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Dipole-Stabilized Carbanions from Thioesters. Secondary α′-Lithio Carbamates and Tertiary α′-Lithio Thioesters

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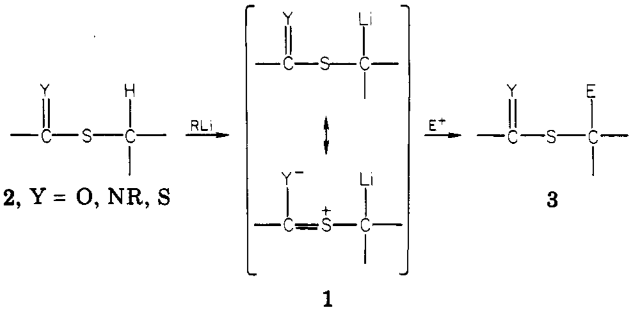
The formations of **5** and **17**, synthetic equivalents of the α-lithioalkylthio and α-lithiodialkylthio functions, respectively, by deprotonations of the corresponding carbamate **4** and thioester **16** are reported. The reactions of these formally dipole-stabilized carbanions with a variety of electrophiles and their use in syntheses of 2,3-substituted thiiranes are demonstrated. The rearrangement of **17** to an α-thiol ketone is shown to be intramolecular by a double labeling experiment. Potentially chiral or conformationally isomeric α′-lithio thioesters are found to be racemized and equilibrated. Formations of secondary α′-lithio thioesters in medium chain, β′-dimethylamino, and allyl systems are reported while β′-alkoxy groups are shown to eliminate to give vinyl thio esters which undergo further metalation. The kinetic acidity of a methyl thioester is shown to be comparable to a propenyl thioester and greater than an ethyl thioester.

The α′-lithio thioesters, **1**, formed by deprotonations of thioesters **2** and converted on reactions with electrophiles to the substituted products **3**, provided early examples of dipole-stabilized carbanions.[1-3] Primary and allyl α′-thio carbanions corresponding to **1** have also been generated by deprotonations of 2-thiothiazolines,[2b-e] 2-thiooxazolines,[2p-r] 2-thioimidazoles,[2f] 2-thiopyridines,[2n] thioimidates,[2v] iminodithiocarbonates,[2s,2t] dithiocarbonates,[2e] mono- and dithiocarbamates,[2g-j] and vinylogous thioesters.[2k-m,q] These carbanions provide the α-lithiomethanethiol synthon and also synthetic equivalents for the allyl,[2c] vinyl,[2h] β-acrolein,[2h] and β-acrylic acid anions[2i,2j] and for the methylene and 1,3-propenone dianions.[2i,2j,4]

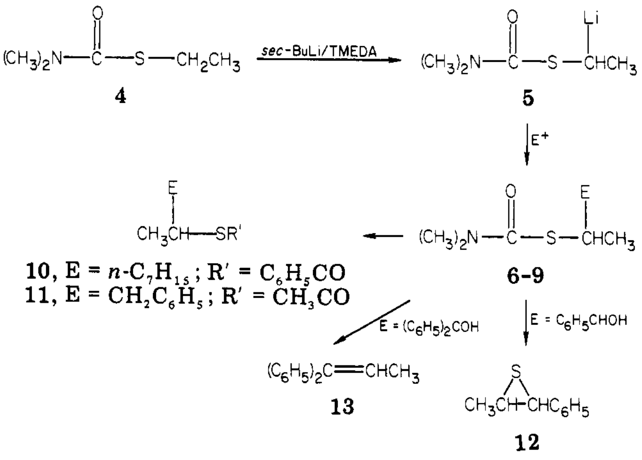


2, Y = O, NR, S

1

3

Scheme I



4

5

6-9

10, E = n-C_7H_{15}; R′ = C_6H_5CO

11, E = $CH_2C_6H_5$; R′ = CH_3CO

12

13

Table I. Reactions from Ethyl *N*,*N*-Dimethylthiocarbamate (**4**)

electrophile	product	yield, %
CH_3OD	**4**-d_1, E = D	85 (98% d_1)
n-$C_7H_{15}I$	**6**, E = n-C_7H_{15}	81
$C_6H_5CH_2Cl$	**7**, E = $C_6H_5CH_2$	66
CH_3CHO	**8**, E = CH_3CHOH	76
C_6H_5CHO	**9**, E = C_6H_5CHOH	50
$(C_6H_5)_2CO$	**13**	67

With the exception of allylically activated cases, lithiations to give secondary derivatives of **1** have been limited to monothiocarbonates and sterically hindered esters while lithations to give tertiary derivatives of **1** have not been reported. We report formation of secondary α′-lithio thiocarbamates and tertiary α′-lithio thioesters and exploration of the chemistry of these novel systems.

Results and Discussion

Lithiation of Thiocarbamates. Ethyl *N*,*N*-dimethylthiocarbamate (**4**) undergoes lithiation to give **5**, which reacts readily with electrophiles to give the expected products **6–9** in useful yields as shown in Scheme I and Table I. Representative conversions of **6–9** have been carried out as shown in the scheme. Hydrolysis gives the substituted thiols which can be converted to thioesters. For example, **6** is converted to **10** in 47% yield on treat-

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[1] (a) Beak, P.; Reitz, D. B. *Chem. Rev.* **1978**, *78*, 275 and references cited therein. For recent cases of dipole stabilized carbanions from amides, amidines, and esters see: (b) Reitz, D. B.; Beak, P.; Tse, A. *J. Org. Chem.* **1981**, *46*, 4316. (c) Meyers, A. I.; TenHove, W. *J. Am. Chem. Soc.* **1980**, *102*, 7125. (d) Beak, P.; Carter, L. G. *J. Org. Chem.* **1981**, *46*, 2363. For a recent summary of α-heterocarbanions in synthesis see: Krief, A. *Tetrahedron* **1980**, *36*, 2531.

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[3] For recent theoretical support for dipole stabilization of carbanions from esters and amides see: Rondan, N. G.; Houk, K. N.; Beak, P.; Zajdel, W. J.; Chendrasekhar, J.; Schleyer, P. v. R. *J. Org. Chem.* **1981**, *46*, 408.

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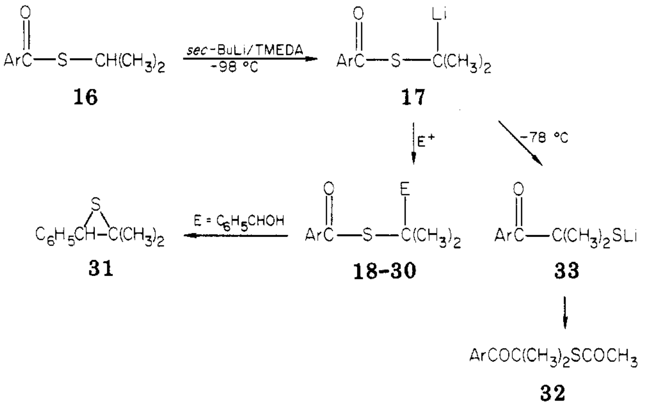
Scheme II[a]



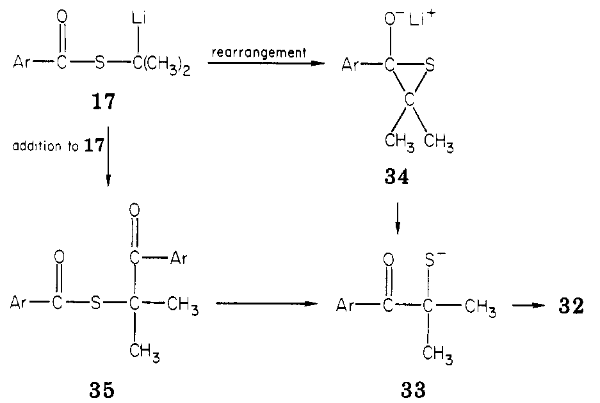
[a] Ar = 2,4,6-triisopropylphenyl.

Table II. Reactions from Isopropyl 2,4,6-Triisopropylthiobenzoate (16)

electrophile	product	yield, %
CH_3OD	16-d_1, E = D	69 (85% d_1)
CH_3I	18, E = CH_3	38[a]
$(CH_3)_3SiCl$	19, E = $(CH_3)_3Si$	25[a]
$CH_3(CH_2)_3I$	20, E = $CH_3(CH_2)_3$	74
$CH_3(CH_2)_4I$	21, E = $CH_3(CH_2)_4$	65
$CH_3(CH_2)_5Br$	22, E = $CH_3(CH_2)_5$	47
$(CH_3)_2C{=}CHCH_2Cl$	23, E = $(CH_3)_2C{=}CHCH_2$	43
CH_3CHO	24, E = CH_3CHOH	72
C_6H_5CHO	25, E = C_6H_5CHOH	51
$(CD_3)_2CO$	26, E = $(CD_3)_2COH$	30
$(CH_3CO)_2O$	27, E = CH_3CO	14
$C_6H_5COOCH_3$	28, E = C_6H_5CO	54
C_2H_5OCOCl	29, E = C_2H_5OCO	29
CO_2	30, E = COOH	35

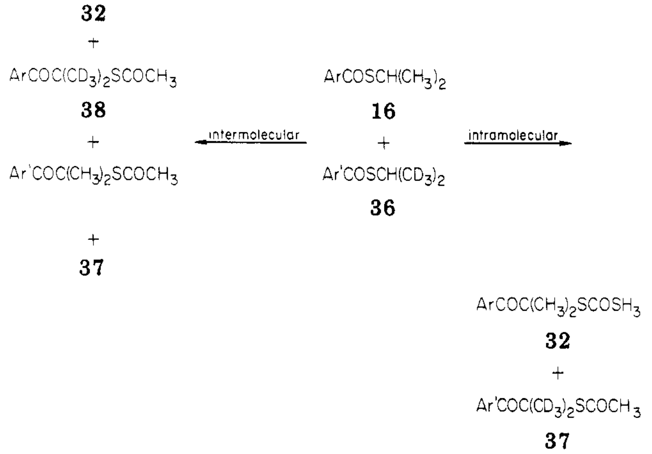
[a] Low yields attributed to difficulties in product isolation.

