Alkylation of Benzothiazolines and the Stevens Rearrangement of the Resulting 2,3,3-Trisubstituted Benzothiazolinium Salts

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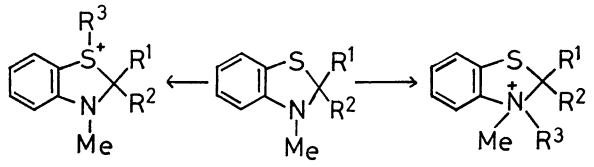
Alkylation of 2-substituted 3-methyl- or 3-ethylbenzothiazolines with Meerwein reagents gave 2-substituted 3,3-dialkylbenzothiazolinium tetrafluoroborates (**3**). The configuration of two alkyl groups on the nitrogen was assigned by NMR spectra and NOE measurement. In the Stevens rearrangement of **3** with lithium diisopropylamide ethyl group showed a much larger migratory aptitude (Et:Me≧20:1) than methyl group irrespective of the configuration of **3**, and cyclic ammonium ylide with planar π-type carbanion was proposed as an intermediate. **3** suffered nucleophilic attack at the ring sulfur atom by butyllithium to afford a ring-opened ammonium ylide, which collapses to a radical pair to give unusual Stevens rearrangement product, where *o*-alkylthiophenyl group migrated selectively in preference to alkyl group, because of stabilization by participation of *o*-alkylthio group.

In an alkylation of a compound containing two hetero atoms such as sulfur and nitrogen, the position of alkylation is dependent on the structure of the compound and the kind of alkylating reagent.

For example, dimorpholino sulfide undergoes *S*-ethylation with triethyloxonium tetrafluoroborate, while it gives *N,N*-dimethylmorpholinium salt with methyl iodide.[1] 1-Pyrrolidinyl *p*-tolyl sulfoxide undergoes *O*-methylation with methyl trifluoromethanesulfonate,[2] and *S*-methyl-*S*-phenylsulfoximine[3] and 2-anilino-3-methylthio-1,4-naphthoquinone[4] *N*- and *S*-methylations with trimethyloxonium tetrafluoroborate, respectively.

In the benzothiazolines (**1**), it is also possible in their alkylation to give thionia (**2**) or azonia compound (**3**), but **3** was obtained in alkylation with Meerwein reagents.[5] Independently, Hori *et al.*[6] reported that **1** suffers *N*-methylation both with trimethyloxonium tetrafluoroborate (**4a**) and methyl iodide, but 2,2,3-trimethylbenzothiazoline *S*-methylation with methyl iodide.



2 1 3

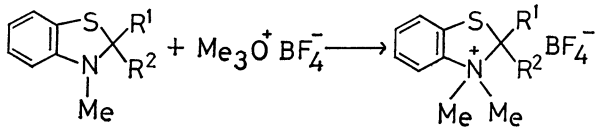
Moreover, it is well known that the quaternary ammonium salts undergo Stevens rearrangement[7] with bases *via* ammonium ylide[8] stereospecifically[9] in intramolecular manner.[10] Because of observation of CIDNP,[11] it is generally accepted that Stevens rearrangement involves a radical pair which recombines in a solvent cage. On the other hand, Dewar[12] have suggested that concerted S_Ni type mechanism, which is forbidden according to the Woodward-Hoffmann rule, is energetically not so unfavorable in gas phase based on the MINDO/3 calculation.

Therefore, we carried out the Stevens rearrangement of **3** (R^1=H, R^3≠Me) of a definite configuration with lithium diisopropylamide (LDA) or butyllithium in order to investigate the steric course and the migratory aptitude.[13]

This paper describes on alkylation of **1**, the structure of the resulting salts (**3**), and their Stevens rearrangement in detail.

Results and Discussion

Methylation of 3-Methylbenzothiazolines (1). Methylation of **1** with **4a** gave 3,3-dimethylbenzothiazolinium salts (**3**). The results are shown in Table 1.



1 4a 3

The structure of **3** was easily determined by NMR. The salts (**3a**—**e**), where the 2-position is asymmetric, show two methyl signals with an equal intensity at δ 3.1 and 3.7 ppm region. Although these two signals may be assigned to *S*- and *N*-methyl groups of the thionia compound (**2**), they should be assigned to the dimethylammonio group because no spectral change could be observed by addition of excess trifluoroacetic acid (TFA) to **3c** and **3e**. The conclusion was confirmed by the fact that **3f** and **3g** which bear the same two substituents at 2-C show a single methyl peak and no spectral change could be also observed by addition of excess TFA.

The chemical shifts of the lower field methyl of **3a**—**e** are almost constant (δ 3.7). On the other hand, these of the higher field methyl are constant for **3a**—**d** (δ 3.12), but a distinct shift to lower field is observed for **3e** (R^2=Me). Hence, it can be concluded that the lower field methyl is assigned to lie *syn* to 2-C–H and the higher field methyl *syn* to 2-C–R. The assignement was supported by NOE measurement (*vide infra*).

