysis are consistent with the established structure.

Reduction of 34 with Lithium Aluminum Hydride. A solution of 4.50 g (13.8 mmol) of **34** was added to 1.58 g (41.6 mmol) of lithium aluminum hydride. The product mixture was chromatographed on silica gel with hexane to give 1.70 g (81%) of 3-phenylpropane-2-thiol which was eluted first as a colorless liquid: bp 106-107 °C (20 mm) (lit.[52] bp 106-108 °C (18 mm)). The IR, NMR, MS, and analysis are consistent with the established structure.

Reaction of 32 (R = CH_3; E = $C_6H_5C(OH)C_2H_5$) with Potassium Hydroxide. A 1.27-g (3.43 mmol) sample of **32** (R = CH_3; E = $C_6H_5C(OH)C_2H_5$) was allowed to stir for 12 h with 10.0 g (178 mmol) of potassium hydroxide in 25 mL of absolute ethanol at reflux under a nitrogen atmosphere. The reaction mixture was poured onto crushed ice, acidified to pH 7, and extracted with ether. The extracts were combined, washed with saturated sodium bicarbonate, dried ($MgSO_4$), and concentrated. The product was purified by molecular distillation to give 260 mg (58%) of α-ethylstyrene: NMR ($CDCl_3$) δ 1.10 (t, 3, J = 7 Hz, CH_2CH_3), 3.50 (q, 2, J = 7 Hz, CH_2CH_3), 4.92-5.08 (m, 1, C=CH), 5.14-5.25 (m, 1, C=CH), 7.10-7.50 (m, 5, ArH); IR (neat) 3090, 3070, 3040, 2980, 2950, 2890, 1695, 1630 (C=C-Ar), 1600, 1575, 1495, 1440-1470, 1380, 1220, 1080, 1030, 900, 780, 760, 705 cm^{-1}; mass spectrum (70 eV) *m/e* (rel intensity) 133 (9), 132 (82), 131 (21), 118 (10), 117 (100), 116 (9), 115 (29), 105 (11), 103 (38), 91 (25), 78 (18), 77 (27), 65 (9), 54 (9), 51 (17), 39 (11).

Anal. Calcd for $C_{10}H_{12}$: C, 90.85; H, 9.15. Found: C, 90.56; H, 9.36.

Reaction of 32 (R = CH_3; E = C_6H_5CHOH) with Sodium Hydride. Reaction was allowed to proceed between 308 mg (6.42 mmol) of 50% oil dispersion sodium hydride after petroleum ether washings, with a THF solution of 2.08 g (5.82 mmol) of **32** (R = CH_3; E = C_6H_5CHOH) at ambient temperature for 6 h under a nitrogen atmosphere. The solvent was removed in vacuo and ether was added. The organic phase was washed with saturated sodium bicarbonate, dried ($MgSO_4$), and concentrated. The product was purified by molecular distillation at 50 °C (0.01 mm) to give 620 mg (71%) of an epimeric mixture of 2-methyl-3-phenylthiirane: NMR ($CDCl_3$) δ 1.22 (d, 1.05, J = 7 Hz, SCHCH_3), 1.65 (d, 1.95, J = 6 Hz, SCHCH_3), 2.90-3.40 (m, 1, SCHCH$_3$), 3.55 (d, 0.65, J = 6 Hz, SCHPh), 4.13 (d, 0.35, J = 7 Hz, SCHPh), 7.20-7.50 (m, 5, ArH); IR (neat) 3090, 3070, 3040, 3010, 2980, 2940, 2880, 1605, 1500, 1455, 1385, 1350, 1195, 1095, 1070, 1030, 1005, 970, 905, 790, 755, 705 cm^{-1}; mass spectrum (10 eV) *m/e* (rel intensity) 152 (4), 151 (17), 150 (100), 149 (42), 136 (7), 135 (67), 121 (5), 118 (22), 117 (29), 115 (8), 105 (9), 91 (14), 59 (17).