Scheme III[a]



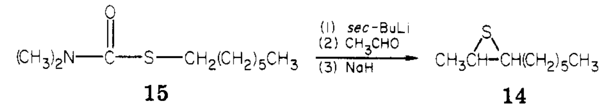
[a] Ar = 2,4,6-triisopropylphenyl.

Scheme IV[a]



[a] Ar = 2,4,6-triisopropylphenyl; Ar′ = 2,6-diisopropylphenyl.

ment with potassium hydroxide and reaction with benzoyl chloride while **7** is converted to **11** in 62% yield when hydrolysis is followed by treatment with acetic anhydride. The β′-hydroxy adduct **9** (E = C_6H_5CHOH) is converted to the thiirane **12** in 81% yield on treatment with sodium hydride. Reaction of **5** with benzophenone followed by base, however, provides the olefin **13** in 62% yield, presumably via the substituted carbamate and the thiirane. The synthesis of **14** from *n*-heptyl *N*,*N*-dimethylthiocarbamate **15** in 76% yield demonstrates the synthesis of a 2,3-disubstituted thiirane without isolation of the intermediates. Attempted metalation of isopropyl *N*,*N*-diethylthiocarbamate was not successful at −98 °C.



These results show that thiocarbamates are useful in the generation of α-lithioalkanethiol synthetic equivalents. The syntheses of thiocarbamates from thiols are straightforward, the metalation and substitution is now established, and the hydrolyses are relatively easy.

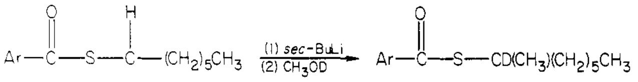
Lithiation of Thioesters. The sterically hindered isopropyl 2,4,6-triisopropylthiobenzoate (**16**) can be lithiated at −98 °C in 2 h to give **17**, which undergoes addition to a variety of electrophiles to give the products **18–30** as shown in Scheme II and Table II. While **17** did not appear to react with acetone, a 30% yield of adduct **26** was obtained on reaction with acetone-d_6, and the recovered ester from this reaction was 70% **17**-d_1. The apparent failure of the reaction with acetone is then attributed to competing enolization. Reaction of **25** with sodium hydride gave 2,2-dimethyl-3-phenylthiirane (**31**). This result and the above thiirane syntheses from the carbamates extend the methodology used to convert aldehydes and ketones to 2-substituted thiiranes[2a,n–s,4] to 2,3-substituted thiiranes. Reduction of **21** with lithium aluminum hydride gives 2,4,6-triisopropylbenzyl alcohol and a volatile material characterized by ^1H NMR as 2-methylheptane-2-thiol. Thus, **17** is an α-lithiodialkanethiol synthetic equivalent.

When the lithiation of **16** was carried out at −78 °C or a solution of **17** was allowed to warm from −98 to −78 °C and acetic anhydride was used as an electrophile, the keto thioester **32** was obtained in 30% yield as shown in Scheme II. The structure of **32** was confirmed by hydrolysis and reduction of the resulting thiol ketone to isopropyl 2,4,6-triisopropylphenyl ketone.

Two paths can be envisioned for the formation of **33**, the precursor of **32** as shown in Scheme III. Intramolecular addition to the carbonyl could provide **33** via the thiirane **34**; intermolecular attack on the carbonyl of a second molecule of **17** could provide **35**, which could give **33**. An analogous intermolecular route was shown to be the pathway of formation of β-diketones from sterically unhindered thioesters.[2a]

These two paths can be distinguished by the double labeling experiment shown in Scheme IV. Lithiation, rearrangement, and acylation of an equimolar mixture of isopropyl 2,4,6-triisopropylthiobenzoate (**16**) with isopropyl-d_6 2,6-diisopropylthiobenzoate (**36**) will give two products, **32** and **37**, in the case of the intramolecular pathway, while four products, **32** and **37–39**, result from the intermolecular processes.[5] The products are readily distinguishable by mass spectrometry. An equimolar mixture of **16** and **36** gave a mixture of products that displayed molecular ions for **32** and **37**, at m/e 312 and 348, but not for **38** and **39**, at m/e 306 and 354. We estimate on this basis that at least 80% of the conversion of **16** to **33** proceeds via **34** on the intramolecular pathway. A similar rearrangement was reported by Hayashi and Baba for the reaction of β-methylallyl and benzyl N,N-dimethyldithiocarbamates with lithium diisopropylamide in HMPA/THF at −60 °C as an intramolecular "thio-Wittig" rearrangement.[6] It is interesting that with the thioesters the tertiary system undergoes rearrangement and the primary, secondary, and allyl systems (vide infra) are stable. In the case of the esters the allyl system rearranged, whereas the primary and secondary organolithiums were stable.[1d]

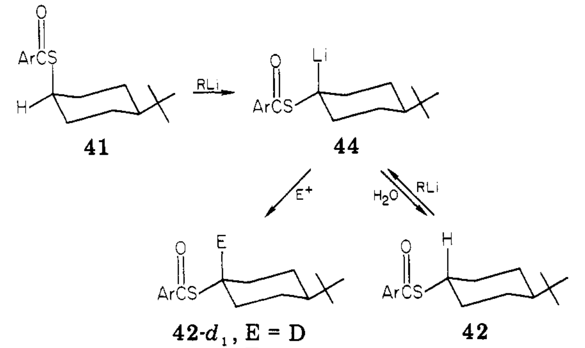
The finding that it is possible to form tertiary α'-lithio thioesters allows the investigation of the configurational stability of these species. Metalation of (S)-2′-octyl 2,4,6-triisopropylthiobenzoate ((S)-**40**) followed by reaction with methanol-d gives a mixture of (S)-**40** and 66% 2-deuterio-2′-octyl 2,4,6-triisopropylthiobenzoate (**40**-d_1). On the basis of the assumption that deuterium has little effect on the optical rotation, the product is 68% racemized.[7] A similar reaction gave material that was 40% **40**-d_1 by mass spectral analysis and 38% racemized as determined by optical rotation.



(S)-**40** (R,S)-**40**-d_1

Ar = 2,4,6-triisopropylphenyl

In a different test of the configurational stability of the α'-lithio thioesters, the metalations of *cis*- and *trans*-4′-*tert*-butylcyclohexyl 2,4,6-triisopropylthiobenzoate (**41** and **42**, respectively) were investigated. Deprotonation of the cis-isomer **41** with *sec*-BuLi/TMEDA followed by reaction with methanol-d gives after chromatographic separation **41** and completely deuterated trans-isomer **42**-d_1 in 47% yield. When **42** is metalated and the anion is quenched with methanol-d, a mixture of **42** (80%) and **42**-d_1 (20%) is obtained. Similarly the metalations of **41** and **42** followed by reaction with iodomethane give a single product, **43**. The stereochemistry of the product **43** is assigned as trans by comparison of the C–S stretch in the IR spectrum with those of **41** and **42**, by the fact that the signals for the methylene groups of **43** in the ^{1}H NMR spectrum are similar to those in the spectrum of **42**, and by analogy to the course of the deuteration. If it is presumed that reactions of the intermediate **44** occur with retention of configuration, the stereochemistry shown, with an axial lithium, may also be assigned. These results show that metalated α'-lithio thioesters are configurationally equilibrated either in the formation of the lithiated species, in the intermediate organometallic, or in quenching the reaction.



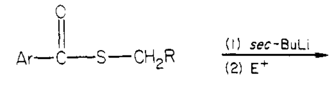
41 **44**

42-d_1, E = D
43, E = CH_3
42

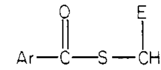
Ar = 2,4,6-triisopropylphenyl

Our studies of α'-lithio esters suggest that medium chain, α' and β' heterosubstituted, and allyl systems give abnormal reactions.[1d] With α'-lithio thioesters only the β'-alkoxy substituents lead to products different from those expected for direct substitution.

Deprotonation of heptyl 2,4,6-triisopropylthiobenzoate (**45**) is accomplished with *sec*-BuLi/TMEDA at −98 °C in THF. Reactions of the intermediate anion with acetone and benzaldehyde give the expected β'-hydroxy thioesters **46** and **47** in 37% and 68% yields, respectively. The medium-length alkyl chain group does not seem to hinder the reaction.



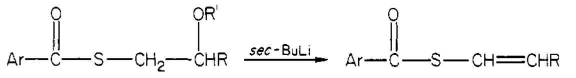
45, R = n-C_6H_{13}
48, R = $CH_2N(CH_3)_2$



46, E = $(CH_3)_2COH$; R = n-C_6H_{13}
47, E = C_6H_5CHOH; R = n-C_6H_{13}
50, E = CH_3; R = $CH_2N(CH_3)_2$

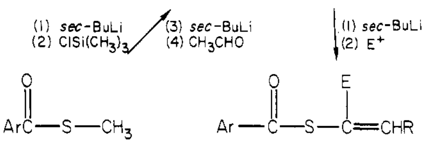
Three thioesters with β'-heteroatom substitution were studied. Metalation of 2′-(diethylamino)ethyl 2,4,6-triisopropylthiobenzoate (**48**) followed by reaction with iodomethane gives the expected product **50** in 66% yield.