From the filtrate in the recrystallization of **3c** obtained by the reaction of **1c** with **4a**, *N*-methyl-*o*-methylthioaniline (10%) and its hydrotetrafluoroborate

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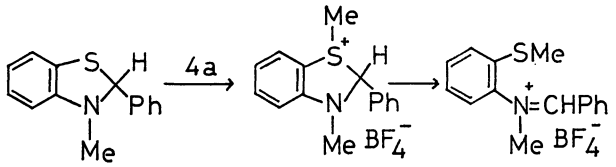
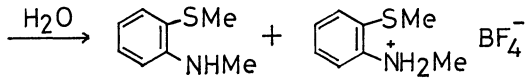
Table 1. Yields, mp, and chemical shifts (in DMSO-d_6) of **3**

3	R^1	R^2	Yield/%	Mp θ_m/°C	δ_{C_2-H}	δ_{N-Me}
3a	H	*p*-$MeOC_6H_4$	65	165—167	6.94	3.12, 3.65
3b	H	*p*-MeC_6H_4	59	195—197	6.94	3.10, 3.66
3c	H	C_6H_5	69	178.5—180.5	6.99	3.11, 3.71
3d	H	*p*-ClC_6H_4	58	196—197	7.00	3.17, 3.71
3e	H	Me	66	117.5—119	5.81	3.35, 3.73
3f	H	H	77	172—173.5	5.34	3.62
3g	Me	Me	72	177—178.5	—	3.53

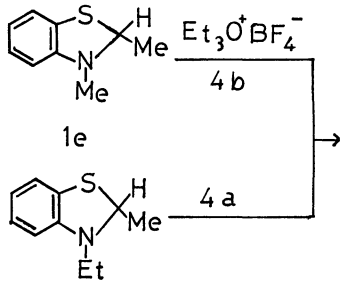
(4.5%) were isolated. These products are probably due to decomposition of *S*-methylated product, because Hori *et al.*[6] have reported isolation of **X** type salt in the methylation of **1g** (R^1=R^2=Me) with methyl iodide.



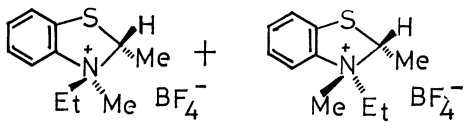
1c X



Alkylation of 3-Alkylbenzothiazolines. Ethylation of 2,3-dimethylbenzothiazoline (**1e**) with triethyloxonium tetrafluoroborate (**4b**) gave a diastereomeric mixture of **5A** and **5B** (**5A**/**5B**=*ca.* 10) in 61% yield, and methylation of 3-ethyl-2-methylbenzothiazoline (**1h**) with **4a** gave a mixture of the same salts (**5A**/**5B**=*ca.* 2) in 43% yield. The pure isomer **5A** could be isolated by repeated recrystallizations of the reaction mixture from **1e**.

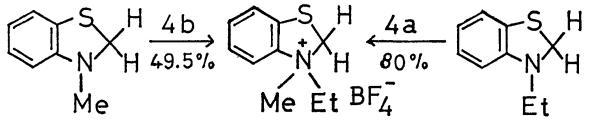


1e 1h



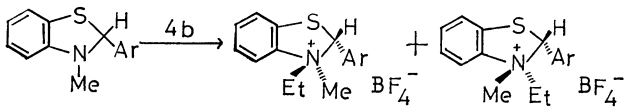
5A 5B

The salt (**6**) obtained by ethylation of 3-methylbenzothiazoline (**1f**) showed identical NMR spectrum with that obtained by methylation of 3-ethyl derivative (**1i**), confirming the structure **6**.



1f 6 1i

Ethylation of **1a—d** with **4b** gave a mixture of **7A** and **7B**. The results are summarized in Table 2.



1a-d 7A 7B

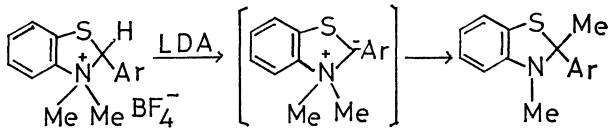
Since in these cases purification of the salts by recrystallization was considerably difficult, the isolated yields were relatively low. But pure **A** type of isomers could be isolated in the cases of **7c** and **7d** by repeated recrystallizations.

Methylations of 3-ethyl-2-phenyl-(**1j**), 2,2-diethyl-3-methyl-(**1k**), 2,3-dimethyl-2-phenyl-(**1l**), and 2-t-butyl-3-phenylbenzothiazolines (**1m**) with **4a** gave only tarry materials which may be decomposition products *via* *S*-methylation, but further identification was not done.

On the other hand, reaction of **1c** with benzyl chloride in the presence of silver perchlorate gave 3-methyl-2-phenylbenzothiazolium perchlorate (**8**), which was also obtained in the reaction with only silver perchlorate.

Determination of Stereochemistry by NOE Measurement. In order to confirm the stereochemistry of **3** and **5**, the NOE measurement was performed. In the NMR spectra of **3c**, **3e**, and **5A**, the increase of intensities of 2-H was observed on irradiation of the alkyl groups on the nitrogen atom resonating at lower field, while little change was observed on irradiation of the substituent resonating at higher field as shown in Table 3, supporting the before-mentioned conclusion.

*Reactions of **3a—d** and **7** with LDA.* Reactions of **3a—d** with LDA in ether or tetrahydrofuran (THF) at −50 °C gave 2-aryl-2,3-dimethylbenzothiazolines (**9a—d**) as product due to Stevens rearrangement through a cyclic ammonium ylide (**10**). The results are summarized in Table 4.



