$PhCH_2$), 106419-85-6; **31** (R_2 = H), 106419-84-5; **31** (R_2 = CH_3), 106419-86-7; **32** (R_2 = $C_{12}H_{25}$), 98506-67-3; **33** (R_2 = $C_{12}H_{25}$), 106419-87-8; **33** (R_2 = $PhCH_2$), 106434-37-1; **33** (R_2 = H), 106419-88-9; **33** (R_2 = CH_3), 106419-89-0; **34** (R_2 = $C_{12}H_{25}$), 106419-90-3; **34** (R_2 = $PhCH_2$), 106419-91-4; **34** (R_2 = H), 106419-92-5; **34** (R_2 = CH_3), 106419-93-6; **35** (R_2 = $C_{12}H_{25}$), 106419-94-7; **35** (R_2 = $PhCH_2$), 106419-95-8; **35** (R_2 = H), 106419-96-9; **35** (R_2 = CH_3), 106419-97-0; **36**, 106419-98-1; **37**, 106419-99-2; **38**, 106420-00-2; **39**, 106420-01-3; **40**, 106420-02-4; **41**, 106420-03-5; $CH_3(CH_2)_{11}CH(COOEt)_2$, 7252-87-1; $PhCH_2CH(COOEt)_2$, 607-81-8; $CH_2(COOEt)_2$, 105-53-3; $CH_3CH(COOEt)_2$, 609-08-5; *o*-$CH_3OC_6H_4CH_2Br$, 52289-93-7; *p*-$CH_3OC_6H_4CH_2Br$, 2746-25-0; *o*-$CH_3OC_6H_4CH_2C(COOEt)_2CH_3$, 106419-75-4; *p*-$CH_3OC_6H_4CH_2C(CH_2OH)_2(CH_2)_{11}CH_3$, 106419-79-8; (*p*-$CH_3C_6H_4SO_2O(CH_2)_2O)_2(CH_2)_3$, 92144-75-7; *o*-$BrCH_2C_6H_4OCH_2Ph$, 103633-30-3; *p*-$CH_3C_6H_4SO_2O(CH_2)_2OCH_3$, 17178-10-8; (*p*-$CH_3C_6H_4SO_2O(CH_2)_2O)_2(CH_2)_2$, 19249-03-7; (*p*-$CH_3C_6H_4SO_2O(CH_2)_2O(CH_2)_2)_2O$, 37860-51-8; $(CH_3)_2NSO_2C_6H_4NH_2$, 1709-59-7; *p*-$O_2NC_6H_4NH_2$, 100-01-6; Li^+, 17341-24-1; Na^+, 17341-25-2; K^+, 24203-36-9; Rb^+, 22537-38-8; Cs^+, 18459-37-5; Mg^{2+}, 22537-22-0; Ca^{2+}, 14127-61-8; Sr^{2+}, 22537-39-9; Ba^{2+}, 22541-12-4; *o*-salicylaldehyde, 90-02-8; *p*-salicylaldehyde, 123-08-0.

Reactions of (Benzothiazol-2-ylthio)(trimethylsilyl)methane. A General Method for α-Mercaptoalkylation by Alkylation and Alkylative Desilylation

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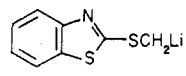
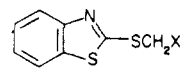
Readily available (benzothiazol-2-ylthio)(trimethylsilyl)methane (**2a**) provides a convenient synthon for $HSCH^{2-}$ and enables the general conversions RR'CO → RR'C(OH)CH(SH)R'' and RBr → $RCH(SH)SiMe_3$. The lithium derivative of **2a** reacts with aldehydes and ketones to give Peterson olefination products which are protected vinyl mercaptans converted into vinyl mercaptans by reaction with methyllithium. This overall conversion is RR'CO → RR'C:CHSH.

We have recently developed[1] a convenient two-step procedure for the mercaptomethylation of alkyl halides, and of aromatic aldehydes and ketones, which involved (i) their treatment with 2-[(lithiomethyl)thio]benzothiazole (**1**) and (ii) subsequent reaction with *n*-butyllithium (nucleophilic attack at the benzothiazole 2-position). This procedure was limited to mercaptomethylation, since carbanions analogous to **1** could not readily be prepared by deprotonation of 2-(ethylthio)benzothiazole (**2b**) or of higher homologues. Although there are alternative



(1)



(2)

a X = $SiMe_3$
b X = Me
c X = H
d X = $PhCH_2$

methods to effect mercaptomethylation,[2-4] no general method for α-mercaptoalkylation, i.e., for the introduction of the group CHRSH, is available. As other results in our laboratories[5] suggest that the second step of our mercaptomethylation sequence could be of general application, we have therefore sought a system **2** where the group X would enhance the acidity of the α-methylene protons and could be easily removed with concomitant introduction of functionality: trimethylsilyl (as in **2a**) suited both these purposes. Carbanions adjacent to both sulfur and silicon have found extensive synthetic applications.[6-9] Furthermore, the reaction of α-heterosubstituted silyl derivatives with aldehydes has yielded the alcohols deriving from the addition of the C–Si bond to the carbonyl group in recent nucleophilic amino- and hydroxymethylations of carbonyl compounds.[10,11]

Table I. Products and Yields from the Reaction of 2a with LDA and Electrophiles

R^1	R^2	product	yield, %
$(CH_2)_3$		**5g**	86
H	Me	**5h**	32
$PhCH_2$		**6a**	90
Me		**6b**	91
n-Hex		**6c**	93
p-MeC_6H_4	H	**11d**	98
$CH_3CH_2CH_2$	H	**11e**	98
$(CH_2)_5$		**11f**	77

We now report the application of **2a** as a synthon for $HSCH^{2-}$, by successive (i) deprotonation with LDA and reaction with electrophiles, (ii) fluoride anion promoted desilylation, followed by reaction with a carbonyl compound, and (iii) nucleophilic attack by alkyllithiums at the benzothiazole 2-position. This sequence provides a general method for the mercaptoalkylation of carbonyl compounds and also opens up a variety of other useful synthetic transformations.