The β'-alkoxyl system 2′-ethoxyethyl 2,4,6-triisopropylthiobenzoate (**49**), on the other hand, undergoes elimination of lithium ethoxide under the same metalation conditions to give vinyl 2,4,6-triisopropylthiobenzoate (**51**). Metalation of **51** followed by electrophilic trapping with methanol-d, iodomethane, or benzaldehyde gives the vinyl thioester products **52–54** in 76% (82% d_1), 86%, and 54% yields. Similarly, deprotonation of 2′-methoxy-1′-propyl 2,4,6-triisopropylthiobenzoate (**55**) gives the propenyl thioester **57** with a Z to E ratio of 1:5.7. Another route to this thioester is deprotonation of the methyl thioester **56** followed by reaction with chlorotrimethylsilane to give (trimethylsilyl)methyl 2,4,6-triisopropylthiobenzoate



49, R = H; R′ = C_2H_5
55, R = CH_3; R′ = CH_3

51, R = H
57, R = CH_3



56

52, E = D; R = H
53, E = CH_3; R = H
54, E = C_6H_5CHOH; R = H
58, E = CH_3CHOH; R = CH_3

Ar = 2,4,6-triisopropylphenyl

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[5] It was established that **36** undergoes lithiation, rearrangement, and acylation to **37** at −78 °C in an independent experiment in the absence of **16**.

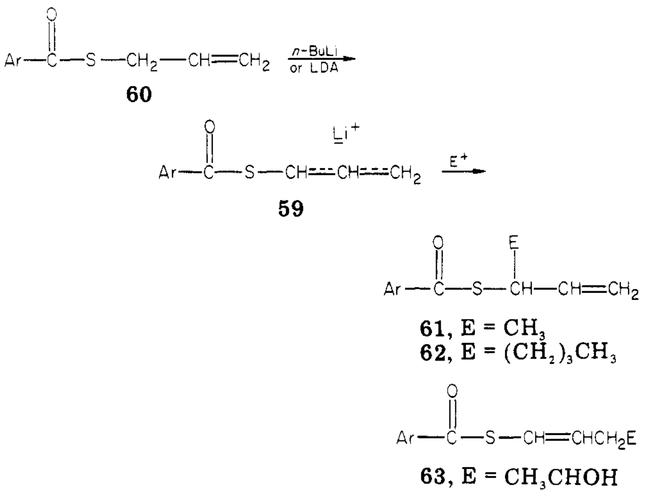
[6] Hayashi, T.; Baba, H. *J. Am. Chem. Soc.* **1975**, *97*, 1608.

[7] Fryzuk, M. D.; Bosnich, B. *J. Am. Chem. Soc.* **1977**, *99*, 6262.

which, in a Peterson olefination,[8] is deprotonated and trapped with acetaldehyde to give **57** with *Z* to *E* ratio of 1:1.5. Reaction of **57** with *sec*-BuLi/TMEDA followed by reaction with acetaldehyde gives **58** in 62% yield.

The eliminations are similar to those previously reported,[1d] and the lithiation is analogous to the reaction of (*S*)-2-methylpropenyl *N*,*N*-dimethylthiocarbamate with *t*-butyllithium recently reported by Hoppe.[9]

It is interesting to note that no product from the deprotonation at the γ-carbon to form an allylic anion was observed in the case of **57**. An α′-lithio thioallyl anion, **59**, was produced, however, when allyl 2,4,6-triisopropylthiobenzoate (**60**) was treated with either *n*-butyllithium or lithium diisopropylamide, at −98 °C in THF. Reaction of **59** with iodomethane and 1-iodobutane gives the α-substituted products **61** (46%) and **62** (45%), respectively, while reaction of **59** with acetaldehyde gives the γ-substituted product (*Z*)-**63** in 62% yield. This regiochemistry is similar to that reported with other α-thioallyl carbanions.[2f–h,10]



60

59

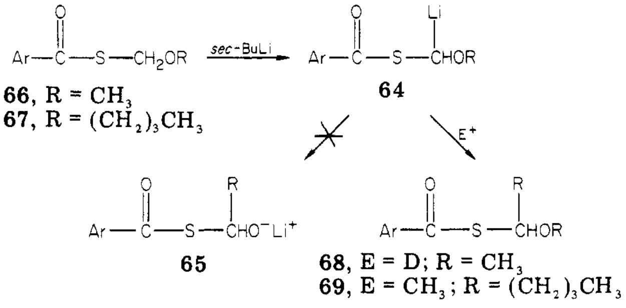
61, E = CH_3

62, E = $(CH_2)_3CH_3$

63, E = CH_3CHOH

Ar = 2,4,6-triisopropylphenyl

Deprotonations of the α′-alkoxy thioesters was briefly investigated because of the interesting possibility that the intermediate **64** could undergo a Wittig rearrangement to **65**, thus providing a novel homologation of an alcohol precursor. We find, however, that deprotonations of the methoxymethyl and butoxymethyl 2,4,6-triisopropylthiobenzoates **66** and **67** give **64** as a stable carbanion at −98 °C. Electrophilic trapping proceeds normally to give **68** in 65% yield (90% d_1) with methanol-*d* from **66** or to give **69** in 72% yield with iodomethane from **67**. Longer reaction times for the anions from **67** give the thiobenzoate as indicated by isolation of **56** after addition of iodomethane. Presumably the latter arises from an α,β′ elimination.[11]



66, R = CH_3

67, R = $(CH_2)_3CH_3$

64

65

68, E = D; R = CH_3

69, E = CH_3; R = $(CH_2)_3CH_3$

Ar = 2,4,6-triisopropylphenyl

Relative Kinetic Acidities of Thioesters. We have previously shown the methyl thioester **56** is thermodynamically more acidic than dimethyl sulfide.[2a] Attempts to similarly determine the relative thermodynamic acidities of these substituted thioesters failed because equilibration appears to be slower than decomposition. Thus, when the anion of ethyl 2,4,6-triisopropylthiobenzoate (**70**) was generated, treated with the methyl thioester **56** and subsequently with methanol-*d*, the the product contained deuterium mostly in the ethyl thioester. However, when a mixture of **70** and **56** was treated with *sec*-BuLi/TMEDA followed by methanol-*d*, the only product obtained was the deuterated methyl thioester **56**-d_1. Addition of *sec*-BuLi/TMEDA to a mixture of **56** and the propenyl thioester **57** gave, after quenching with methanol-*d*, thioesters containing comparable amounts of deuterium.

These experiments show that the methyl thioester **56** is kinetically more acidic than the ethyl thioester **70** and that **56** has a kinetic acidity comparable to the vinyl proton of the propenyl thioester **57**.

Summary. The present studies of the lithiations of thiocarbamates and thioesters provide α′-lithio thio intermediates that are synthetic equivalents for the α-lithioalkanethiol and α-lithiodialkanethiol species. The use of these species in thiirane synthesis is demonstrated. In addition, the formation and electrophilic trapping of primary, vinyl, and allyl α′-lithio thioesters is reported. Neither configurational nor conformational stability is found with tertiary α′-lithio thioesters.

Experimental Section[12]

General Methods. Materials and solvents from commercial sources were used without further purification with the following exceptions: tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl, *N,N,N′,N′*-tetramethylethylenediamine (TMEDA) was distilled from calcium hydride, and hexane used for chromatography was bulk grade distilled from molecular sieves. The activities of the *sec*-butyllithium (*sec*-BuLi) and *n*-butyllithium (*n*-BuLi) were determined by titration with 2-butanol using 1,10-phenanthroline as indicator.

Thiocarbamates and thioesters were in general prepared by reaction of the thiol with sodium hydride in diethyl ether followed by addition of the appropriate acid chloride, extractive workup, and medium pressure liquid chromatography (MPLC) or distillation.[12b] The preparation of **16** is representative.

Isopropyl 2,4,6-Triisopropylthiobenzoate (16). A solution of 10.0 g (40.3 mmol) of 2,4,6-triisopropylbenzoic acid[13] and excess thionyl chloride was stirred for 18 h and heated at reflux for 5 h, and the thionyl chloride was removed by distillation. To the residue were added 50 mL of 2-propanethiol and 120 mmol of sodium hydride, and the mixture was heated at reflux for 40 h. The 2-propanethiol was removed by distillation and the residue

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dissolved in diethyl ether, washed with aqueous NH_4Cl, and dried ($MgSO_4$). The solvent was removed at reduced pressure and the residue distilled at reduced pressure ((145–152 °C (1 torr)) to give 9.95 g (81%) of **16** as an oil, which on standing formed crystals: mp 52 °C; IR (neat) 2930, 1663, 1605, 1460, 1385, 1211, 947, 901, 835, 772 cm^{-1}; ^1H NMR (CCl_4) δ 1.23 (d, 18, *J* = 7 Hz, Ar $CH(CH_3)_2$), 1.39 (d, 6, *J* = 7 Hz, $SCH(CH_3)_2$), 2.9 (m, 3, *J* = 7 Hz, Ar $CH(CH_3)_2$), 3.76 (m, 3, *J* = 7 Hz, $SCH(CH_3)_2$), 6.83 (s, 2, Ar H); mass spectrum (70 eV), *m/e* (rel intensity) 306 (0.35), 232 (20), 231 (100), 217 (10), 129 (4), 91 (4), 43 (5), 41 (3). Anal. ($C_{19}H_{30}OS$) C, H, S.