Anal. Calcd for $C_9H_{10}S$: C, 71.95; H, 6.71; S, 21.34. Found: C, 72.07; H, 6.52; S, 21.23.

The basic extracts were combined, acidified, and extracted with ether. The organic phase was washed with water, dried ($MgSO_4$), and concentrated to give 936 mg (78%) of 2,4,6-triethylbenzoic acid, mp 112-114 °C.

Equilibration of 35 with Lithiomethyl 2,4,6-Triisopropylthiobenzoate-TMEDA at −78 °C. In a drybox under an atmosphere of argon, 14.279 mg (0.077 49 mmol) of **35** was weighed into an NMR tube. The tube was sealed with a septum cap, removed from the drybox, and cooled to −78 °C in a dry ice/acetone bath. The sample was then dissolved in 250 μL of THF-d_8, to which 50 μL of benzene was added to provide a lock signal, and placed in the probe of an HA-100 NMR spectrometer which was maintained at −78 °C. A 21.586-mg (0.077 52 mmol) sample of **27c** was dissolved in 250 μL of THF and added by syringe to the tube. The course of the equilibration was monitored periodically by obtaining spectra, and after 11 days the anion solution was quenched with 50 μL of methanol-d_1.

The solvent was removed in vacuo and ether was added. The ethereal solution was washed with water, dried ($MgSO_4$), and concentrated. The product was purified by sublimation at 75° (0.01 mm) to give 16 mg (74%) of recovered **29c**: NMR ($CDCl_3$) δ 1.22 (d, 18, J = 7 Hz, CH(CH_3)$_2$), 2.45 (t, 2.17, J = 2 Hz, SCH_2D), 2.92 (m, 3, J = 7 Hz, CH(CH$_3$)$_2$), 2.45 (t, 2.17, J = 2 Hz, SCH_2D), 2.92 (m, 3, J = 7 Hz, CH(CH$_3$)$_2$), 6.98 (s, 2, ArH); mass spectrum (10 eV) *m/e* (rel intensity **27c**/rel intensity **29c**) 280 (6.5/20.9), 279 (20.3/100), 278 (100/36.7), 232 (19.2/19.2), 231 (100/100).

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Supplementary Material Available: An appendix describing the reactions of **27a-c** and **28** with *n*-butyllithium and **27c**, **27d**, and **28** with *sec*-butyllithium (3 pages). Ordering information is given on any current masthead page.