Results and Discussion

Reactions of 2a with LDA and Electrophiles. The trimethylsilyl derivative **2a** was previously prepared by the

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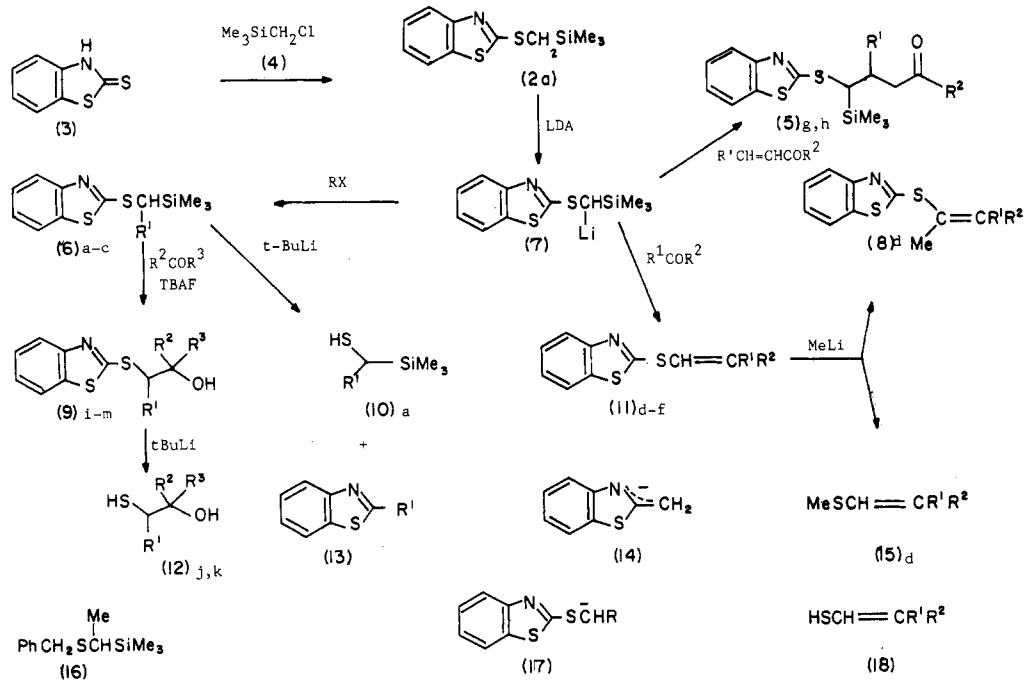
0022-3263/87/1952-0844$01.50/0

Scheme I



a, R^1 = $PhCH_2$
b, R^1 = Me
c, R^1 = *n*-Hex
d, R^1 = *p*-MeC_6H_4, R^2 = H
e, R^1 = *n*-Pr, R^2 = H
f, R^1, R^2 = $(CH_2)_5$
g, R^1, R^2 = $(CH_2)_3$
h, R^1 = H, R^2 = Me
i, R^1 = H, R^2 = *p*-MeC_6H_4, R^3 = H
j, R^1 = $PhCH_2$, R^2 = *p*-MeC_6H_4, R^3 = H
k, R^1 = Me, R^2 = *p*-MeC_6H_4, R^3 = H
l, R^1 = Me, R^2 = *n*-Pr, R^3 = H
m, R^1 = Me, R^2 = R^3 = Ph
n, R^1 = *n*-Bu
o, R^1 = *t*-Bu
p, R^1 = Et

Table II. Products and Yields from the Reactions of 2a and 6 with Carbonyl Compounds. Effect of Solvent and Catalyst

substr	carbonyl compound	solv	*T*, °C	catal. (equiv)	reacn time, h	yield of **2**, %	yield of **9**, %
2a	*p*-MeC_6H_4CHO	DMF	25	CsF (1)	20	(**2c**) 13	(**9i**) 60
2a	*p*-MeC_6H_4CHO	DMF	25	TBAF (0.05)	20	(**2c**) 10	(**9i**) 72
2a	*p*-MeC_6H_4CHO	THF	25	TBAF (0.05)	20	(**2c**) 18	(**9i**) 75
6a	*p*-MeC_6H_4CHO	THF	25	TBAF (0.05)	20	(**2d**) 15	(**9j**) 65
6b	*p*-MeC_6H_4CHO	DMF	25	CsF (1)	24	(**2b**) 10	(**9k**) <5
6b	*p*-MeC_6H_4CHO	THF	25	CsF (1)	48	(**2b**) 12	(**9k**) 5
6b	*p*-MeC_6H_4CHO	THF	25	TBAF (0.05)	24	(**2b**) 15	(**9k**) 75
6b	*p*-MeC_6H_4CHO	CH_2Cl_2	−78→25	$TiCl_4$	4	(**2b**) 0	(**9k**) 0
6b	*p*-MeC_6H_4CHO	CH_2Cl_2	25	$AlCl_3$	4	(**2b**) 0	(**9k**) 0
6b	*n*-BuCHO	THF	25	TBAF (0.05)	20	(**2b**) 19	(**9l**) 65
6b	Ph_2CO	THF	25	TBAF (0.05)	48	(**2b**) 43	(**9m**) 22

alkylation of 2-[(lithiomethyl)thio]benzothiazole (**1**) with chlorotrimethylsilane.[1] However, for multigram preparations of **2a**, it is more conveniently obtained by the reaction of benzothiazole-2-thione (**3**) with (chloromethyl)trimethylsilane (**4**) and potassium carbonate in acetone (Scheme I).

The treatment of **2a** with equimolar LDA in THF at −78 °C affords a light yellow solution of the corresponding α-lithio derivative **7**, which was trapped with various electrophiles to give products, generally in good yields (Table I). The alkylation of **7** succeeds with both activated and unactivated alkyl halides, to give **6a–c** (Scheme I). Addition of **7** to the carbonyl group of aldehydes and ketones gives Peterson olefination products **11d–f**, whereas with α,β-unsaturated ketones Michael addition occurs forming **5g,h** (Scheme I). However, no reaction took place with propylene oxide or ethyl acrylate, and ethyl 2-bromoacetate gave a complex mixture of products.

Alkylative Desilylation. The alkylative desilylations of **2a** and its derivatives **6a,b** take place smoothly at 25 °C in THF or DMF in the presence of excess of a carbonyl compound and a catalytic amount of tetrabutylammonium fluoride (TBAF). Good yields of the corresponding alcohols **9i–l** (Scheme I) are obtained with aromatic or aliphatic aldehydes and **2a** or **6a,b** (Table II); however, the yield of product **9m** formed from benzophenone with **6b** is much lower. Benzyl bromide and ethyl acrylate did not react with **6b** under these conditions; the starting material **6b** was completely consumed after a prolonged reaction time but the only product obtained in these cases was 2-(ethylthio)benzothiazole (**2b**). Variable amounts of compounds **2b–d** were generally obtained as byproducts in the preparations of **9i–m**. Compounds **2b–d** probably originate by protonation of the intermediate carbanionic species **17** by the solvent.

Variation of the solvent and the catalyst in the reactions between **2a** or **6b** and *p*-tolualdehyde (Table II) gave comparable results for THF and DMF. However, THF was generally the solvent of choice because of the simplicity of the workup. Whereas both cesium and tetrabutylammonium fluoride gave good yields of alcohol **9i** (Table II) for reaction of **2a** with *p*-tolualdehyde, only TBAF proved useful for reaction of the substituted derivative **6b**. Attempts to use $TiCl_4$ or $AlCl_3$ in methylene chloride with **6b** resulted in the recovery of the starting materials. Potassium *tert*-butoxide gave a complex mixture.