3a-d 10 9a-d

Table 2. Ethylation products (**7A** and **7B**) from **1a—d**

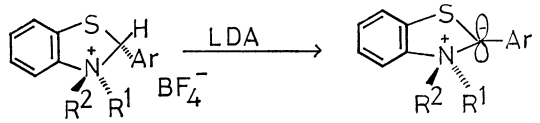
7	Ar	Yield/%	7A/7B	Mp θ_m/°C	δ_{N-Me} A	δ_{N-Me} B
7a	*p*-$MeOC_6H_4$	39	*ca.* 1	145.5—149.5	3.10	3.53
7b	*p*-MeC_6H_4	37	*ca.* 1	158—161	3.11	3.57
7c	C_6H_5	34	*ca.* 10	147—148.5	3.12	3.57
7d	*p*-ClC_6H_4	35	*ca.* 10	139—141	3.17	3.58

Table 3. NOE measurements of **3c**, **3e**, and **5A**

Salt	Irradiated group (δ)	Relative intensity of C_2-H/%
3c	3.71 (*N*-Me)	128±1
	3.11 (*N*-Me)	99±1
3e	3.73 (*N*-Me)	140±2
	3.35 (*N*-Me)	111±2
	1.86 (2-Me)	98±1
5A	3.8—4.3 (*N*-CH_2)	120±2
	3.41 (*N*-Me)	105±1
	1.78 (2-Me)	97±1

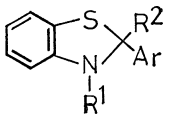
The salts (**3**) where the 2-substituent is an alkyl group was mostly recovered under the same conditions, probably because of much lower acidity of the 2-H.

The salts (**7A** and **7B**) should be very suitable models to study the stereochemical relation between the migratory group and the carbanion of the ylide, if the anion retains sp^3 type. If the migration occurs *via* concerted S_Ni type mechanism, **7A** and **7B** should give 2-aryl-2-ethyl-3-methyl-(**11**) and 2-aryl-3-ethyl-2-methylbenzothiazolines (**12**), respectively.



7A: R^1=Me, R^2=Et
7B: R^1=Et, R^2=Me

13

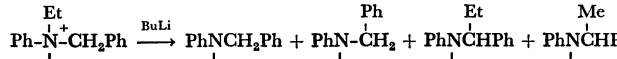


11: R^1=Me, R^2=Et
12 R^1=Et, R^2=Me

As was expected, reactions of pure **7cA** and **7dA** with LDA gave only **11** in 22 (in ether) and 33% (in THF) yields, respectively, and no **12** could be detected by NMR and GLC. However, a similar reaction of a 1:1 mixture of **7aA** and **7aB** or **7bA** and **7bB** in THF gave also only the corresponding **11** in 54 and 30% yields, respectively, being inconsistent with concerted S_Ni type mechanism. These facts indicate that ethyl group migrates exclusively irrespective of the stereochemistry of the starting salt.

In order to realize these phenomena, it is necessary to invoke not only a planar carbanion (**13**) conjugated with the aryl group as the intermediate, because inversion of sp^3 type carbanion is known to be slow enough to retain its configuration,[14] but also a preferential migration of ethyl group than methyl group.

Furthermore, in order to examine the difference of the migratory aptitudes of ethyl and methyl groups in general, benzylethylmethylphenylammonium tetrafluoroborate (**14**) was allowed to react with butyllithium to give **15**—**17** whose yields were estimated by GLC as shown below.



	14	**15**	**16**	**17**	**18**
in Et_2O		34%	6%	20%	—
in THF		35%	6%	12%	—

The compounds, **15** and **16**, are products due to decomposition of ylides resulting by deprotonation of the ethyl and the methyl groups, respectively, and **17** is the product resulting from the migration of the ethyl group. The product **18** due to methyl migration could not be detected.

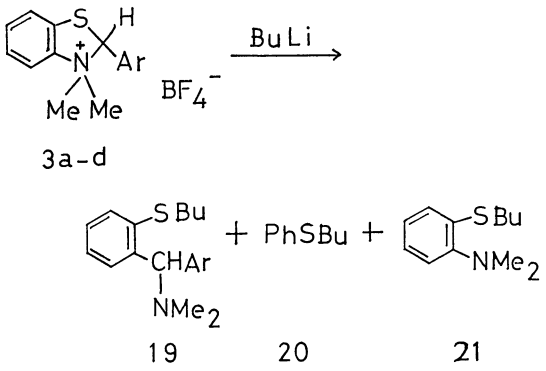
Judged from the sensitivity of glc, the ratio of migratory aptitude of ethyl group to that of methyl group is estimated to be more than 20. This value is nearly consistent with that for Wittig rearrangement (Et/Me=39)[15] which is generally accepted to proceed by radical pair mechanism as in Stevens rearrangement. Therefore, the remarkable difference between the migratory aptitudes of the ethyl and the methyl groups

Table 4. Yields of Stevens rearrangement products

3	Ar	With LDA		With BuLi		
		9(in Et_2O)/%	**9**(in THF)/%	**19**/%	**20**/%	**21**/%
a	*p*-$MeOC_6H_4$	14	20	33	12	8
b	*p*-MeC_6H_4		47	27		
c	C_6H_5	45	41	38	14	6
d	*p*-ClC_6H_4	59	62	13		

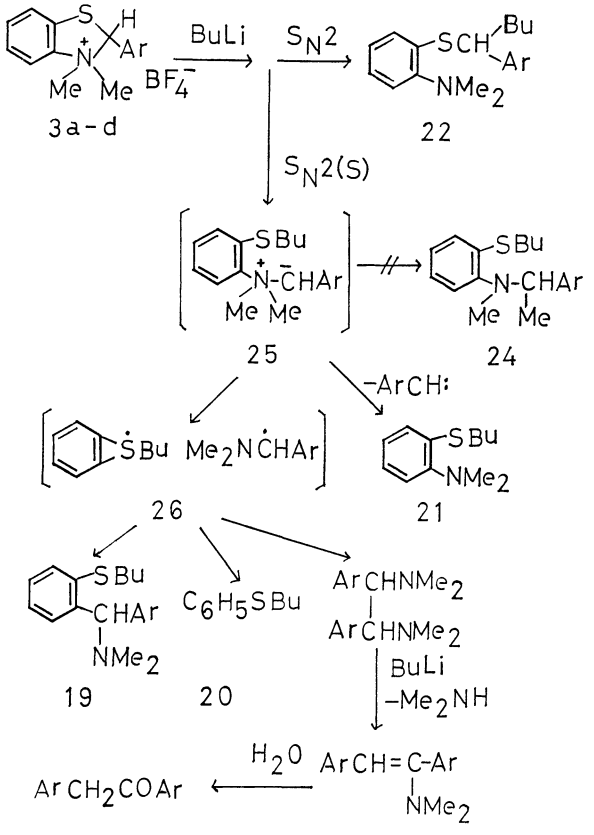
should be attributed to the radical stability in the radical pair during Stevens rearrangement.[16]