Ethyl *N,N*-dimethylthiocarbamate (4) was obtained from ethanethiol and *N,N*-dimethylcarbamyl chloride as a liquid in 89% yield; IR (neat) 2900, 1650 (C=O), 1360, 1260, 1100, 920 cm^{-1}; ^1H NMR (CCl_4) δ 1.27 (t, 3, *J* = 7 Hz, SCH_2CH_3), 2.87 (q, 2, *J* = 7 Hz, SCH_2CH_3), 3.02 (s, 6, $N(CH_3)_2$); mass spectrum (70 eV), *m/e* (rel intensity) 133 (16.1), 105 (5.7), 100 (4.7), 72 (100), 58 (4.9), 43 (9.9), 42 (7.3). Anal. (C_5H_7NOS) C, H, N, S.

Heptyl *N,N*-dimethylthiocarbamate (15) was obtained from 1-heptanethiol and *N,N*-dimethylcarbamyl chloride in 80% yield as a colorless liquid: IR (neat) 2900, 1650 (C=O), 1360, 1100, 940, 685 cm^{-1}; ^1H NMR (CCl_4) δ 0.87 (m, 3, $(CH_2)_6CH_3$), 1.3 (m, 10, $CH_2CH_2)_5CH_3$), 2.78 (t, 2, *J* = 7 Hz, SCH_2CH_2), 2.96 (s, 6, $N(CH_3)_2$). Anal. ($C_{10}H_{21}NOS$) C, H, N, S.

2′-Octyl 2,4,6-triisopropylthiobenzoate (40) was prepared from 2-octanethiol and 2,4,6-triisopropylbenzoyl chloride in 60% yield as a pale yellow viscous oil: IR (neat) 2930, 1663 (C=O) 1605, 1460, 1385, 1210, 947, 901, 835, 772, 725 cm^{-1}; ^1H NMR (CCl_4) δ 0.75–1.75 (34, Ar $CH(CH_3)_2$ and $SCH(CH_3)(n\text{-}C_6H_{13})$), 2.9 (m, 3, *J* = 7 Hz, Ar $CH(CH_3)_2$), 3.67 (m, 1, *J* = 7 Hz, $SCH(CH_3)(n\text{-}C_6H_{13})$), 6.81 (s, 2, Ar H). Anal. ($C_{24}H_{40}OS$) C, H, S.

(*S*)-2′-Octyl 2,4,6-triisopropylthiobenzoate ((*S*)-40) was prepared from (*S*)-2-octanethiol[14] and 2,4,6-triisopropylbenzoyl chloride in 43% yield; $[\alpha]^{25}_D$ 20.62 ± 1.79° (*c* 0.1, cyclohexane); IR and ^1H NMR spectra are identical with those of the racemic material. Anal. ($C_{24}H_{40}OS$) C, H, S.

***cis*-4′-*tert*-Butylcyclohexyl 2,4,6-triisopropylthiobenzoate (41)** was prepared from 2,4,6-triisopropylbenzoyl chloride and *cis*-4-*tert*-butylcyclohexanethiol[14] in 41% yield; mp 91–92.5 °C; IR (mull) 2950, 1680 (C=O), 1460, 1360, 1205, 900, 772 (C–S), 762 (C–S); ^1H NMR (CCl_4) δ 0.87 (s, 9, $C(CH_3)_3$), 1.27 (d, 18, *J* = 7 Hz, Ar $CH(CH_3)_2$), 1.2–2.1 (m, 9, cyclohexyl), 2.9 (m, 3, *J* = 7 Hz, Ar $CH(CH_3)_2$), 4.12 (m, 1, *J* = 2 Hz, $SCH(CH_2)_2$), 6.86 (s, 2, Ar H); ^{13}C NMR ($CDCl_3$) δ 23.3 (cyclohexyl-3,5), 23.9 (Ar CC-4), 24.4 (2,6-(Ar CC-2,6), 27.3 (*t*-Bu), 30.6 (Ar CC-2, 6), 32.0 (cyclohexyl-2,6), 32.5 (*t*-Bu), 34.4 (4-Ar CC-4), 42.3 (cyclohexyl-1), 47.8 (cyclohexyl-4) 121.0 (Ar C-3,5), 136.1 (Ar C-1), 144.4 (Ar C-2,6), 150.2 (Ar C-4), 197.7 (C=O). Anal. ($C_{26}H_{42}OS$) C, H, S.

***trans*-4′-*tert*-Butylcyclohexyl 2,4,6-triisopropylthiobenzoate (42)** was prepared from 2,4,6-triisopropylbenzoyl chloride and *trans*-4-*tert*-butylcyclohexanethiol[15] in 4% yield; mp 88–90 °C; IR (oil mull) 2900, 1680 (C=O), 1460, 1370, 1210, 945, 900, 767 (C–S) cm^{-1}; ^1H NMR (CCl_4) δ 0.88 (s, 9, $C(CH_3)_3$), 1.21 (d, 12, *J* = 7 Hz, Ar $CH(CH_3)_2$), 1.24 (d, 6, *J* = 7 Hz, Ar CH $(CH_3)_2$), 1.1–2.4 (m, 9, cyclohexyl H), 2.95 (m, 3, Ar $CH(CH_3)_2$), 3.46 (m, 1, $J_{H_{ax}H_{ax}}$ = 12 Hz, $J_{H_aH_{eq}}$ = 4 Hz, $SCH(CH_2)_2$), 6.85 (s, 2, Ar H); ^{13}C NMR ($CDCl_3$) δ 23.9 (Ar CC), 24.4 (Ar CC-2,6), 27.5 (*t*-Bu), 27.7 (cyclohexyl-3,5), 30.6 (2,6-(Ar 2,6-CC), 32.4 (*t*-Bu), 33.5 (cyclohexyl-3,5), 34.4 (4-(Ar CC-4), 43.5 (cyclohexyl-1), 47.3 (cyclohexyl-4), 121.0 (Ar C-3,5), 136.0 (Ar C-1), 144.5 (Ar C-2,6) 150.2 (Ar C-4), 198.3 (C=O). Anal. ($C_{26}H_{42}OS$) C, H, S.

Heptyl 2,4,6-triisopropylthiobenzoate (45) was prepared from 2,4,6-triisopropylbenzoyl chloride and 1-heptanethiol[16] in 88% yield as a colorless oil: IR (neat) 2960, 1680 (C=O), 1460, 1210, 945, 895, 835, 765 cm^{-1}; ^1H NMR (CCl_4) δ 0.75–1.9 (m, 13, $SCH_2\text{-}n\text{-}C_6H_{13}$), 1.22 (d, 18, *J* = 7 Hz, Ar $CH(CH_3)_2$), 2.9 (m, 3, *J* = 7 Hz, Ar $CH(CH_3)_2$), 2.95 (t, 2, *J* = 7 Hz, $SCH_2\text{-}n\text{-}C_6H_{13}$), 6.82 (s, 2, Ar H). Anal. ($C_{23}H_{38}OS$) C, H, S.

2′-(Diethylamino)ethyl 2,4,6-triisopropylthiobenzoate (48) was prepared from 2,4,6-triisopropylbenzoyl chloride and (diethylamino)ethanethiol in 83% yield as a pale yellow solid: IR (mull) 2900, 1680 (C=O), 1460, 1210, 900, 770 cm^{-1}; ^1H NMR (CCl_4) δ 1.04 (t, 6, *J* = 7 Hz, NCH_2CH_3), 1.23 (d, 18, *J* = 7 Hz, Ar $CH(CH_3)_2$), 23–2.7 (m, 6, $CH_2NCH_2CH_3$), 2.7–3.1 (m, 5, Ar $CH(CH_3)_2$, SCH_2CH_2), 6.83 (s, 2, Ar H). Anal. ($C_{22}H_{37}ONS$) C, H, N, S.

2′-Ethoxyethyl 2,4,6-triisopropylthiobenzoate (49) was prepared from 2,4,6-triisopropylbenzoyl chloride and ethoxyethanethiol[14,17] in 75% yield as a waxy solid: mp 43–46 °C; IR (mull) 2910, 1680 (C=O), 1460, 1380, 1110, 950, 900, 770 cm^{-1}; ^1H NMR (CCl_4) δ 1.10 (t, 3, *J* = 7 Hz, OCH_2CH_3), 1.22 (d, 18, *J* = 7 Hz, Ar $CH(CH_3)_2$), 2.90 (m, 3, *J* = 7 Hz, Ar $CH(CH_3)_2$), 3.13 (t, 2, *J* = 6 Hz, SCH_2CH_2O), 3.42 (q, 2, *J* = 7 Hz, OCH_2CH_3), 3.54 (t, 2, *J* = 6 Hz, SCH_2CH_2O), 6.83 (s, 2, Ar H). Anal. ($C_{20}H_{32}O_2S$) C, H, S.

Isopropyl-*d*₆ 2,6-diisopropylthiobenzoate (36) and 2′-methoxypropyl 2,4,6-triisopropylthiobenzoate (55) were prepared by lithiation and electrophilic trapping of the appropriate methyl thioesters.