Alkyllithium Reactions, Mercaptan Formation. We have previously shown[1] that *n*-butyllithium attacks the

Table III. Products and Yields from the Reactions of 6, 9, and 11 with Alkyllithiums

R^1	R^2	R^3	no.	alkyllithium (equiv)	product	yield, %
$PhCH_2$			**6a**	*t*-BuLi (1)	**10a**	98
Me			**6b**	*t*-BuLi (1)	**16**	97
$PhCH_2$	*p*-MeC_6H_4	H	**9j**	*t*-BuLi (2)	**12j**	73
Me	*p*-MeC_6H_4	H	**9k**	*t*-BuLi (2)	**12k**	86
p-MeC_6H_4	H		**11d**	MeLi (2)	**15d**	61

benzothiazole 2-position of 2-(alkylthio)benzothiazole derivatives, releasing the corresponding alkane thiols. In effect the benzothiazole group therefore acts as a protecting group for the thiol functionality. Consequently, the derivatives **6**, **9**, and **11** are protected thiols that can be deprotected by alkyllithium reagents (Table III).

Indeed, the reaction of the alcohols **9j,k** with 3 equiv[12] of *n*-butyllithium in THF at −78 °C afforded the expected 2-butylbenzothiazole (**13n**) in high yield (as estimated by TLC) and presumably the β-hydroxyalkyl mercaptans **12j,k** (Scheme I). However, the isolation of the mercaptans **12j,k** was complicated in these cases by the presence of small amounts of byproducts which probably arose from *n*-butyllithium attack at the sulfur atom. This dual reactivity was previously observed in some of the *n*-butyllithium reactions of 2-(methylthio)benzothiazole derivatives.[1,5] The presence of byproducts was minimized by the use of 2 equiv of *tert*-butyllithium instead of *n*-butyllithium, and the desired β-hydroxy mercaptans **12j** and **12k** were isolated in yields of 73% and 86%, respectively.

Likewise, the treatment of **6a,b** with 1 equiv of *tert*-butyllithium afforded 2-*tert*-butylbenzothiazole (**13o**) (ca. 96%) and the α-(trimethylsilyl)alkyl mercaptans **10a** (isolated in 96% yield) and **10b**, which was isolated and characterized as its benzyl sulfide derivative **16** (97%) (Scheme I). Few methods are available for the synthesis of α-alkyl-α-silyl mercaptans. The addition of mercapto groups to vinyl silanes is Markovnikov both under radical and basic conditions.[13] Recently, these compounds have been prepared in low yields by reaction of (lithiochloromethyl)trimethylsilane and alkyl halides followed by treatment with thiourea and alkaline hydrolysis.[14] Good yields can be obtained in a rather lengthy three-step process that involves consecutive alkylations of 2-(methylthio)tetrahydropyran, and hydrolysis with silver nitrate and hydrogen sulfide.[4]

The alkyllithium cleavage of the benzothiazole alkenyl sulfides **11** derived from aldehydes presented a further complication due to the relatively high acidity of the alkenyl proton on the carbon bearing the sulfur.[15] Thus, when **11d** was treated with 2 equiv of *n*-butyllithium followed by 2 equiv of methyl iodide, the expected methyl alkenyl sulfide **15d** was obtained in only 20% yield; the major product of the reaction was the alkenyl sulfide **8d** (40%), as a consequence of the predominant deprotonation over nucleophilic attack. As expected, a substantially better result was obtained when *n*-butyllithium was replaced by the less basic methyllithium. This raised the yield of **15d** to 61%, whereas **8d** was obtained in only 28% yield.

The source of the *S*-methyl group in **15d** was unambiguously established as methyl iodide by the isolation from the same reaction of a 52% yield of 2-ethylbenzothiazole (**13p**), formed by reaction of methyl iodide with the resonance stabilized carbanion **14** derived from 2-methylbenzothiazole (**13b**). Therefore, the reaction of methyllithium with benzothiazole alkenyl sulfides derived from aldehydes provides a method for the preparation of alkenyl thiols **18**, stable tautomers of thio aldehydes, and precursors[16] of these well-established intermediates.[17]

Conclusion. The ability of alkyllithiums to convert 2-(alkylthio)- and 2-(alkenylthio)benzothiazoles into alkyl and alkenyl mercaptans has now been further exploited by utilizing the reactivity of the trimethylsilyl group in 2-[(α-silylalkyl)thio]benzothiazoles. We have been able then to offer new approaches to functionalized alkyl mercaptans and to alkenyl mercaptans.

Experimental Section

Melting points were determined on a Kofler hot-stage microscope and are uncorrected. IR spectra were recorded on a Perkin-Elmer 283B spectrophotometer. ^1H (200-MHz) and ^{13}C (50-MHz) NMR spectra were recorded on a Varian XL200 (FT mode) spectrometer. Mass spectra were obtained at 70 eV on a AEI MS 30 spectrometer operating with a DS-55 data system. Elemental analyses were performed under the supervision of Dr. R. W. King of this Department.

Tetrahydrofuran (THF) was dried by distillation from sodium–benzophenone ketyl. Diisopropylamine was distilled over calcium hydride and then stored over sodium hydroxide under an argon atmosphere. Acetone was dried over calcium sulfate and distilled prior to use. Dimethyl formamide (DMF) was dried by azeotropic distillation with benzene followed by distillation under reduced pressure.

All reactions were carried out in a dry argon atmosphere.

Column chromatography was carried out with MCB silica gel (230–400 mesh).

(Benzothiazol-2-ylthio)(trimethylsilyl)methane (2a). (Chloromethyl)trimethylsilane (28 mL, 200 mmol) was added to a stirred mixture of potassium carbonate (33.2 g, 240 mmol) and **3** (33.4 g, 200 mmol) in dry acetone (240 mL) at 25 °C. The mixture was stirred under these conditions for 12 h, after which it was filtered and the solvent evaporated to yield an oil, which was distilled to give 40 g (79%) of **2a** as a colorless oil that solidified on standing, bp 110 °C (1.1 mmHg) [lit.[1] bp 120 (1.3 mmHg)].