*Reactions of **3a—d** with Butyllithium.* Reactions of **3a—d** with butyllithium in ether at −50 °C followed quite different course and gave butyl *o*-(α-dimethylaminobenzyl)phenyl sulfide derivatives (**19**) together with butyl phenyl sulfide (**20**) and *o*-butylthio-*N*,*N*-dimethylaniline (**21**). The results were shown in Table 4. The structure of **19** was determined by unequivocal synthesis of **19c** (see Experimental).



In the case of **3a**, *o*-[1-(*p*-methoxyphenyl)pentylthio]-*N*,*N*-dimethylaniline (**22**) (4%) was also obtained, and in the case of **3c**, *o*-butylthio-*N*-methylaniline (**23**) (6%) and benzyl phenyl ketone (3%) were also obtained.

A plausible reaction scheme is depicted as shown in Scheme 1.

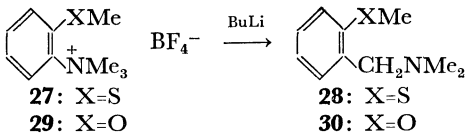


Scheme 1.

The normal product (**9**) derived from cyclic ammonium ylide (**10**) could not be obtained at all in contrast with the reaction with LDA. Formation of **19** can be rationalized by the formation of a ring-opened ammonium ylide (**25**) which then collapses to a radical pair (**26**) or decomposes to give **21** and arylcarbene. The radical pair (**26**) recombines to give **19** and also can afford **20** as an escape product. The starting salt (**3a—d**) is also attacked by butyllithium at the 2-position to a small extent to give **22**.

The most interesting point is that the product is not **24** but **19**, although an expected Stevens rearrangement product is **24**, because of higher migratory aptitude of alkyl groups than that of aryl groups in Stevens rearrangement.[7] However, **19** is the product due to migration of *o*-butylthiophenyl group.

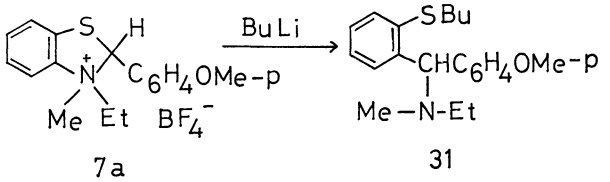
The reason for this unusual aryl migration can be ascribed to participation of the adjacent sulfur atom in stabilizing the aryl radical as shown in **26**. This possibility was supported by reference reaction of trimethyl[*o*-(methylthio)phenyl]ammonium tetrafluoroborate (**27**) to give *N*,*N*-dimethyl-*o*-(methylthio)benzylamine (**28**) due to aryl migration as a major product (22%) under the same conditions, while *o*-methoxyphenyltrimethylammonium salt (**29**) did not give **30** under the same conditions.



27: X=S
29: X=O
28: X=S
30: X=O

A similar attack on the divalent sulfur atom by butyllithium has been reported in the reactions of 1-methyl-2-nitrosoimino-1,2-dihydrobenzothiazole[17] and diphenylphosphinodithioate esters.[18]

A similar reaction of **7a** gave **31** as a mian product (11%).



When there is no aryl group at 2-C, a similar reaction gave a complicated mixture and product such as **19** was not obtained.

Experimental

All the melting and boiling points are not corrected. IR spectra were measured with a Hitachi EPI-G2 spectrophotometer, ^{1}H NMR spectra with Hitachi R-24B and R-20B spectrometers using TMS as an internal standard, and MS and high-resolution MS (HMS) with Hitachi RMU-6L and JEOL D-300 mass spectrometers at 70 V, respectively.

Materials. Trimethyl-(**4a**)[19] and triethyloxonium tetrafluoroborates (**4b**),[20] 2,2,3-trimethyl-(**1g**),[21] 2,3-dimethyl-2-phenyl-(**1l**=**9c**),[22] and 2-*t*-butyl-3-phenylbenzothiazolines (**1m**)[23] were prepared according to the reported methods.

*Syntheses of Benzothiazolines (**1**) by Grignard Reaction.*[24] *General Procedure*: To a suspension of 3-methyl-(**32a**),[25] 3-ethyl-(**32b**),[21] or 3-methyl-2-methylthiobenzothiazolium io-

dide (**32c**)[22] (0.1 mmol) in ether (90—120 ml) was added dropwise an appropriate Grignard reagent (0.11—0.12 mmol) in ether (90—200 ml), filtered through a tube with glass wool, under nitrogen at −40 °C. The mixture was stirred at room temp for several hours and then refluxed for 0.5 h. The reaction mixture was washed with aq NH_4Cl and the ethereal layer was dried ($MgSO_4$). The solvent was evaporated *in vacuo* and the residue was recrystallized from ethanol, distilled, or purified by column chromatography (CC) (SiO_2, C_6H_6).

*2-(p-Methoxyphenyl)-3-methylbenzothiazoline (**1a**)*: 34% yield from **32a**, pale yellow crystals, mp 106.5—108.5 °C; NMR ($CDCl_3$): δ 2.58 (s, 3H), 3.79 (s, 3H), 5.94 (s, 1H), and 6.25—7.75 (m, 8H). Found: C, 69.87; H, 5.60; N, 5.52%. Calcd for $C_{15}H_{15}NOS$: C, 70.00; H, 5.87; N, 5.44%.