Allyl 2,4,6-triisopropylthiobenzoate (60), methoxymethyl 2,4,6-triisopropylthiobenzoate (66), and butoxymethyl 2,4,6-triisopropylthiobenzoate (67) were prepared by displacements of 2,4,6-triisopropylthiobenzoate on the appropriate halide. Details are available.[12b,18]

General Procedure for Reaction of Thiocarbamates and Thioesters with *sec*-BuLi/TMEDA or *n*-BuLi. Glassware was oven-dried at 150 °C and allowed to cool under a nitrogen atmosphere prior to use. The thiocarbamate or thioester was dissolved in THF and cooled to −78 °C (dry ice/2-propanol) or −98 °C (liquid nitrogen/methanol). After addition of 1.1–2 equiv excess of *sec*-BuLi and TMEDA or *n*-BuLi the solution was allowed to stir for 0.5–4 h before the electrophile was added. After being allowed to stir an additional 0.5–1 h, the reactants were allowed to warm to room temperature. The solution was diluted with diethyl ether, washed with saturated ammonium chloride and dried ($MgSO_4$). The diethyl ether was removed at reduced pressure, and the product was purified by distillation on a Kügelrohr apparatus or by MPLC. Reactants, yields of analytically pure products, and spectral characterization will be given here. Other details are available.[12b,18]

1-Deuterioethyl *N,N*-dimethylthiocarbamate (4-*d*) was obtained from **4** and methanol-*d* in 88% yield; IR (neat) 2900, 2150 (C–D), 1650 (C=O), 1350, 1090, 910, 695 cm^{-1}; ^1H NMR (CCl_4) δ 1.23 (d, 3, *J* = 7 Hz, $SCHDCH_3$), 2.74 (q of t, 1.1, J_{HD} = 2 Hz, J_{HH} = 7 Hz, $SCHDCH_3$), 2.9 (s, 6, $N(CH_3)_2$); mass spectrum (70 eV) oscillograph trace, *m/e* (rel intensity) 136 (4.9), 135 (7.5), 134 (100), 133 (1.78).

2-Nonyl *N,N*-dimethylthiocarbamate (6) was obtained as a liquid from **4** and 1-iodoheptane in 81% yield; ^1H NMR (CCl_4) δ 0.9 (m, 3, $(CH_2)_6CH_3$), 1.2–1.6 (m, 15, $SCH(CH_3)(CH_2)_6$), 2.95 (s, 6, $N(CH_3)_2$), 3.4 (m, 1, SCH). The thioester **6** was converted to the liquid **10** by hydrolysis and reaction with benzoyl chloride in 58% yield; IR (neat) 2900, 1660 (C=O), 1210, 915, 775, 690 cm^{-1}; ^1H NMR (CCl_4) δ 0.9 (m, 3, $(CH_2)_6CH_3$), 1.2–1.6 (m, 15, $SCH(CH_3)(CH_2)_6$), 3.75 (m, 1, SC*H*), 7.3–8.0 (m, 5, C_6H_5).

2-Phenylethyl *N,N*-dimethylthiocarbamate (7) was obtained as a liquid from **4** and benzoyl chloride in 66% yield; ^1H NMR (CCl_4) δ 1.2 (d, 3, *J* = 7 Hz, $SCHCH_3$), 2.55 (d of d, 1, *J* = 13 Hz, *J* = 9 Hz, $SCHCH_AH_BPh$), 2.95 (s, 6, $N(CH_3)_2$), 3.10 (d of d, 1, *J* = 13 Hz, *J* = 6 Hz, $SCHCH_AH_BPh$), 3.65 (m, 1, SCH), 7.2 (br s, 5, C_6H_5). The thioester **7** was converted to **11** by hydrolysis and reaction with acetic anhydride in 70% yield; IR (neat) 2950, 1680 (C=O), 1120, 960, 755, 705 cm^{-1}; ^1H NMR (CCl) 1.2 (d, 3, *J* = 7 Hz, $SCHCH_3$), 2.2 (s, 3, $C{=}OCH_3$), 2.5–3.1 (m, 2, $SCHCH_2Ph$), 3.7 (m, 1, SCH), 7.15 (br s, 5, C_6H_5).

3-Hydroxy-2-butyl *N,N*-dimethylthiocarbamate (8) was obtained as a liquid from **4** and acetaldehyde in 76% yield; IR (neat) 3400 (OH), 2950, 1640 (C=O), 1100, 920 cm^{-1}; ^1H NMR (CCl_4) δ 1.1–1.4 (m, 6, $SCH(CH_3)CHCH_3$), 2.8 (s, 1, OH), 3.0 (s, 6, $N(CH_3)_2$), 3.4–4.0 (m, 2, $SCH(CH_3)CHCH_3$).

1-Hydroxy-1-phenyl-2-propyl *N,N*-dimethylthiocarbamate (9) was obtained as a solid from **4** and benzaldehyde in 50% yield; ^1H NMR (CCl_4) δ 1.05 (d, 3, *J* = 7 Hz, $SCHCH_3$), 2.9 (s, 6,

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(18) Details are available as supplementary material, which appears in the microfilm edition of this journal.

$N(CH_3)_2$), 3.4 (s, 1, OH), 3.7 (m, 1, SCH), 4.9 (d, 1, J = 2 Hz, SCHCHPh), 7.1–7.4 (m, 5, Ar H).

2-Methyl-3-phenylthiirane (12), obtained as a single diastereomer from **9** in 81% yield and as a 23:77 mixture of diastereomers from **4** without purification of intermediates, had analytical and spectral properties consistent with the established structure.[2a]

1,1-Diphenylpropene (13) was obtained from **4** and benzophenone heated at reflux in ethanol in 62% yield; mp 47.5–48.5 °C; (lit.[19] mp 52 °C).

2-Hexyl-3-methylthiirane (14) was obtained as a liquid mixture of diastereomers from **15** and acetaldehyde in 67% yield as described for **12**;[2a] IR (neat) 2950, 1460, 1070, 790 cm^{-1}; ^{1}H NMR (CCl_4) δ 0.90 (m, 3, $(CH_2)_5CH_3$), 1.3 (m, 10, $(CH_2)_5$), 1.5 (d, 3, J = 6 Hz, $SCHCH_3$), 2.5 (m, 0.8, $\overline{\mathrm{SCHC}}\mathrm{H}$), 2.8 (m, 1.2, $\overline{\mathrm{SCHC}}\mathrm{H}$).

2′-Deuterio-2′-propyl 2,4,6-triisopropylthiobenzoate (16-*d*$_1$) was obtained from **16** and methanol-*d* in 69% yield; mp 51.5–52.5 °C; IR (neat) 2930, 2190 (C–D), 1660 (C=O), 1605, 1460, 1385, 1211, 947, 901, 835 cm^{-1}; ^{1}H NMR (CCl_4) δ 1.22 (d, 18, J = 7 Hz, Ar $CH(CH_3)_2$), 1.39 (s, 6, $SCD(CH_3)_2$), 2.9 (m, 3, J = 7 Hz, Ar $CH(CH_3)_2$), 6.8 (s, 2, Ar H); mass spectrum (70 eV), m/e (rel intensity) 232 (21), 231 (100), 217 (7), 213 (4), 129 (5), 91 (7), 43 (21), 41 (9); oscillograph trace (8.6 eV), m/e (rel intensity) 310 (1.36), 309 (6.72), 308 (21.34), 307 (100), 306 (8.72).

***tert*-Butyl 2,4,6-triisopropylthiobenzoate (18)** was obtained from **16** and iodomethane in 38% yield; mp 74–76 °C; IR (mull) 2920, 1660 (C=O), 1460, 1360, 1210, 1160, 945, 900, 885, 835, 772 (C–S) cm^{-1}; ^{1}H NMR (CCl_4) δ 1.25 (d, 18, J = 7 Hz, Ar $CH(CH_3)_2$, 1.56 (s, 9, $SC(CH_3)_3$), 2.95 (m, 3, J = 7 Hz, Ar $CH(CH_3)_2$), 6.82 (s, 2, Ar H).

2′-(Trimethylsilyl)propyl 2,4,6-triisopropylthiobenzoate (19) was obtained from **16** and chlorotrimethylsilane in 25% yield; mp 58–62 °C; IR (mull) 2960, 1675 (C=O), 1605, 844 cm^{-1}; ^{1}H NMR (CCl_4) δ 0.08 (s, 9, $Si(CH_3)_3$), 1.27 (d, 18, J = 7 Hz, Ar $CH(CH_3)_2$), 1.63 (s, 6, $SC(CH_3)_2Si$), 2.9 (m, 3, J = 7 Hz, Ar $CH(CH_3)_2$), 6.78 (s, 2, Ar H).

2′-Methyl-2′-hexyl 2,4,6-triisopropylthiobenzoate (20) was obtained from **16** and iodopentane in 65% yield as a colorless oil: ^{1}H NMR (CCl_4) δ 0.90 (m, 3, $(CH_2)_4CH_3$), 1.20 (d, 18, J = 7 Hz, Ar $CH(CH_3)_2$), 1.2–1.8 (m, 8, $(CH_2)_4$), 1.55 (s, 6, $SC(CH_3)_2$), 3.0 (m, 3, J = 7 Hz, Ar $CH(CH_3)_2$), 6.85 (s, 2, Ar H).