General Procedure for the Lithiation of 2a and Reaction with Electrophiles. A solution of **2a** (1.27 g, 5 mmol) in THF (30 mL) was added dropwise to a solution of LDA [prepared from diisopropylamine (0.8 mL, 5.7 mmol) and *n*-butyllithium (2.5 M in hexane, 2 mL, 5 mmol)] in THF (25 mL) at −78 °C, and the resulting light yellow solution was stirred at that temperature for 2 h. To this solution of the lithio derivative **7** was added a solution of the electrophile (5 mmol) in THF (5 mL), and the resulting solution stirred at −78 °C for the appropriate time (see below). The reaction mixture was then poured into saturated aqueous ammonium chloride (50 mL), the layers were separated, the aqueous layer was extracted with ether (3 × 10 mL), the combined organic extracts were washed with water and dried ($MgSO_4$), and the solvent was evaporated to give the crude product as an oil, which was purified as indicated below.

3-[(Benzothiazol-2-ylthio)(trimethylsilyl)]methyl]cyclohexanone (5g). The reaction of **7** with 2-cyclohexen-1-one gave

(12) Three equivalents of *n*-butyllithium are required for total conversions. See ref 1.
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after 4 h and the general workup an oil, which was purified by column chromatography (hexane/chloroform, 3/1) to afford **5g** (86%) as a ca. 60/40 mixture of diastereoisomers: bp (mixture) 145 °C (0.3 mmHg) [Kugelrohr]; IR (neat) 2950, 2860, 1710 (CO), 1460, 1425, 1250, 985, 840, 755 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.97–7.81 (m, 2 H), 7.55–7.34 (m, 2 H), 3.83 (d, J = 2 Hz, 1 H, major isomer), 3.73 (d, J = 3 Hz, 1 H minor isomer), 2.59–1.71 (m, 9 H), 0.3 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 211.5, 211.0, 168.3, 168.1, 152.8, 152.7, 135.4, 135.3, 125.8, 124.1, 121.3, 121.2, 120.8, 120.7, 47.4, 45.7, 41.4, 41.2, 40.8, 40.7, 40.3, 40.2, 30.6, 28.6, 25.0, 24.7, −1.6.

Anal. Calcd for $C_{17}H_{23}NOS_2Si$: C, 58.41; H, 6.63; N, 4.01. Found: C, 58.47; H, 6.64; N, 3.99.

5-(Benzothiazol-2-ylthio)-5-(trimethylsilyl)pentan-2-one (5h). Obtained from **7** and methyl vinyl ketone. Reaction time 7 h. The usual workup gave an oil that was purified by column chromatography (hexane/chloroform, 2/1). This afforded **5h** (32%) as a clear oil: bp 136 °C (0.5 mmHg) [Kugelrhor]; IR (neat) 3060, 2950, 2900, 1715 (CO), 1460, 1425, 1250, 990, 840, 755 cm^{-1}; ^1H NMR δ 7.78 (dd, J = 7, 1 Hz, 1 H), 7.69 (dd, J = 8, 1 Hz, 1 H), 7.36–7.23 (m, 2 H), 3.37 (dd, J = 11, 3 Hz, 1 H), 2.84–2.52 (m, 2 H), 2.37–2.20 (m, 1 H), 2.02 (s, 3 H), 1.84–1.64 (m, 1 H), 0.15 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 208.1, 168.5, 152.9, 135.4, 125.8, 124.0, 121.1, 120.8, 41.6, 33.7, 29.9, 25.1, −2.8.

Anal. Calcd for $C_{15}H_{21}NOS_2Si$: C, 55.68; H, 6.54; N, 4.33. Found: C, 55.77; H, 6.58; N, 4.29.

1-(Benzothiazol-2-ylthio)-2-phenyl-1-(trimethylsilyl)-ethane (6a). The general procedure (reaction time 4 h) with **7** and benzyl bromide afforded after column chromatography (chloroform/hexane, 1/3) **6a** (90%) as a yellowish oil: bp 170 °C (0.07 mmHg) [Kugelrhor]; IR (neat) 3030, 2950, 2800, 1605, 1495, 1455, 1425, 1310, 1250, 1125, 1075, 980, 840, 750 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.07 (dd, J = 8, 1 Hz, 1 H), 7.83 (dd, J = 8, 1 Hz, 1 H), 7.64–7.28 (m, 7 H), 3.90 (t, J = 7 Hz, 1 H), 3.39 (d, J = 7 Hz, 1 H), 0.1 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 167.7, 153.0, 139.8, 135.3, 129.1, 127.9, 126.2, 125.6, 123.8, 121.1, 120.6, 37.8, 35.8, −2.3.

Anal. Calcd for $C_{18}H_{21}NS_2Si$: C, 62.92; H, 6.16; N, 4.07. Found: C, 63.07; H, 6.27; N, 4.01.

1-(Benzothiazol-2-ylthio)-1-(trimethylsilyl)ethane (6b). **6b** was prepared from **7** and methyl iodide (reaction time 4 h). After the usual workup the crude product was distilled in Kugelrhor to give **6b** (91%) as a colorless oil: bp 119–120 °C (0.1 mmHg); IR (neat) 3080, 2960, 2925, 2900, 2860, 1560, 1460, 1425, 1310, 1250, 1120, 1070, 990, 840, 750, 720 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.86 (dd, J = 8, 1 Hz, 1 H), 7.74 (dd, J = 7.5, 1 Hz, 1 H), 7.44–7.36 (m, 1 H), 7.31–7.23 (m, 1 H), 3.30 (q, J = 7 Hz, 1 H), 1.57 (d, J = 7 Hz, 3 H), 0.15 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 168.2, 153.3, 135.3, 125.7, 123.8, 121.2, 120.7, 28.5, 16.9, −3.15.

Anal. Calcd for $C_{12}H_{17}NS_2Si$: C, 53.88; H, 6.41; N, 5.24. Found: C, 54.04; H, 6.42; N, 5.16.

1-(Benzothiazol-2-ylthio)-1-(trimethylsilyl)heptane (6c). Hexyl iodide and **7** (reaction time 6 h) gave after the usual workup and purification by column chromatography (hexane/chloroform, 3/1) **6c** as a light yellow oil (93%): bp 145 (0.8 mmHg) [Kugelrhor]; IR (neat) 3060, 2960, 2920, 2850, 1560, 1460, 1425, 1300, 1250, 1120, 1070, 985, 845, 750, 720 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.95 (dd, J = 7, 1 Hz, 1 H), 7.82 (dd, J = 7, 1 Hz, 1 H), 7.51 (t of d, J = 7, 1 Hz, 1 H), 7.37 (t of d, J = 7, 1 Hz, 1 H), 3.50 (dd, J = 8, 5 Hz, 1 H), 2.16–1.80 (m, 2 H), 1.70–1.58 (m, 2 H), 1.50–1.30 (m, 6 H), 0.98 (t, J = 7 Hz, 3 H), 0.3 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 168.9, 153.3, 135.4, 125.7, 121.2, 120.7, 34.8, 31.6, 29.2, 28.2, 22.6, 14.0, −2.4.