References and Notes

(1) P. Beak and B. G. McKinnie, *J. Am. Chem. Soc.*, **99**, 5213 (1977).
(2) P. Beak, B. G. McKinnie, and D. B. Reitz, *Tetrahedron Lett.*, 1839 (1977).
(3) For a general review of the possible members of the family of stabilized carbanions see P. Beak and D. B. Reitz, *Chem. Rev.*, **78**, 275 (1978).
(4) D. Seebach and W. Lubosch, *Angew. Chem., Int. Ed. Engl.*, **15**, 313 (1976).
(5) R. Schlecker and D. Seebach, *Helv. Chim. Acta*, **60**, 1459 (1977).
(6) (a) K. Hirai, H. Matsuda, and Y. Kishida, *Tetrahedron Lett.*, 4359 (1971); (b) C. R. Johnson, A. Nakanishi, N. Nakanishi, and K. Tanaka, *Ibid.*, 2865 (1975).
(7) (a) A. I. Meyers and M. E. Ford, *Tetrahedron Lett.*, 2861 (1975); (b) A. I. Meyers and M. E. Ford, *J. Org. Chem.*, **41**, 1735 (1976).
(8) K. Hirai and Y. Kishida, *Heterocycles*, **2**, 185 (1974).
(9) C. R. Johnson and K. Tanaka, *Synthesis*, 413 (1976).
(10) D. Hoppe, *Angew. Chem., Int. Ed. Engl.*, **14**, 424 (1975).
(11) K. Hirai and Y. Kishida, *Tetrahedron Lett.*, 2743 (1972).
(12) E. Negishi, T. Yoshida, A. Silveira, Jr., and B. L. Chiou, *J. Org. Chem.*, **40**, 814 (1975).
(13) P. Beak and R. Farney, *J. Am. Chem. Soc.*, **95**, 4771 (1973).
(14) R. A. Olofson and C. M. Dougherty, *J. Am. Chem. Soc.*, **95**, 582 (1973).
(15) R. Kow and M. W. Rathke, *J. Am. Chem. Soc.*, **95**, 2715 (1973); C. C. Kissel and B. Rickborn, *J. Org. Chem.*, **37**, 2060 (1972).
(16) M. Oki, W. Funakoshi, and A. Nakamura, *Bull. Chem. Soc. Jpn.*, **44**, 828 (1971); M. Oki and W. Funakoshi, *Ibid.*, **44**, 832 (1971).
(17) P. Beak, G. R. Brubaker, and R. F. Farney, *J. Am. Chem. Soc.*, **98**, 3621 (1976).
(18) A. Nickon, J. C. Lambert, J. E. Oliver, D. F. Covery, and J. Morgan, *J. Am. Chem. Soc.*, **98**, 2593 (1976), and references cited therein.
(19) The calculated primary isotope effect at −98 °C is k_H/k_D = 27. For another case see A. I. Meyers and E. D. Mihelich, *J. Org. Chem.*, **40**, 3158 (1975).
(20) It was shown by mass spectrometry of specifically labeled **8**-d_5 that both benzoyl groups were lost from the molecular ion with comparable facility.
(21) This conversion must involve reduction of the ketone followed by migration of the benzoyl group and intramolecular displacement of benzoate by sulfur. That sequence is analogous to the previously noted thiirane syntheses.[6b,7,8] It was established by reduction and mass spectrometry of specifically labeled **8**-d_5 that the phenyl attached to the ketone carbonyl was retained in the thiirane. The lithium benzoate undergoes further reduction to benzyl alcohol which also carries the label as expected.
(22) P. Beak and E. M. Monroe, *J. Org. Chem.*, **34**, 589 (1969).
(23) (a) J. P. Marino, M. Neisser, and W. Butler, private communication; (b) Abstracts, 175th National Meeting of the American Chemical Society, Anaheim, Calif., March 1978, No. ORGN-22.
(24) J. P. Marino and J. C. Kostosyk, ref 23b, No. ORGN-23.
(25) D. W. Slocum and D. I. Sugarman, *Adv. Chem. Ser.*, **130**, 222-247 (1974); H. W. Gschwend and A. Hamden, *J. Org. Chem.*, **40**, 2008 (1975); P. Beak and R. A. Brown, *ibid.*, **42**, 1823 (1977), and references cited therein.
(26) P. Beak and C. J. Upton, unpublished results.
(27) The lack of deuteration at the benzylic positions could be attributed in part to a rotation of the carbonyl group to a position orthogonal to the benzene ring such that the expected conjugative stabilization is reduced. It should be noted that *N,N*-dialkyl-*o*-toluamides are metalated by *n*-butyllithium or LiTMP at the benzylic position: R. E. Ludt, J. S. Griffiths, K. N. McGrath, and C. R. Hauser, *J. Org. Chem.*, **38**, 1668 (1973).