Reduction of 21 with lithium aluminum hydride gave a low-boiling liquid that was identified by NMR as 2-methyl-heptane-2-thiol and a highboiling residue in 76% yield identified as 2,4,6-triisopropylbenzyl alcohol: mp 89–90 °C; IR (mull) 3200 (OH), 1605, 1005, 880 cm^{-1}; ^{1}H NMR (CCl_4) δ 1.2 (d, 18, J = 7 Hz, Ar $CH(CH_3)_2$), 2.8 (m, 1, J = 7 Hz, Ar $CH(CH_3)_2$), 3.3 (m, 2, J = 7 Hz, $ArCH(CH_3)_2$), 4.5 (d, 2, J = 3 Hz, CH_2OH), 6.9 (s, 2, Ar*H*).

2′-Methyl-2′-octyl 2,4,6-triisopropylthiobenzoate (22) was obtained from **16** and 1-bromohexane as a colorless oil in 47% yield; IR (neat) 2940, 1680 (C=O), 1460, 1210, 945, 895, 765 cm^{-1}; ^{1}H NMR (CCl_4) δ 1.22 (d, 18, J = 7 Hz, Ar $CH(CH_3)_2$), 1.5 (s, 6, $SC(CH_3)_2CH_2$), 2.92 (m, 3, J = 7 Hz, Ar $CH(CH_3)_2$), 6.85 (s, 2, Ar H).

5′-Methyl-2′-hex-4′-enyl 2,4,6-triisopropylthiobenzoate (23) was obtained from **16** and 1-chloro-3-methyl-2-butene as a colorless oil in 43% yield; IR (neat) 2960, 1680 (C=O), 1460, 945, 895, 770 cm^{-1}; ^{1}H NMR (CCl_4) δ 1.25 (d, 18, J = 7 Hz, Ar $CH(CH_3)_2$), 1.52 (s, 6, $SC(CH_3)_2CH_2$), 1.66 (s, 3, $CH{=}C(CH_3)CH_3$), 1.73 (s, 3, $CH{=}C(CH_3)CH_3$), 2.58 (d, 2, J = 7 Hz, $CH_2CH{=}C$), 2.95 (m, 3, J = 7 Hz, Ar $CH(CH_3)_2$), 5.22 (t, 1, J = 7 Hz, $CH_2CH{=}C$), 6.87 (s, 2, Ar H).

3′-Hydroxy-2′-methyl-2′-butyl 2,4,6-triisopropylthiobenzoate (24) was obtained from **16** and acetaldehyde in 72% yield; mp 77–80 °C; IR (mull) 3450 (O–H), 2950, 1680 (C=O), 1460, 1380, 1075, 945, 895 cm^{-1}; NMR (CCl_4) δ 1.30 (d, 21, J = 7 Hz, Ar $CH(CH_3)_2$ and $CH(OH)CH_3$), 1.42 (s, 3, $SC(CH_3)(CH_3)CH$), 1.58 (s, 3, $SC(CH_3)(CH_3)CH$), 2.95 (m, 4, J = 7 Hz, Ar $CH(CH_3)_2$ and OH), 4.04 (q, 1, J = 7 Hz, $CH(OH)CH_3$), 6.90 (s, 2, Ar H).

3′-Hydroxy-3′-phenyl-2′-methyl-2′-propyl 2,4,6-triisopropylthiobenzoate (25) was obtained from **16** and benzaldehyde as an oil which solidified on standing in 51% yield; IR (neat) 3460 (O–H), 2980, 1675 (C=O), 1460, 1150, 900, 770 cm^{-1}; ^{1}H NMR (CCl_4) δ 1.27 (d, 18, J = 7 Hz, Ar $CH(CH_3)_2$), 1.37 (s, 3, $SC(CH_3)(CH_3)$), 1.54 (s, 3, $SC(CH_3)(CH_3)$), 2.95 (m, 3, J = 7 Hz, Ar $CH(CH_3)_2$), 3.38 (d, 1, J = 3 Hz, OH), 5.10 (d, 1, J = 7 Hz, PhCHOH), 6.92 (s, 2, Ar H), 7.1–7.4 (m, 5, C_6H_5CHOH).

2,2-Dimethyl-3-phenylthiirane (31). To 0.95 g (2.31 mmol) of **25** was added 0.40 g (9.5 mmol) of sodium hydride (57%, washed with hexane). After the mixture was stirred in THF at room temperature for 19 h, the solvent was removed in vacuo, and the product was dissolved in diethyl ether and washed with water and HCl (1 M). Chromatography on silica gel and elution with diethyl ether/hexane mixtures gave 0.5151 g (90%) of triisopropylbenzoic acid and an oil which was purified by distillation using a Kugelrohr apparatus 70 °C (1 mm)) to give 0.2359 g (62%) of **31** as a clear liquid: IR (neat) 2950, 1605, 1495, 1450, 1090, 795, 735, 695 cm^{-1}; NMR (CCl_4) δ 1.22 (s, 3, *cis*-$SC(CH_3)$), 1.72 (s, 3, *trans*-$SC(CH_3)$), 3.83 (s, 1, $SCHC_6H_5$), 7.20 (m, 5, C_6H_5). Anal. ($C_{10}H_{12}S$) C, H, S.

2′-Hydroxy-2′-methyl-*d*$_3$-3′-methyl-3′-butyl-1′-*d*$_3$ 2,4,6-triisopropylthiobenzoate (26) was obtained from **16** and acetone-*d*$_6$ in 30% yield; mp 81–84 °C; IR (mull) 3450 (OH), 2900, 2230 weak (C–D), 1650 (C=O), 1460, 1370, 950, 905, 768 cm^{-1}; ^{1}H NMR (CCl_4) δ 1.22 (d, 18, J = 7 Hz, Ar $CH(CH_3)_2$), 1.53 (s, 6, $SC(CH_3)_2C$), 2.95 (m, 3, J = 7 Hz, Ar $CH(CH_3)_2$), 3.38 (s, 1, OH), 6.87 (s, 2, Ar H).

2′-Methyl-3′-oxo-2′-butyl 2,4,6-triisopropylthiobenzoate (27) was obtained from **16** and acetic anhydride in 14% yield; mp 105–105.5 °C; IR (mull) 1706 (C=O), 1660 (C=O), 1605, 1121, 899, 770 cm^{-1}; ^{1}H NMR (CCl_4) δ 1.23 (d, 18, J = 7 Hz, Ar $CH(CH_3)_2$), 1.57 (s, 6, $SC(CH_3)_2C{=}O$), 2.3 (s, 3, $C{=}OCH_3$), 2.9 (m, 3, J = 7 Hz, Ar $CH(CH_3)_2$), 6.87 (s, 2, Ar H); mass spectrum (70 eV), m/e (rel intensity) 263 (0.7), 232 (17.4), 231 (100), 213 (5.0), 139 (3.47), 91 (3.98), 43 (12.5) 28 (12.7).

2′-Methyl-1′-phenyl-1′-oxo-2′-propyl 2,4,6-triisopropylthiobenzoate (28) was obtained from **16** and methyl benzoate in 54% yield; mp 96–100 °C; IR (mull) 2960, 1680 (C=O), 1475, 900, 720 cm^{-1}; ^{1}H NMR (CCl_4) δ 1.02 (d, 12, J = 7 Hz, Ar $CH(CH_3)_2$), 1.20 (d, 6, J = 7 Hz, Ar $CH(CH_3)_2$), 1.85 (s, 6, $SC(CH_3)_2$), 2.39 (m, 2, J = 7 Hz, Ar $CH(CH_3)_2$), 2.77 (m, 1, J = 7 Hz, Ar $CH(CH_3)_2$), 6.8 (s, 2, Ar H), 7.2–7.45 (m, 3, H_{3-5} of PhCO), 7.9–8.1 (m, 2, $H_{2,6}$ of PhCO).

2′-Carbethoxy-2′-propyl 2,4,6-triisopropylthiobenzoate (29) was obtained from **16** and ethyl chloroformate as an oil in 29% yield. IR (neat) 2980, 1730 (C=O), 1680 (C=O), 1460, 1275, 1160, 950, 900, 770 cm^{-1}; ^{1}H NMR (CCl_4) δ 1.27 (d, 18, J = 7 Hz, Ar $CH(CH_3)_2$), 1.33 (t, 3, J = 7 Hz, OCH_2CH_3), 1.67 (s, 6, $SC(CH_3)_2C$), 2.95 (m, 3, J = 7 Hz, Ar $CH(CH_3)_2$), 4.17 (q, 2, J = 7 Hz, OCH_2CH_3), 6.91 (s, 2, Ar H).

2′-Carboxy-2′-propyl 2,4,6-triisopropylthiobenzoate (30) was obtained from **16** and CO_2 in 35% yield; mp 157–159 °C; IR (mull) 2950, 1700 (C=O), 1680 (C=O), 1460, 1280, 1170, 895, 770 cm^{-1}; ^{1}H NMR (CCl_4) δ 1.25 (d, 18, J = 7 Hz, Ar $CH(CH_3)_2$), 1.7 (s, 6, $SC(CH_3)_2CO$), 3.0 (m, 3, J = 7 Hz, Ar $CH(CH_3)_2$), 6.88 (s, 2, Ar H), 12.06 (s, 1, COOH).