*3-Methyl-2-p-tolylbenzothiazoline (**1b**)*: 68% yield from **32a**, pale yellow crystals, mp 86—89 °C; NMR ($CDCl_3$) : δ 2.37 (s, 3H), 2.64 (s, 3H), 5.99 (s, 1H), and 6.3—7.6 (m, 8H). Found: C, 74.90; H, 6.11; N, 5.82%. Calcd for $C_{15}H_{15}NS$: C, 74.65; H, 6.26; N, 5.80%.

*3-Methyl-2-phenylbenzothiazoline (**1c**)*: 72% yield from **32a**, pale yellow crystals, mp 112—114 °C (lit,[25] 112—113 °C).

*2-(p-Chlorophenyl)-3-methylbenzothiazoline (**1d**)*: 55% yield from **32a**, colorless crystals, mp 77—79 °C; NMR ($CDCl_3$): δ 2.65 (s, 3H), 5.99 (s, 1H), and 6.35—7.7 (m, 8H). Found: C, 64.01; H, 4.80; N, 5.25%. Calcd for $C_{14}H_{12}NSCl$: C, 64.24; H, 4.62; N, 5.35%.

*2,3-Dimethylbenzothiazoline (**1e**)*: 67% yield from **32a**, pale yellow oil, bp 69 °C/0.2 mmHg (1 mmHg=133.322 Pa) (lit,[21] 120—121 °C/10 mmHg).

*3-Ethyl-2-methylbenzothiazoline (**1h**)*: 27% yield from **32b**, yellow oil, bp 95 °C/0.2 mmHg; NMR ($CDCl_3$): δ 1.15 (t, J=6 Hz, 3H), 1.53 (d, J=6 Hz, 3H), 3.21 (br q, J=7 Hz, 2H), 5.23 (q, J=6 Hz, 1H), and 6.2—7.2 (m, 4H). Found: C, 67.27; H, 7.25; N, 7.71%. Calcd for $C_{10}H_{13}NS$: C, 67.00; H, 7.31; N, 7.81%.

*3-Ethyl-2-phenylbenzothiazoline (**1j**)*: 33% yield from **32b**, yellow oil, bp 120 °C/0.25 mmHg; NMR ($CDCl_3$): δ 1.02 (t, J=7 Hz, 3H), 3.11 (m, 2H), 6.22 (s, 1H), and 6.3—7.7 (m, 9H). Found: C, 74.50; H, 6.42; N, 5.63%. Calcd for $C_{15}H_{15}NS$: C, 74.65; H, 6.26; N, 5.80%.

*2,2-Diethyl-3-methylbenzothiazoline (**1k**)*: 83% yield from **32c**, yellow oil;[26] NMR ($CDCl_3$): δ 0.95 (t, J=7 Hz, 6H), 1.82 (br q, J=7 Hz, 4H), 2.65 (s, 3H), and 6.0—7.1 (m, 4H).

*3-Methylbenzothiazoline (**1f**)*. To **32a** (3.31 g, 11.9 mmol) in THF (80 ml), $NaBH_4$ (487 mg, 12.9 mmol) was added portionwise at −10 °C. The solution was stirred for 2 h at room temp, and usual work-up gave yellow oil (0.724 g, 40%); bp 90 °C/0.1 mmHg (lit,[25] 133 °C/11 mmHg).

*3-Ethylbenzothiazoline (**1i**)* was prepared from **32b** by a similar method to that of **1f** as pale yellow oil in 65% yield; bp 81 °C/0.1 mmHg; NMR ($CDCl_3$): δ 1.28 (t, J=7 Hz, 3H), 3.18 (q, J=7 Hz, 2H), 4.65 (s, 2H), and 6.3—7.1 (m, 4H). Found: C, 65.63; H, 6.60; N, 8.34%. Calcd for $C_9H_{11}NS$: C, 65.41; H, 6.60; N, 8.34%.

*Alkylations of **1** with Meerwein Reagents (**4**). General Procedure*: To **1** (7 mmol) in CH_2Cl_2 (20—30 ml) was added a slightly excess of **4a** or **4b**. After stirring at room temp for several hours, the reaction was quenched with a few ml of ethanol. The solvent was evaporated *in vacuo*, the residue was washed well with dry ether, and recrystallized to give colorless crystals unless otherwise noticed. The NMR spectra were determined in DMSO-d_6.

Methylation: **3a**: yield 69%, mp 165—167 °C (decomp) (from CH_2Cl_2–Et_2O); NMR: δ 3.12 (s, 3H), 3.65 (s, 3H), 3.87 (s, 3H), 6.94 (s, 1H), and 7.0—8.1 (m, 8H). Found: C, 53.31; H, 5.10; N, 3.73%. Calcd for $C_{16}H_{18}BF_4NOS$: C, 53.50; H, 5.05; N, 3.90%.

3b: pale yellow crystals, yield 59%, mp 195—197 °C (decomp) (from MeOH–Et_2O); NMR: δ 2.42 (s, 3H), 3.10 (s, 3H), 3.66 (s, 3H), 6.94 (s, 1H), and 7.2—8.1 (m, 8H). Found: C, 55.38; H, 5.16; N, 3.99%. Calcd for $C_{16}H_{18}BF_4NS$: C, 56.00; H, 5.29; N, 4.08%.