Anal. Calcd for $C_{17}H_{27}NS_2Si$: C, 60.48; H, 8.06; N, 4.15. Found: C, 60.59; H, 8.09; N, 4.15.

1-(Benzothiazol-2-ylthio)-2-(4-methylphenyl)ethene (11d). The same procedure used for **6b** gave with **7** and *p*-tolualdehyde the alkenes **11d** (98%) as a *E*–*Z* mixture. The isomers were separated by column chromatography (benzene/ethyl acetate, 19/1). The *E*/*Z* ratio was ca. 60/40. First eluted was (*Z*)-**11d**: mp 106–107 °C; IR ($CHBr_3$) 1600, 1455, 1420, 1325, 1305, 995, 850, 815, 750, 720 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.94 (dd, J = 8, 1 Hz, 1 H), 7.79 (dd, J = 8, 2 Hz, 1 H), 7.50–7.20 (m, 6 H), 7.12 (d, J = 11 Hz, 1 H), 6.85 (d, J = 11 Hz, 1 H), 2.36 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 164.7, 153.0, 137.8, 132.7, 130.5, 129.1, 128.7, 126.1, 124.4, 121.8, 120.9, 117.6, 21.2.

Anal. Calcd for $C_{16}H_{13}NS_2$: C, 67.81; H, 4.62; N, 4.94. Found: C, 67.91; H, 4.68; N, 4.89.

Physical data for (*E*)-**11d**: mp 95–96 °C; IR ($CHBr_3$) 1600, 1505, 1455, 1420, 1310, 995, 855, 815, 750, 720 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.91 (dd, J = 10, 2 Hz, 1 H), 7.77 (dd, J = 8, 1 Hz, 1 H), 7.48–7.15 (m, 8 H), 7.03 (d, J = 16 Hz, 1 H), 2.4 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 166.6, 153.6, 138.8, 137.7, 135.2, 132.7, 129.4, 126.6, 126.1, 124.4, 121.8, 120.9, 115.8, 21.3.

Anal. Calcd for $C_{16}H_{13}NS_2$: C, 67.81; H, 4.62; N, 4.94. Found: C, 67.65; H, 4.59; N, 4.83.

1-(Benzothiazol-2-ylthio)pent-1-ene (11e). The procedure was as that for **6b**, from butyraldehyde and **7**. The alkene **11e** (98%) was obtained as a ca. 50/50 mixture of the *E* and *Z* isomers: bp (mixture) 120 °C (0.8 mmHg) [Kugelrhor]. The isomers were separated by column chromatography (hexane/chloroform, 3/1). First eluted was (*Z*)-**11e**: IR (neat) 3060, 2960, 2930, 2870, 1560, 1460, 1420, 1310, 1235, 1003, 990, 950, 750, 720 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.85 (dd, J = 7, 1 Hz, 1 H), 7.72 (dd, J = 7, 1 Hz, 1 H), 7.42–7.21 (m, 4 H), 6.68 (d of t, J = 9, 1 Hz, 1 H), 6.06 (d of t, J = 9, 7 Hz, 1 H), 2.25 (q of d, J = 7, 1 Hz, 2 H), 1.47 (pseudosextet, J = 7 Hz, 2 H), 0.96 (t, J = 7 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 165.8, 153.3, 137.2, 135.0, 125.9, 124.1, 121.5, 120.7, 117.7, 31.4, 21.9, 13.5. Data for (*E*)-**11e**: IR (neat 3060, 2960, 2930, 2860, 1610, 1560, 1460, 1420, 1310, 1240, 1120, 1070, 990, 850, 750, 720 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.88 (dd, J = 7, 1 Hz, 1 H), 7.72 (dd, J = 7, 1 Hz, 1 H), 7.40 (t of d, J = 7, 1 Hz, 1 H), 7.25 (t of d, J = 7, 1 Hz, 1 H), 6.43 (d of t, J = 15, 1 Hz, 1 H), 6.26 (d of t, J = 15, 7 Hz, 1 H), 2.21 (q of d, J = 7, 1 Hz, 2 H), 1.50 (pseudosextet, J = 7 Hz, 2 H), 0.96 (t, J = 7 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 167.6, 156.7, 143.1, 135.0, 126.0, 124.0, 121.5, 120.7, 116.4, 35.0, 21.7, 13.0.

Anal. Calcd for $C_{12}H_{13}NS_2$: C, 61.24; H, 5.57; N, 5.95. Found (mixture of isomers): C, 61.16; H, 5.48; N, 6.08.

2-[(Cyclohexylidenemethyl)thio]benzothiazole (11f) was obtained (77%) from **7** and cyclohexanone (reaction time 6 h) as a colorless oil after purification by column chromatography (hexane/chloroform, 1/3): bp 142 °C (0.5 mmHg) [Kugelrhor]; IR (neat) 3060, 2930, 2850, 1605, 1560, 1460, 1425, 1385, 1310, 1235, 1180, 1120, 1080, 1015, 1000, 930, 900, 850, 805, 750, 720 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.83 (dd, J = 7, 1 Hz, 1 H), 7.65 (dd, J = 7, 1 Hz, 1 H), 7.38 (t of d, J = 7, 1 Hz, 1 H), 7.22 (t of d, J = 7, 1 Hz, 1 H), 6.21 (s, 1 H), 2.36 (m, 4 H), 1.58 (m, 6 H); ^{13}C NMR ($CDCl_3$) δ 161.7, 147.2, 146.8, 128.0, 118.8, 116.7, 114.4, 113.6, 100.5, 29.6, 23.6, 20.9, 20.2, 19.0.

Anal. Calcd for $C_{14}H_{15}NS_2$: C, 64.33; H, 5.78; N, 5.36. Found: C, 64.26; H, 5.81; N, 5.31.

General Procedure for the F^--Catalyzed Reaction of 2a and 6 with Carbonyl Compounds. A 1 M solution of TBAF in THF (0.1 mL, 0.1 mmol) was added at 25 °C to a solution of the carbonyl compound (10 mmol) and **2a** or **6** (5 mmol) in dry THF (15 mL). The mixture was stirred at 25 °C. After ca. 6 h a further portion of TBAF (1 M in THF, 0.1 mL, 0.1 mmol) was added and the mixture stirred at 25 °C for the appropriate time (see Table II). Water (10 mL) and 1 N HCl were added, the layers were separated, the aqueous layer was extgracted with ether (3 × 5 mL), and the combined organic extracts were washed with water and dried ($MgSO_4$). Evaporation of the solvent gave an oil, which was purified by column chromatography to afford products **9**.

Reaction of 2a with *p*-Tolualdehyde. Elution with hexane/ethyl acetate (9/1) of the crude reaction mixture afforded in successive order of elution **2c**[18] (18%) and the alcohol **9i** (75%), mp 79–82 °C (lit.[1] mp 81–84 °C).