(*S*)-Acetyl-2′-thio-2′-propyl 2,4,6-triisopropylphenyl ketone (32) was obtained as a viscous liquid in 30% yield if **16** and *sec*-BuLi/TMEDA were allowed to stand 2 h at −78 °C before addition of acetic anhydride; IR (neat) 2930, 2690 (C=O), 1605, 1460, 1380, 1360, 1106, 957, 877 cm^{-1}; ^{1}H NMR (CCl_4) δ 1.07 (d, 6, J = 7 Hz, Ar $CH(CH_3)_2$), 1.23 (d, 6, J = 7 Hz, Ar $CH(CH_3)_2$), 1.29 (d, 6, J = 7 Hz, Ar $CH(CH_3)_2$), 1.73 (s, 6, $C{=}OC(CH_3)_2S$), 2.15 (s, 3, $SC{=}OCH_3$), 2.75 (m, 3, J = 7 Hz, Ar $CH(CH_3)_2$), 6.84 (s, 2, Ar H); mass spectrum (70 eV), m/e (rel intensity) 348 (0.23), 232 (18), 231 (100), 217 (18), 129 (5), 91 (6), 43 (12), 41 (6). The details of the hydrolysis and reduction of **32**, lithiations and rearrangements of **36** and of a mixture of **16** and **36**, and lithiations and deuterations of (*S*)-**40**, -**41**, and -**42** are described in supplementary material.[12b,18]

***trans*-1′-Methyl-4′-*tert*-butylcyclohexyl 2,4,6-triisopropylthiobenzoate, 43 from 41.** To 0.3169 g (0.79 mmol) of **41** at −98 °C was added 1.58 mmol of *sec*-BuLi/TMEDA. After 2 h iodomethane (1 mL) was added. The product was purified by chromatography on silica gel. Elution with hexane gave 0.1582 g (48%) of **43** as a colorless solid: mp 137–140 °C; IR (mull) 2950,

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[19] Weast, R. C., Ed. "Handbook of Chemistry and Physics", 56th ed.; CRC Press: Cleveland, OH, 1975.

1660 ($\mathrm{C{=}O}$), 1460, 1370, 1210, 1095, 945, 895, 767 $\mathrm{cm^{-1}}$; ^{1}H NMR ($\mathrm{CCl_4}$) δ 0.91 (s, 9, $\mathrm{C(CH_3)_3}$), 1.26 (d, 18, J = 7 Hz, Ar $\mathrm{CH(C\mathbf{H}_3)_2}$), 1.3–2.3 (m, 9, cyclohexyl H), 1.60 (s, 3, $\mathrm{SC(CH_3)}$), 3.0 (m, 3, J = 7 Hz, Ar $\mathrm{C\mathbf{H}(CH_3)_2}$), 6.86 (s, 2, Ar H); ^{13}C NMR ($\mathrm{CDCl_3}$) δ 22.2 ($\mathrm{SCCH_3}$), 23.3 (cyclohexyl *C*-3,5), 23.9 (Ar C*C*-4), 24.5 (ArCC-2,6), 27.5 (*t*-Bu), 30.4 (Ar **C**C-2,6), 32.4 (*t*-Bu), 34.4 (Ar **C**C-4), 37.3 (cyclohexyl C-2,4), 47.6 (cyclohexyl C-4), 52.8 (cyclohexyl C-1), 120.9 (Ar C-3,5), 136.0 (Ar C-1), 144.4 (Ar C-2,6) 150.1 (Ar C-4), 198.9 ($\mathrm{C{=}O}$). Anal. ($\mathrm{C_{27}H_{44}OS}$) C, H, S.

43 from 42. To 0.3403 g (0.85 mmol) of **42** at –98 °C was added 1.69 mmol of *sec*-BuLi/TMEDA. After 4 h iodomethane (0.13 mL) was added. The product was purified by chromatography on silica gel. Elution with hexane gave 0.3087 g (90%) of a colorless solid which is an 88:12 mixture of **42** and **43** as shown by ^{13}C NMR and ^{1}H NMR.

2′-Hydroxy-2′-methyl-3′-nonyl 2,4,6-triisopropylthiobenzoate (46) was obtained from **45** and acetone in 37% yield as a pale-yellow oil purified by preparative plate chromatography: IR (neat) 3450 (OH), 2950, 1680 ($\mathrm{C{=}O}$), 1650, 1460, 1210, 990, 900, 770 $\mathrm{cm^{-1}}$; ^{1}H NMR ($\mathrm{CCl_4}$) δ 0.9 (m, 3, $\mathrm{(CH_2)_5C\mathbf{H}_3}$), 1.27 (d, 18, J = 7 Hz, Ar $\mathrm{CH(C\mathbf{H}_3)_2}$), 1.32 (s, 6, $\mathrm{COH(C\mathbf{H}_3)_2}$), 1.3–2.0 (m, 10, $\mathrm{(CH_2)_5}$), 2.27 (s, 1, OH), 2.97 (m, 3, J = 7 Hz, Ar $\mathrm{C\mathbf{H}(CH_3)_2}$), 3.7 (m, 1, $\mathrm{SC\mathbf{H}CH_2}$), 6.90 (s, 2, Ar H).

1′-Hydroxy-1′-phenyl-2′-octyl 2,4,6-triisopropylthiobenzoate (47) was obtained from **45** and benzaldehyde in 68% yield as an oil which solidified on standing; IR (mull) 3500 (O–H), 2900, 1660 ($\mathrm{C{=}O}$), 1460, 1210, 900 $\mathrm{cm^{-1}}$; ^{1}H NMR ($\mathrm{CCl_4}$) δ 0.88 (t, 3, $\mathrm{(CH_2)_5C\mathbf{H}_3}$), 1.20 (d, 6, J = 7 Hz, Ar $\mathrm{CH(C\mathbf{H}_3)_2}$), 1.26 (d, 12, J = 7 Hz, Ar $\mathrm{CH(C\mathbf{H}_3)_2}$, 1.25–1.9 (m, 10, $\mathrm{CH_2)_5}$), 2.16 (d, 1, J = 3 Hz, OH), 2.8 (m, 3, J = 7 Hz, Ar $\mathrm{C\mathbf{H}(CH_3)_2}$), 4.02 (m, 1, $\mathrm{SC\mathbf{H}CH_2}$), 4.84 (m, 1, $\mathrm{HOC\mathbf{H}Ph}$), 6.85 (s, 2, Ar H), 7.15–7.5 (m, 5, $\mathrm{C_6H_5}$).

1′-(Diethylamino)-2′-propyl 2,4,6-triisopropylthiobenzoate (50) was obtained from **48** and iodomethane in 66% yield as an oil which solidifies on standing; ^{1}H NMR ($\mathrm{CCl_4}$) δ 1.03 (t, 6, J = 7 Hz, $\mathrm{NCH_2C\mathbf{H}_3}$), 1.25 (d, 18, J = 7 Hz, Ar $\mathrm{CH(C\mathbf{H}_3)_2}$), 1.37 (d, 3, J = 7 Hz, $\mathrm{SCHC\mathbf{H}_3}$), 2.6 (m, 6, $\mathrm{CH_2NC\mathbf{H}_2CH_3}$), 3.0 (m, 3, J = 7 Hz, Ar $\mathrm{C\mathbf{H}(CH_3)_2}$), 3.75 (m, 1, J = 7 Hz, SCH), 6.86 (s, 2, Ar H).

Vinyl-1′-d_1 2,4,6-triisopropylthiobenzoate (52) was obtained from **49** and deuterium oxide in 76% yield as an oil: IR (neat) 2910, 2270 (C–D) weak, 1680 ($\mathrm{C{=}O}$), 1460, 1210, 945, 895, 770 $\mathrm{cm^{-1}}$; ^{1}H NMR ($\mathrm{CCl_4}$) δ 1.25 (d, 18, J = 7 Hz, Ar $\mathrm{CH(C\mathbf{H}_3)_2}$), 2.93 (m, 3, J = 7 Hz, Ar $\mathrm{C\mathbf{H}(CH_3)_2}$), 5.40 (s, 1, $\mathrm{SCD{=}CH_{\mathit{E}}\boldsymbol{H}_{\mathit{Z}}}$), 5.46 (s, 1, $\mathrm{SCD{=}C\mathbf{H}_{\mathit{E}}\mathit{H}_{\mathit{Z}}}$), 6.86 (s, 2, Ar H); deuterium analysis, 3.15 mol% (82% d_1).

Isopropenyl 2,4,6-triisopropylthiobenzoate (53) was obtained from **49**, excess *sec*-BuLi/TMEDA, and iodomethane in 86% yield; mp 89–89.5 °C; IR (mull) 2900, 1680, ($\mathrm{C{=}O}$), 1460, 1380, 1365, 1210, 1175, 945, 915, 895, 880, 835, 772 $\mathrm{cm^{-1}}$; ^{1}H NMR ($\mathrm{CCl_4}$) δ 1.26 (d, 18, J = 7 Hz, Ar $\mathrm{CH(C\mathbf{H}_3)_2}$), 2.18 (s, 3, $\mathrm{SC(C\mathbf{H}_3){=}CH_2}$), 2.98 (m, 3, J = 7 Hz, Ar $\mathrm{C\mathbf{H}(CH_3)_2}$), 5.38 (s, 1, $\mathrm{C{=}C\mathbf{H}_AH_B}$), 5.53 (s, 1, $\mathrm{C{=}CH_A\mathbf{H}_B}$), 6.85 (s, 2, Ar H).