3c: yield 69%, mp 178.5—180.5 °C (decomp) (from MeOH–Et_2O); NMR: δ 3.11 (s, 3H), 3.71 (s, 3H), 6.99 (s, 1H), and 7.4—8.1 (m, 9H). Found: C, 54.50; H, 5.00; N, 4.11%. Calcd for $C_{15}H_{16}BF_4NS$: C, 54.73; H, 4.90; N, 4.26%. After collection of **3c**, the filtrate and washings were evaporated to be subjected to CC (SiO_2, CH_2Cl_2). *N*-Methyl-*o*-methylthioaniline[6] (IR (neat): 3360 cm^{-1} (NH); NMR ($CDCl_3$): δ 2.17 (s, 3H), 2.70 (s, 3H), 4.76 (br s, 1H), 6.3—6.8, and 6.95—7.45 (m, 4H)) and its hydrotetrafluoroborate (NMR: δ 2.47 (s, 3H), 2.97 (s, 3H), 7.0—7.7 (m, 4H), and 8.01 (br s, 2H)) were obtained in 10 and 4.5% yields, respectively. The NMR spectrum of the latter was in agreement with that of authentic sample obtained from *N*-methyl-*o*-methylthioaniline and tetrafluoroboric acid.

3d: yield 70%, mp 196—197 °C (decomp) (from EtOH–Et_2O); NMR: δ 3.17 (s, 3H), 3.71 (s, 3H), 7.00 (s, 1H), and 7.4—8.1 (m, 8H). Found: C, 49.65; H, 4.05; N, 3.59%. Calcd for $C_{15}H_{15}BClF_4NS$: C, 49.55; H, 4.16; N, 3.85%.

3e: yield 66%, mp 117.5—119.0 °C (decomp) (from CH_2Cl_2–Et_2O); NMR: δ 1.86 (d, J=7 Hz, 3H), 3.35 (s, 3H), 3.73 (s, 3H), 5.81 (q, J=7 Hz, 1H), and 7.3—8.0 (m, 4H). Found: C, 45.24; H, 5.42; N, 5.24%. Calcd for $C_{10}H_{14}BF_4NS$: C, 44.97; H, 5.28; N, 5.24%.

3f: yield 77%, mp 172—173.5 °C (decomp) (from EtOH–Et_2O); NMR: δ 3.62 (s, 6H), 5.34 (s, 2H), and 7.3—8.0 (m, 4H). Found: C, 42.55; H, 4.69; N, 5.71%. Calcd for $C_9H_{12}BF_4NS$: C, 42.72; H, 4.78; N, 5.53%.

3g: yield 71.5%, mp 177—178.5 °C (decomp) (from CH_2Cl_2); NMR: δ 1.95 (s, 6H), 3.55 (s, 6H), and 7.4—8.1 (m, 4H). Found: C, 47.22; H, 5.84; N, 5.27%. Calcd for $C_{11}H_{16}BF_4NS$: C, 47.00; H, 5.74; N, 4.98%.

5 (from **1h**): recryst from EtOH–Et_2O, yield 43% (**5A**/**5B**=*ca.* 2) (see below).

6 (from **1i**): recryst from EtOH–Et_2O, yield 80% (see below).

Ethylation: **5** (from **1e**): yield 61% (**5A**/**5B**=*ca.* 10); NMR: **5A**: δ 1.24 (t, J=7 Hz, 3H), 1.78 (d, J=7.5 Hz, 3H), 3.41 (s, 3H), 3.8—4.3 (m, 2H), 5.81 (q, J=7.5 Hz, 1H), and 7.3—8.0 (m, 4H); **5B**: δ 1.15 (t, J=7 Hz, 3H), 1.91 (d, J=7.5 Hz, 3H), 3.65 (s, 3H), 3.8—4.3 (m, 2H), *ca.* 5.9 (q, J=7.5 Hz, 1H), and 7.3—8.3 (m, 4H). Pure **5A**: mp 160—161.5 °C (decomp) (three times from CH_2Cl_2). Found: C, 47.12; H, 6.01; N, 5.25%. Calcd for $C_{11}H_{16}BF_4NS$: C, 47.00; H, 5.74; N, 4.98%.

6 (from **1f**): yield 49.5%, mp 93.5—95.0 °C (decomp) (from EtOH–Et_2O); NMR: δ 1.40 (t, J=7 Hz, 3H), 3.62 (s, 3H), 4.02 (dq, J=7 Hz and 2 Hz, 2H), 5.31 (s, 2H), and 7.2—7.9 (m, 4H). Found: C, 44.98; H, 5.23; N, 5.32%. Calcd for $C_{10}H_{14}BF_4NS$: C, 44.97; H, 5.28; N, 5.24%.

7aA+**7aB**: pale yellow crystals, yield 39%, mp 145.5—149.5 °C (from CH_2Cl_2–Et_2O) (**A**/**B**=*ca.* 1); NMR: **7aA**: δ 1.42 (t, J=7 Hz, 3H), 3.10 (s, 3H), 3.5—4.2 (m, 2H), 6.86 (s, 1H), and 6.95—8.0 (m, 8H); **7aB**: δ 1.09 (t, J=7 Hz, 3H), 3.53 (s, 3H), 3.5—4.5 (m, 2H), and 6.95—8.0 (m, 9H). Found (mixture): C, 54.65; H, 5.48; N, 3.71%. Calcd for $C_{17}H_{20}BF_4NOS$: C, 54.71; H, 5.40; N, 3.75%.

7bA+**7bB**: pale yellow crystals, yield 37%, mp 158—161 °C (**A**/**B**=*ca.* 1); NMR: **7bA**: δ 1.46 (t, J=7 Hz, 3H),

3.11 (s, 3H), 3.5—4.5 (m, 2H), 6.80 (s, 1H), and 7.2—8.0 (m, 8H); **7bB**: δ 1.13 (t, J=7 Hz, 3H), 3.57 (s, 3H), 3.5—4.5 (m, 2H), 7.07 (s, 1H), and 7.2—8.0 (m, 8H). Found (mixture): C, 57.43; H, 5.86; N, 4.09%. Calcd for $C_{17}H_{20}BF_4NS$: C, 57.16; H, 5.64; N, 3.92%.