Reaction of 6a with *p*-Tolualdehyde. This afforded in successive order of elution (hexane/ethyl acetate, 9/1) **2d**[18] (15%) and **2-(benzothiazol-2-ylthio)-1-(4-methylphenyl)-3-phenylpropan-1-ol (9j)** (as a 50/50 mixture of diastereoisomers) (65%). Data for **9j**: oil that could not be distilled without decomposition; IR (neat) 3350 (b, OH), 3025, 2965, 2930, 2870, 1600, 1560, 1515, 1500, 1450, 1420, 1310, 1240, 1075, 995, 810, 755, 725, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.9–7.0 (m, 13 H), [5.40 (d), 5.05 (d, J = 5 Hz), 1 H], [4.30 (m), 4.1 (m), 1 H], 3.38–2.80 (m, 3 H), [2.31 (s), 2.27 (s), 3 H]; ^{13}C NMR ($CDCl_3$) δ 166.6, 166.4, 152.3, 139.5, 138.6, 138.5, 138.2, 137.1, 137.0, 135.3, 135.1, 129.1, 128.9, 128.8, 128.3, 128.1, 126.5, 126.3, 126.2, 126.0, 124.4, 121.2, 120.8, 75.6, 74.5, 59.4, 58.9, 37.6, 33.5, 21.0.

(18) Identical in spectral (^1H and ^{13}C NMR) properties with an authentic sample; see ref 1.

Anal. Calcd for $C_{23}H_{21}NOS_2$: C, 70.55; H, 5.41; N, 3.58. Found: C, 70.68; H, 5.30; N, 3.73.

Reaction of 6b with *p*-Tolualdehyde. This afforded in successive order of elution (hexane/ethyl acetate, 1/1) **2b**[18] (15%) and **2-(benzothiazol-2-ylthio)-1-(4-methylphenyl)-propan-1-ol (9k)** (as a 50/50 mixture of diastereoisomers) (75%). Data for **9k**: oil that decomposes on distillation; IR (neat) 3370 (b, OH), 3075, 2980, 2930, 2880, 1560, 1510, 1450, 1425, 1310, 1240, 1035, 1020, 1000, 800, 755, 720 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.88–7.65 (m, 2 H), 7.42–7.08 (m, 6 H), 5.33–4.75 (m, 2 H), 4.25–3.97 (m, 1 H), [2.31 (s), 2.29 (s), 3 H], 1.38–1.28 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ 166.6, 166.4, 152.3, 152.2, 139.5, 138.6, 138.5, 138.2, 137.1, 137.0, 135.3, 135.1, 129.1, 128.9, 128.8, 128.3, 128.1, 126.5, 126.3, 126.0, 125.9, 124.4, 121.2, 120.8, 75.6, 74.5, 59.4, 58.8, 37.6, 33.5, 21.0, 20.9.

Anal. Calcd for $C_{17}H_{17}NOS_2$: C, 64.73; H, 5.43; N, 4.44. Found: C, 65.01; H, 5.41; N, 4.25.

Reaction of 6b with Butyraldehyde. Obtained in successive order of elution were **2b**[18] (19%) and **2-(benzothiazol-2-ylthio)hexan-3-ol (9l)** (65%) (as a 50/50 mixture of diastereoisomers). Data for **9l**: oil; IR (neat) 3390 (b, OH), 2955, 2930, 2865, 1555, 1450, 1420, 1305, 1235, 1070, 890, 840, 750 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.87–7.69 (m, 2 H), 7.40–7.27 (m, 2 H), 4.27–3.78 (m, 3 H), 1.70–1.30 (m, 7 H), 0.99–0.89 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ 166.7, 166.4, 152.7, 152.6, 135.4, 135.3, 126.1, 124.5, 124.4, 121.3, 120.9, 74.5, 74.1, 50.6, 50.4, 37.6, 36.0, 19.3, 19.0, 18.2, 15.0, 14.0.

Anal. Calcd for $C_{13}H_{17}NOS_2$: C, 58.39; H, 6.41; N, 5.24. Found: C, 58.29; H, 6.52; N, 5.15.

Reaction of 6b and Benzophenone. Obtained in successive order of elution were **2b**[18] (43%) and **2-(benzothiazol-2-ylthio)-1,1-diphenylpropan-1-ol (9m)** (22%). Data for **9m**: IR ($CHBr_3$) 3200 (b, OH), 1600, 1490, 1450, 1420, 1310, 1240, 1070, 1030, 1000, 755 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.94 (d, J = 8 Hz, 1 H), 7.68–7.57 (m, 5 H), 7.44–7.12 (m, 8 H), 5.91 (brs, 1 H, OH), 4.84 (q, J = 7 Hz, 1 H), 1.52 (d, J = 7 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 165.5, 152.4, 147.0, 144.9, 135.6, 128.2, 128.0, 126.2, 125.8, 125.6, 124.6, 121.3, 120.9.

Anal. Calcd for $C_{22}H_{19}NOS_2$: C, 69.99; H, 5.07; N, 3.71. Found: C, 69.78; H, 5.05 N, 3.82.

General Procedure for the Reaction of Benzothiazoles 6 and 9 with Alkyllithiums. In a typical experiment, to a stirred solution of **6** or **9** (2 mmol) in THF (20 mL) at −78 °C was added *tert*-butyllithium (2 or 4 mmol, respectively). After 5 min the orange solution was poured into saturated aqueous ammonium chloride (20 mL). The layers were separated, the aqueous layer was extracted with ether (3 × 5 mL), and the combined organic extracts were washed with water and dried ($MgSO_4$). Evaporation of the solvent left an oil, which contained 2-*tert*-butylbenzothiazole (**13o**) and the mercaptan. These two products were separated by column chromatography.

1-(Trimethylsilyl)-2-phenylethanethiol (10a). 10a was obtained (98%) from **6a** after elution with hexane. First eluted was **13o**: bp 85 °C (0.8 mmHg) [Kugelrhor] [lit.[19] bp 255–260 °C (760 mmHg)]; IR (neat) 1610, 1450, 1435, 1360, 1280, 1245, 1085, 1040, 1005, 805, 755, 725 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.0 (m, 2 H), 7.80 (m, 2 H), 7.44–7.21 (m, 2 H), 1.50 (s, 9 H). Data for **10a**: colorless oil IR (neat) 3080, 3060, 3020, 2950, 2900, 2840, 1600, 1590, 1490, 1450, 1250, 1120, 1070, 1020, 840, 750 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.35–7.12 (m, 5 H), 3.14 (dd, J = 14, 4 Hz, 1 H), 2.61–2.21 (m, 2 H), 1.15 (d, J = 6.5 Hz, 1 H), 0.12 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 140.3, 129.0, 128.3, 126.3, 40.1, 26.9, −3.1.