1′-Hydroxy-1′-phenyl-2′-propenyl 2,4,6-triisopropylthiobenzoate (54) was obtained from **49** and benzaldehyde in 54% yield; IR (neat) 3400 (O–H), 2950, 1680 ($\mathrm{C{=}O}$), 1605, 1460, 1210, 1060, 945, 895, 880, 835, 767, 700 $\mathrm{cm^{-1}}$; ^{1}H NMR ($\mathrm{CCl_4}$) δ 1.20 (d, 6, J = 7 Hz, Ar $\mathrm{CH(C\mathbf{H}_3)_2}$), 1.26 (d, 12, J = 7 Hz, Ar $\mathrm{CH(C\mathbf{H}_3)_2}$), 2.85 (m, 3, J = 7 Hz, Ar $\mathrm{C\mathbf{H}(CH_3)_2}$), 3.65 (s, 1, OH) 5.42 (s, 1, $\mathrm{C{=}C\mathbf{H}_AH_B}$), 5.66 (s, 1, $\mathrm{C{=}CH_A\mathbf{H}_B}$) 6.12 (s, 1, $\mathrm{HOC\mathbf{H}Ph}$), 6.85 (s, 2, Ar H), 7.1–7.4 (m, 5, $\mathrm{C_6H_5}$).

Propenyl 2,4,6-triisopropylthiobenzoate (57) was obtained from **55** and water in 56% yield as an oil: IR (neat) 2950, 1680 ($\mathrm{C{=}O}$), 1460, 1210, 945, 895, 765 (C–S) $\mathrm{cm^{-1}}$; ^{1}H NMR ($\mathrm{CCl_4}$) δ 1.22 (d, 18, J = 7 Hz, Ar $\mathrm{CH(C\mathbf{H}_3)_2}$), 1.75 (d, 0.45, J = 7 Hz, $\mathrm{CH{=}CH(C\mathbf{H}_3)_{\mathit{Z}}}$), 1.90 (d, 2.55, J = 7 Hz, $\mathrm{CH{=}CH(C\mathbf{H}_3)_{\mathit{E}}}$), 2.93 (m, 3, J = 7 Hz, Ar $\mathrm{C\mathbf{H}(CH_3)_2}$), 5.77 (m, 1, $\mathrm{SCH{=}C\mathbf{H}(CH_3)}$), 6.54 (d, 0.85, J = 17 Hz, $\mathrm{SC\mathbf{H}{=}CH(CH_3)_E}$), 6.86 (s, 2, Ar H). (The signals for $\mathrm{SC\mathbf{H}{=}CH}$, Z isomer, appear at δ 6.7 in the crude product.) Anal. ($\mathrm{C_{19}H_{28}OS}$) C, H, S. The ester **56** was also produced as a *Z,E* mixture from the methyl thioester **56** by lithiation, silylation, lithiation, and addition to acetaldehyde.[12b,18]

2-Hydroxy-3′-pent-3′-enyl 2,4,6-triisopropylthiobenzoate (58) was obtained from **55** and acetaldehyde as an oil in 62% yield; IR (neat) 3450 (O–H), 2920, 1680 ($\mathrm{C{=}O}$), 1460, 1210, 945, 985, 860, 835, 790, 765 $\mathrm{cm^{-1}}$; ^{1}H NMR ($\mathrm{CCl_4}$) δ 1.27 (d, 21, J = 7 Hz, Ar $\mathrm{CH(C\mathbf{H}_3)_2}$ and $\mathrm{HOCHC\mathbf{H}_3}$), 1.97 (d, 3, J = 7 Hz, $\mathrm{C{=}CHC\mathbf{H}_3}$), 2.98 (m, 4, J = 7 Hz, Ar $\mathrm{C\mathbf{H}(CH_3)_2}$ and OH), 4.87 (q, 1, J = 7 Hz, $\mathrm{HOC\mathbf{H}CH_3}$), 6.03 (q, 1, J = 7 Hz, $\mathrm{C{=}C\mathbf{H}CH_3}$), 6.89 (s, 2, Ar H).

3′-But-2′-enyl 2,4,6-triisopropylthiobenzoate (61) was obtained from **60** and iodomethane in 46% yield as an oil: IR (neat) 2970, 1680 ($\mathrm{C{=}O}$), 1460, 1210, 945, 895, 830, 765 $\mathrm{cm^{-1}}$; ^{1}H NMR ($\mathrm{CCl_4}$) δ 1.22 (d, 18, J = 7 Hz, Ar $\mathrm{CH(C\mathbf{H}_3)_2}$), 1.45 (d, 3, J = 7 Hz, $\mathrm{SCHC\mathbf{H}_3}$), 2.88 (m, 3, J = 7 Hz, Ar $\mathrm{C\mathbf{H}(CH_3)_2}$), 4.25 (m, 1, J = 7 Hz, $\mathrm{SC\mathbf{H}CH_3}$), 4.98 (d, 1, J = 10 Hz, $\mathrm{CH{=}C\mathbf{H}_{\mathit{Z}}\mathit{H}_{\mathit{E}}}$), 5.15 (d, 1, J = 17 Hz, $\mathrm{CH{=}CH_{\mathit{Z}}\boldsymbol{C}\boldsymbol{H}_{\mathit{E}}}$), 5.83 (m, 1, $\mathrm{C\mathbf{H}{=}CH_2}$), 6.82 (s, 2, Ar H).

3′-Hept-2′-enyl 2,4,6-triisopropylthiobenzoate (62) was obtained from **60** and iodobutane in 45% yield as a colorless oil: IR (neat) 2920, 1680 ($\mathrm{C{=}O}$), 1605, 1460, 1210, 897, 835, 770 $\mathrm{cm^{-1}}$; ^{1}H NMR ($\mathrm{CCl_4}$) δ 0.93 (t, 3, J = 7 Hz, $\mathrm{(CH_2)_3C\mathbf{H}_3}$), 1.23 (d, 18, J = 7 Hz, Ar $\mathrm{CH(C\mathbf{H}_3)_2}$), 1.2–1.6 (m, 4, $\mathrm{CH_2(C\mathbf{H}_2)_2CH_3}$), 1.70 (t, 2, J = 7 Hz, $\mathrm{C\mathbf{H}_2(CH_2)_2CH_3}$), 2.95 (m, 3, J = 7 Hz, Ar $\mathrm{C\mathbf{H}(CH_3)_2}$, 4.22 (q, 1, J = 7 Hz, $\mathrm{SC\mathbf{H}(CH_2)CH{=}CH_2}$), 5.07 (d, 1, J = 10 Hz, $\mathrm{CHCH{=}C\mathbf{H}_{\mathit{E}}\mathit{H}_{\mathit{Z}}}$), 5.26 (d, 1, J = 17 Hz, $\mathrm{CH{=}CH_{\mathit{E}}\boldsymbol{H}_{\mathit{Z}}}$), 5.82 (m, $\mathrm{C\mathbf{H}{=}CH_2}$), 6.88 (s, 2, Ar H).

4′-Hydroxy-1′-pentenyl 2,4,6-Triisopropylthiobenzoate (63) was obtained from **60** and acetaldehyde in 62% yield as an oil: IR (neat) 3400 (O–H), 2950, 1680, ($\mathrm{C{=}O}$), 1460, 1210, 1120, 950, 895, 835, 780 $\mathrm{cm^{-1}}$; ^{1}H NMR ($\mathrm{CCl_4}$) δ 1.04 (d, 3, J = 6 Hz, $\mathrm{HOCHC\mathbf{H}_3}$), 1.24 (d, 18, J = 7 Hz, Ar $\mathrm{CH(C\mathbf{H}_3)_2}$), 2.19 (t, 2, J = 7 Hz, $\mathrm{CHC\mathbf{H}_2CH}$), 2.5 (s, 1, OH), 2.92 (m, 3, J = 7 Hz, Ar $\mathrm{C\mathbf{H}(CH_3)_2}$), 3.80 (m, 1, J = 6 Hz, $\mathrm{CHC\mathbf{H}OHCH_3}$), 5.88 (m, 1, J = 10 Hz, $\mathrm{SCH{=}C\mathbf{H}}$), 6.74 (d, 1, J = 10 Hz, $\mathrm{SC\mathbf{H}{=}CH}$), 6.90 (s, 2, Ar H).

Methoxymethyl-d_1 2,4,6-triisopropylthiobenzoate (68) was obtained from **66** and deuterium oxide.[12b,18]

1′-*n*-Butoxyethyl 2,4,6-triisopropylthiobenzoate (69) was obtained from **67** and iodomethane in 77% yield as an oil which crystallized on standing; IR (neat) 2950, 1680 ($\mathrm{C{=}O}$), 1110, 895, 835, 770 $\mathrm{cm^{-1}}$; ^{1}H NMR ($\mathrm{CCl_4}$) δ 0.93 (m, 3, $\mathrm{(CH_2)_3C\mathbf{H}_3}$), 1.25 (d, 18, J = 7 Hz, Ar $\mathrm{CH(\mathbf{CH}_3)_2}$), 1.5 (m, 4, $\mathrm{OCH_2(C\mathbf{H}_2)_2}$), 163 (d, 3, J = 6.5 Hz, $\mathrm{SCHC\mathbf{H}_3}$), 2.95 (m, 3, J = 7 Hz, Ar $\mathrm{C\mathbf{H}(CH_3)_2}$), 3.6 (m, 2, $\mathrm{OCH_2}$), 6.53 (q, 1, J = 6.5 Hz, $\mathrm{SC\mathbf{H}CH_3}$), 6.9 (s, 2, Ar H).

Reactions of ethyl 2,4,6-trithiobenzoate (70) with *sec*-BuLi/TMEDA followed by addition of 56, of a mixture of 56 and 70 with *sec*-BuLi/TMEDA, and of a mixture of 56 and 57 with *sec*-BuLi/TMEDA are described in the supplementary material.[12b,18]

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Supplementary Material Available: Experimental details for individual products (20 pages). Ordering information is given on any current masthead page.