7cA+**7cB**: yield 34% (**A**/**B**=*ca.* 10); NMR: **7cA**: δ 1.43 (t, J=7 Hz, 3H), 3.12 (s, 3H), 3.5—4.5 (m, 2H), 6.93 (s, 1H), and 7.4—8.0 (m, 9H); **7cB**: δ 1.08 (t, J=7 Hz, 3H), 3.57 (s, 3H), 3.5—4.5 (m, 2H), 7.17 (s, 1H), and 7.4—8.0 (m, 9H). Pure **7cA**: mp 144—145 °C (decomp) (three times from EtOH–Et_2O). Found: C, 55.76; H, 5.42; N, 3.91%. Calcd for $C_{16}H_{18}BF_4NS$: C, 56.00; H, 5.29; N, 4.08%.

7dA+**7dB**: pale yellow crystals (from CH_2Cl_2–Et_2O) (**A**/**B**=*ca.* 10), yield 35%; NMR: **7dA**: δ 1.42 (t, J=7 Hz, 3H), 3.17 (s, 3H), 3.7—4.6 (m, 2H), 6.89 (s, 1H), and 7.3—8.0 (m, 8H); **7dB**: δ 1.09 (t, J=7 Hz, 3H), 3.58 (s, 3H), 3.7—4.6 (m, 2H), 7.17 (s, 1H), and 7.3—8.0 (m, 8H). Pure **7dA**: mp 139—141 °C (three times from CH_2Cl_2–Et_2O). Found: C, 51.00; H, 4.38; N, 4.00%. Calcd for $C_{16}H_{17}BClF_4NS$: C, 50.89; H, 4.54; N, 3.71%.

Reaction of ***1c*** *with Silver Perchlorate.* 3-Methyl-2-phenylbenzothiazoline (**1c**) (1.1 g, 4.87 mmol) was subjected to the reaction with $AgClO_4$ (1.01 g, 4.89 mmol) in CH_2Cl_2 (20 ml) and $MeNO_2$ (10 ml). After usual work-up, recrystallization from MeOH gave **8** quantitatively, mp 219—223 °C (lit,[27] 219—220 °C).

Reactions of ***3a—d*** *and* ***7*** *with LDA. General Procedure*: To a suspension of the salt (**3a—d** and **7**) (1 mmol) in THF (5 ml) or ether (20 ml) at −40 °C was added LDA (1.1—2 mmol) in THF (5 ml) or ether (5 ml) under nitrogen. The mixture was stirred for 0.5 h at this temp, for 1.5 h at room temp, and then slightly heated. After removal of the solvent *in vacuo* and addition of water, the reaction mixture was extracted with ether. The ethereal layer was dried ($MgSO_4$) and evaporated to be subjected to dry column chromatography (DCC) (**9a**: SiO_2, CCl_4–CH_2Cl_2 (4:1); **9b**: SiO_2, CCl_4–CH_2Cl_2 (10:1); **9c**: SiO_2, CCl_4; **9d**: SiO_2, CCl_4–CH_2Cl_2 (3:1); **11a** and **11b**: SiO_2, hexane–Et_2O (3:1); **11c**: SiO_2, hexane–Et_2O (10:1); **11d**: SiO_2, CCl_4). The results were shown in Table 4 and in the text. These products were identified by a comparison of NMR spectra with authentic samples prepared independently (see below).

Independent Syntheses of ***9***, ***11***, *and* ***12***. *General Procedure*: To a suspension of 2-aryl-3-ethyl- or -3-methylbenzothiazolium perchlorate[27] (5 mmol) in ether (25—70 ml) at −40 °C was added an ethereal solution of Grignard reagent (8.5—10 mmol) under nitrogen. The mixture was stirred for several hours at room temp. After usual work-up, the residue was subjected to DCC (SiO_2, C_6H_6) to give **9** (as colorless crystals), **11** (as yellow viscous oil), and **12**.

9a: yield 68%, mp 58.5—59.5 °C (from EtOH); NMR ($CDCl_3$): δ 1.90 (s, 3H), 2.49 (s, 3H), 3.68 (s, 3H), and 6.1—7.6 (m, 8H). Found: C, 70.58; H, 6.47; N, 5.22%. Calcd for $C_{16}H_{17}NOS$: C, 70.81; H, 6.31; N, 5.16%.

9b: yield 61%, mp 104—105 °C (from EtOH); NMR ($CDCl_3$): δ 1.92 (s, 3H), 2.30 (s, 3H), 2.54 (s, 3H), and 6.1—7.6 (m, 8H). Found: C, 75.04; H, 6.65; N, 5.38%. Calcd for $C_{16}H_{17}NS$: C, 75.25; H, 6.71; N, 5.48%.

9d: yield 84%, mp 95.5—96.5 °C (from EtOH–hexane); NMR ($CDCl_3$): δ 1.95 (s, 3H), 2.55 (s, 3H), and 6.15—7.65 (m, 8H). Found: C, 65.27; H, 5.03; N, 5.25%. Calcd for $C_{15}H_{14}ClNS$: C, 65.32; H, 5.12; N, 5.08%.

11a: yield 68%; NMR ($CDCl_3$): δ 1.05 (t, J=7 Hz, 3H), 2.29 (q, J=7 Hz, 2H), 2.57 (s, 3H), 3.73 (s, 3H), and 6.1—7.6 (m, 8H); HMS: Found: *m/e* 285.1187. Calcd for $C_{17}H_{19}NOS$: 285.1187.