Anal. Calcd for $C_{11}H_{18}SSi$: C, 62.79; H, 8.62. Found: C, 63.04; H, 8.85.

Benzyl 1-(Trimethylsilyl)ethyl Sulfide (16). 16 was obtained from **6b**. The general procedure was modified as follows: after addition of *tert*-butyllithium the reaction mixture was stirred for 1 h at −78 °C, benzyl bromide (3 mmol) was added, and the mixture was stirred at −78 °C a further 2 h. The usual workup gave an oil, which was purified by column chromatography (hexane/chloroform, 3/1). This afforded **16** (97%) as an oil: bp 75 °C (0.8 mmHg) [Kugelrhor] [lit.[13] bp 97–98 °C (1.6 mmHg)]; IR (neat) 3080, 3060, 3020, 2950, 2920, 2900, 2860, 1600, 1490, 1450, 1370, 1250, 1070, 1030, 1005, 830 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.65–7.40 (m, 5 H), 4.01 (s, 2 H) 2.10 (q, J = 7 Hz, 1 H), 1.55 (d, J = 7 Hz, 3 H), 0.30 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 138.5, 128.9, 128.3, 126.6, 35.4, 24.1, 16.1, −3.2.

Anal. Calcd for $C_{12}H_{20}SSi$: C, 64.22; H, 8.98. Found: C, 64.23; H, 8.98.

2-Mercapto-1-(4-methylphenyl)-3-phenylpropan-1-ol (12j). 12j was obtained (73%, mixture of diastereoisomers) from **9j** after elution with hexane/dichloromethane (1/1) as an oil: IR (neat) 3400 (b, OH), 2920, 2860, 1600, 1510, 1490, 1420, 1310, 1230, 1120, 1030, 990, 940, 810, 750 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.40–7.00 (m, 9 H), 4.79–4.60 (m, 1 H), 3.54–3.34 (m, 1 H), 3.21–3.14 (m, 1 H), 2.67–2.50 (m, 2 H), [2.36 (s), 2.35 (s), 3 H], [1.28 (d), 1.27 (d), 1 H]; ^{13}C NMR ($CDCl_3$) δ 138.9, 137.9, 137.7, 129.3, 129.1, 129.0, 128.3, 126.6, 126.4, 77.3, 49.0, 38.7, 21.1.

Anal. Calcd for $C_{16}H_{18}OS$: C, 74.38; H, 7.02. Found: C, 74.59; H, 7.01.

2-Mercapto-1-(4-methylphenyl)-1-propan-1-ol (12k). 12k was obtained (86%, as a 60/40 mixture of diastereoisomers) from **9k** after elution with hexane/chloroform (1/2): bp (mixture, partial decomposition) 75 °C (0.5 mmHg) [Kugelrohr]; IR (neat) 3430 (b, OH), 2985, 2920, 2885, 1510, 1450, 1375, 1190, 1030, 1010, 815 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.28–7.10 (m, 4 H), [4.61 (m, major isomer), 4.34 (m, minor isomer), 1 H], 3.20 (m, 1 H), [2.97 (d, J = 4 Hz, minor isomer), 2.69 (d, J = 3 Hz, major isomer), 1 H], 2.35 (s, 3 H), [1.60 (d, J = 7 Hz, minor isomer), 1.43 (d, J = 7 Hz, major isomer), 1 H], [1.21 (d, J = 7 Hz), 1.19 (d), J = 7 Hz), 3 H]; ^{13}C NMR ($CDCl_3$) δ 138.0, 137.6, 137.4, 129.0, 128.8, 126.4, 126.3, 79.1, 78.1, 43.5, 41.7, 21.1, 21.0, 18.7.

Anal. Calcd for $C_{10}H_{14}OS$: C, 65.89; H, 7.74. Found: C, 65.57; H, 7.61.

Reaction of 11d with Methyllithium. To a solution of **11d** (1.13 g, 4 mmol) in THF (40 mL) was added methyllithium (1.4 M in hexane, 5.8 mL, 8.2 mmol) at −78 °C. The resulting red solution was stirred at −78 °C for 2 h, methyl iodide (0.51 mL, 8 mmol) added, and the mixture stirred at −78 °C a further 4 h. After the usual workup the crude mixture was separated by column chromatography (hexane/chloroform, 4/1). In successive order of elution, **15d** (61%), **8d** (28%), and **13p** (52%) were obtained.

Data for **15d** (50/50 *E*–*Z* mixture): colorless oil, IR (neat) 2920, 1640, 1590, 1560, 1505, 1430, 1360, 1310, 1180, 1115, 1100, 1035, 950, 920, 850, 815, 780, 770, 680 cm^{-1}; ^1H NMR[20] ($CDCl_3$) δ 7.37–7.02 (m, 4 H), [6.67 (d, J = 15.5 Hz, *E* isomer), 6.36 (d, J = 11 Hz, *Z* isomer), 1 H], [6.24 (d, J = 15.5 Hz, *E* isomer), 6.06 (d, J = 11 Hz, *Z* isomer), 1 H], 2.30 (s, 3 H), 2.28 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 136.2, 136.1, 134.2, 134.0, 129.1, 128.7, 128.4, 127.8, 125.1, 125.0, 124.6, 124.4, 21.0, 20.9, 18.6, 14.6.

Anal. Calcd for $C_{10}H_{12}S$: C, 73.12; H, 7.36. Found: C, 73.20; H, 7.48.

Data for **8d** (*E*–*Z* mixture): colorless oil; IR (neat) 3060, 3020, 2920, 1610, 1560, 1510, 1460, 1430, 1310, 1240, 1190, 1130, 1080, 1020, 1000, 880, 810, 760, 730 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.92 (d, J = 8 Hz, 1 H), 7.66 (d, J = 8 Hz, 1 H), 7.45–7.06 (m, 6 H), 6.93 (s, 1 H), 2.32 (s, 3 H), 2.26 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 167.2, 165.1, 153.7, 153.6, 140.1, 137.6, 137.4, 137.2, 135.7, 135.6, 132.9, 132.6, 129.2, 129.0, 128.9, 128.7, 128.6, 127.8, 126.4, 126.0, 125.9, 125.8, 124.2, 124.1, 121.7, 121.5, 120.6, 26.4, 21.0.

Anal. Calcd for $C_{17}H_{15}NS_2$: C, 68.65; H, 5.08; N, 4.71. Found: C, 68.51; H, 5.12; N, 4.84.