(28) D. J. Cram, "Fundamentals of Carbanion Chemistry", Academic Press, New York, N.Y., 1965, Chapter 2; D. J. Peterson, *Organomet. Chem. Rev., Sect. A*, **7**, 295 (1972); M. Schlosser, "Struktur und Reaktivität Polarer Organometalle", Springer-Verlag, West Berlin, 1973, Chapter 2; E. Buncel, "Carbanions: Mechanistic and Isotopic Aspects", American Elsevier, New York, N.Y., 1975, Chapter 2.
(29) S. Wolfe, *Acc. Chem. Res.*, **5**, 102 (1972); J. Lehn and G. Wipff, *J. Am. Chem. Soc.*, **98**, 7498 (1976); N. D. Epiotis, R. L. Yates, F. Bernardi, and S. Wolfe, *ibid.*, **98**, 5435 (1976); A. Streitwieser, Jr., and J. E. Williams, Jr., *ibid.*, **97**, 191 (1975).
(30) F. G. Bordwell, J. E. Bares, J. E. Bartmess, G. E. Drucker, J. Gerhold, G. J. McCollum, M. Van Der Puy, N. R. Vanier, and W. S. Matthews, *J. Org. Chem.*, **42**, 326 (1977); F. G. Bordwell, M. Van Der Puy, and N. R. Vanier, *ibid.*, **41**, 1885 (1976).
(31) (a) T. M. Dolak and T. A. Bryson, *Tetrahedron Lett.*, 1961 (1971); (b) D. Peterson, *J. Org. Chem.*, **32**, 1717 (1967); (c) E. J. Corey and D. Seebach, *ibid.*, **31**, 4097 (1966).
(32) This approach avoids the doubtful practice of quenching the anions at equilibrium with an electrophile and making the assumption that the relative amounts of trapped products reflect the relative concentrations of the organometallics in solution. For cases in which reaction of organolithiums with water appears to be slower than other reactions see R. Taylor, *Tetrahedron Lett.*, 435 (1975); R. Levine, M. J. Karten, and W. M. Kadunce, *J. Org. Chem.*, **40**, 1770 (1975); K. Smith, *Annu. Rep. Prog. Chem., Sect. B*, **72**, 189 (1976).
(33) The fact that **29c** is 73% monodeuterated is attributed to competing loss of activity by the 1 equiv of **35** initially added. Initial formation of some dimethyl sulfide as observed before **27c** was added.
(34) The presumption that the relative stabilities of organolithiums will qualitatively follow the order of carbanion stabilities appears to be useful if the states of aggregation are similar. Presumably TMEDA exhibits a leveling effect on aggregation; see G. R. Brubaker and P. Beak, *J. Organomet. Chem.*, **136**, 147 (1977), and references cited for discussion.
(35) Melting points were determined on a Thomas-Hoover melting point apparatus and are uncorrected. Boiling points, taken from distillations, are likewise uncorrected. Chemical shifts are reported in δ (ppm) relative to an internal tetramethylsilane standard unless otherwise noted. Elemental analyses were performed by J. Nemeth and associates. Mass spectra were obtained on a Varian MAT CH-5 spectrometer by J. Wrona under the supervision of C. Cook.
(36) S. C. Watson and J. F. Eastham, *J. Organomet. Chem.*, **9**, 165 (1967).
(37) L. S. Pratt and E. E. Reid, *J. Am. Chem. Soc.*, **37**, 1934 (1915).
(38) R. Mayer, S. Scheithauer, and D. Kunz, *Chem. Ber.*, **99**, 1393 (1966).
(39) R. Otto and R. Lüders, *Chem. Ber.*, **13**, 1283 (1880).
(40) B. Groth, *Ark. Kemi*, **9**, 50 (1924).
(41) R. Ireland and J. A. Marshall, *J. Org. Chem.*, **27**, 1615 (1962).
(42) R. P. Barnes, *Org. Synth.*, **21**, 77 (1941).
(43) R. C. Fuson and J. Corse, *J. Am. Chem. Soc.*, **60**, 2063 (1938).
(44) R. C. Fuson and E. C. Horning, *J. Am. Chem. Soc.*, **62**, 2962 (1940).
(45) M. S. Newman, *J. Am. Chem. Soc.*, **63**, 2431 (1941).
(46) E. E. Betts and L. R. C. Barclay, *Can. J. Chem.*, **33**, 1768 (1955).
(47) A. Sieglitz and O. Horn, *Chem. Ber.*, **84**, 607 (1951).
(48) R. D. Abell, *J. Chem. Soc.*, **79**, 928 (1901).
(49) See paragraph at end of paper regarding supplementary material.
(50) J. Braun, *Chem. Ber.*, **45**, 1563 (1912).
(51) C. L. Arcus and P. A. Hallgarten, *J. Chem. Soc.*, 2987 (1956).