Data for **13p**: colorless oil, bp 75 °C (2 mmHg) [lit.[21] bp 128 °C (16 mmHg)]; IR (neat) 3060, 2980, 2940, 2880, 1530, 1460, 1440, 1310, 1280, 1240, 1170, 1160, 1130, 1070, 1020, 950, 760, 730 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.95 (dd, J = 8, 1.5 Hz, 1 H), 7.79 (dd, J = 8, 1.5 Hz, 1 H), 7.41 (t of d, J = 8, 1.5 Hz, 1 H), 7.29 (t of d, J = 8, 1.5 Hz, 1 H), 3.10 (q, J = 7.5 Hz, 2 H), 1.43 (t, J = 7.5, 3 H); ^{13}C NMR ($CDCl_3$) δ 173.3, 153.1, 134.9, 125.7, 124.4, 122.3, 121.3, 27.6, 13.6.

Registry No. 2a, 106296-62-2; **2b**, 2757-92-8; **2c**, 615-22-5; **2d**, 93366-73-5; **3**, 149-30-4; **4**, 2344-80-1; **5g** (isomer 1), 106296-63-3; **5g** (isomer 2), 106296-64-4; **5h**, 106296-65-5; **6a**, 106296-66-6; **6b**,

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106296-67-7; **6c**, 106296-68-8; (*E*)-**8d**, 106296-84-8; (*Z*)-**8d**, 106318-60-9; **9i**, 106296-74-6; **9j** (isomer 1), 106296-75-7; **9j** (isomer 2), 106296-85-9; **9k** (isomer 1), 106296-76-8; **9k** (isomer 2), 106296-86-0; **9l** (isomer 1), 106296-77-9; **9l** (isomer 2), 106318-61-0; **9m**, 106296-78-0; **10a**, 106296-79-1; (*E*)-**11d**, 106296-69-9; (*Z*)-**11d**, 106296-70-2; (*E*)-**11e**, 106296-71-3; (*Z*)-**11e**, 106296-72-4; **11f**, 106296-73-5; **12j** (isomer 1), 106296-80-4; **12j** (isomer 2), 106296-81-5; **12k** (isomer 1), 106296-82-6; **12k** (isomer 2), 106296-83-7; **13o**, 17626-88-9; **13p**, 936-77-6; (*E*)-**15d**, 55059-13-7; (*Z*)-**15d**, 55059-14-8; **16**, 18032-18-3; $CH_3C(O)CH{=}CH_2$, 78-94-4; $PhCH_2Br$, 100-39-0; MeI, 74-88-4; $CH_3(CH_2)_5I$, 638-45-9; *p*-MeC_6H_4CHO, 104-87-0; $CH_3(CH_2)_2CHO$, 123-72-8; $CH_3(CH_2)_3CHO$, 110-62-3; Ph_2CO, 119-61-9; *t*-BuLi, 594-19-4; MeLi, 917-54-4; 2-cyclohexen-1-one, 930-68-7; cyclohexanone, 108-94-1.

Synthesis of the Major Metabolic Dihydrodiols of Benzo[*j*]fluoranthene

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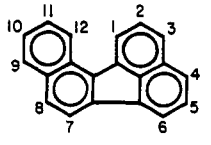
Syntheses are described for the major dihydrodiol metabolites of benzo[*j*]fluoranthene. *trans*-4,5-Dihydro-4,5-dihydroxybenzo[*j*]fluoranthene was prepared via 9-methoxy-11*H*-benzo[*a*]fluorene. Two of the intermediates in this synthetic sequence, 4-hydroxybenzo[*j*]fluoranthene and benzo[*j*]fluoranthene-4,5-dione, are also suspect metabolites of the parent hydrocarbon. An improved synthesis for *trans*-9,10-dihydro-9,10-dihydroxybenzo[*j*]fluoranthene is described. The key steps in this preparation are the Wittig reaction of acenaphthenequinone with (3-methoxyphenethyl)triphenylphosphonium bromide and the cyclization–dehydration of the intermediate, forming 10-methoxybenzo[*j*]fluoranthene exclusively. The synthesis of *trans*-2,3-dihydro-2,3-dihydroxybenzo[*j*]fluoranthene was accomplished through the intermediacy of 1,12c-dihydrobenzo[*j*]fluoranthen-3(2*H*)-one. This ketone was converted to its α-phenylseleno derivative which underwent selenoxide elimination in basic hydrogen peroxide, forming benzo[*j*]fluoranthene-2,3-dione directly. In each synthesis reduction of the appropriate quinone with potassium borohydride afforded the desired dihydrodiol.

Introduction

Benzo[*j*]fluoranthene (**1**) is a nonalternant polycyclic aromatic hydrocarbon[1] which is found throughout the environment in sources such as air, cigarette smoke condensate, soot, soil, drinking water, and smoked foods.[2-7] This compound is active as a tumor initiator and complete carcinogen on mouse skin and is carcinogenic in rat lung.[3,8-10] Studies in our laboratories have shown that **1** is metabolized to two dihydrodiols in rat liver homogenate. One of these has been identified, by comparison



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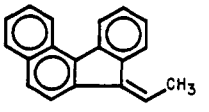

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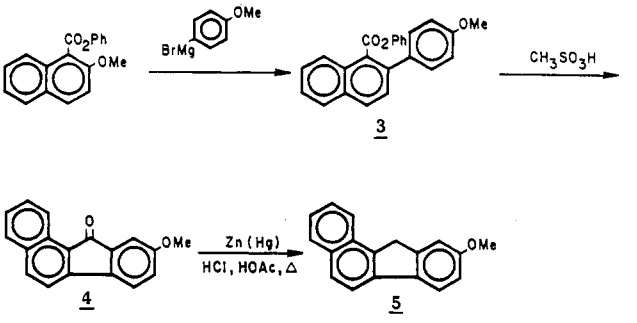
with a synthetic standard, as *trans*-9,10-dihydro-9,10-dihydroxybenzo[*j*]fluoranthene.[11,12] This dihydrodiol is mutagenic in *S. typhimurium* and is active as a tumor initiator on mouse skin.[8] The second dihydrodiol has been tentatively identified as *trans*-4,5-dihydro-4,5-dihydroxybenzo[*j*]fluoranthene by comparison of its UV spectrum with that of 7-ethylidine-7*H*-benzo[*c*]fluorene (**2**).[13] In this paper we describe for the first time the synthesis of the 4,5-dihydrodiol of **1**. Improved syntheses for the 9,10-dihydrodiol and the 2,3-dihydrodiol are also detailed.

Scheme I. Preparation of 9-Methoxy-11*H*-benzo[*a*]fluorene (5), the Key Intermediate in the Synthesis of the 4,5-Dihydrodiol of Benzo[*j*]fluoranthene



Results and Discussion

The key intermediate for the syntheses of the 4,5-dihydrodiol of benzo[*j*]fluoranthene is 9-methoxy-11*H*-benzo[*a*]fluorene. This compound was prepared by the general method of Fuson and Wassmundt[14] as illustrated

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