11b: yield 97%; NMR ($CDCl_3$): δ 1.08 (t, J=7 Hz, 3H), 2.32 (s, 3H), 2.33 (q, J=7 Hz, 2H), 2.62 (s, 3H), and 6.15—7.55 (m, 8H). Found: C, 75.73; H, 7.11; N, 5.28%. Calcd for $C_{17}H_{19}NS$: C, 75.79; H, 7.11; N, 5.20%.

11c: yield 77.5%; NMR ($CDCl_3$): δ 1.10 (t, J=7 Hz, 3H), 2.33 (q, J=7 Hz, 2H), 2.61 (s, 3H), and 6.1—7.65 (m, 9H). HMS: *m/e* 255.1109. Calcd for $C_{16}H_{17}NS$: 255.1082.

11d: yield 95%, bp 164 °C/0.1 mmHg; NMR ($CDCl_3$): δ 1.05 (t, J=7 Hz, 3H), 2.26 (q, J=7 Hz, 2H), and 6.1—7.6 (m, 8H). Found: C, 66.05; H, 5.42; N, 5.03%. Calcd for $C_{16}H_{16}ClNS$: C, 66.31; H, 5.56; N, 4.83%.

12a: colorless crystals, yield 92%, mp 78—79 °C (from EtOH–hexane); NMR ($CDCl_3$): δ 1.05 (t, J=7 Hz, 3H), 1.96 (s, 3H), 2.94 (q, J=7 Hz, 2H), 3.68 (s, 3H), and 6.1—7.7 (m, 8H). Found: C, 71.61; H, 7.00; N, 5.00%. Calcd for $C_{17}H_{19}NOS$: C, 71.54; H, 6.71; N, 4.91%.

12b: yellow viscous oil, yield 78%; NMR ($CDCl_3$): δ 1.11 (t, J=7 Hz, 3H), 2.04 (s, 3H), 3.04 (q, J=7 Hz, 2H), and 6.25—7.75 (m, 9H). Found: C, 75.12; H, 6.72; N, 5.46%. Calcd for $C_{16}H_{17}NS$: C, 75.25; H, 6.71; N, 5.48%.

Reactions of ***3a—d*** *and* ***7*** *with Butyllithium. General Procedure*: To a suspension of the salt (**3a—d** and **7**) (2 mmol) in ether (20 ml) under nitrogen at −60 °C was added butyllithium (2.2—2.4 mmol) and the mixture was stirred for 5 h at room temp. After usual work-up, the residue was subjected to DCC and/or TLC.

Reaction of ***3a***: DCC (SiO_2, CH_2Cl_2) afforded two fractions, R_f 0.1—0.2 and 0.5—0.9. TLC (SiO_2, Et_2O) of the former gave pale yellow viscous oil (**19a**) in 32% yield. TLC (SiO_2, hexane–C_6H_6 (1:1)) of the latter fraction gave **20** (12%), **21** (8%), and **22** (4%) as pale yellow oils. **19a**: NMR ($CDCl_3$): δ 0.91 (br t, J=7 Hz, 3H), 1.2—1.8 (m, 4H), 2.19 (s, 6H), 2.65—3.0 (br t, J=7 Hz, 2H), 3.70 (s, 3H), 4.72 (s, 1H), and 6.65—7.9 (m, 8H); MS: *m/e* 329 (M^+, 40%), 314 (M^+−Me, 100), 285 (M^+−NMe_2, 37), 272 (M^+−Bu, 49), and 164 ($Me_2\overset{+}{N}CH$–C_6H_4OMe, 77). **20**: NMR ($CDCl_3$): δ 0.90 (br t, J=7 Hz, 3H), 1.1—1.9 (m, 4H), 2.90 (br t, J=7 Hz, 2H), and 7.0—7.5 (m, 5H). **21**: NMR ($CDCl_3$): δ 0.91 (br t, J=7 Hz, 3H), 1.2—1.9 (m, 4H), 2.7—3.1 (br t, J=7 Hz, 2H), 2.76 (s, 6H), and 6.8—7.4 (m, 4H); MS: *m/e* 209 (M^+, 62%), 153 (M^+−Bu+H, 100), 152 (M^+−Bu, 46), 137 (56), 136 (54), and 120 (M^+−SBu, 32). **22**: NMR ($CDCl_3$): δ 0.83 (br t, J=7 Hz, 3H), 1.1—1.5 (m, 4H), 1.7—2.2 (m, 2H), 2.77 (s, 6H), 3.76 (s, 3H), 4.33 (t, J=7.5 Hz, 1H), and 6.7—7.4 (m, 8H); MS: *m/e* 329 (M^+, 4%), 209 (M^+−$Me_2NC_6H_4$, 58), 177 ($MeOC_6H_4\overset{+}{C}HBu$, 23), and 153 ($Me_2NC_6H_4SH^+$, 100).

Reaction of ***3b***: DCC (SiO_2, CH_2Cl_2) gave pale yellow viscous oil (**19b**) (27%); NMR ($CDCl_3$): δ 0.90 (br t, J=7 Hz, 3H), 1.1—1.9 (m, 4H), 2.18 (s, 6H), 2.23 (s, 3H), 2.7—3.0 (br t, J=7 Hz, 2H), 4.73 (s, 1H), and 6.9—7.9 (m, 8H).

Reaction of ***3c***: DCC (SiO_2, CCl_4–CH_2Cl_2 (2:1)) gave **19c** (38%), benzyl phenyl ketone (3%) (by IR and NMR), and a fraction of R_f 0.8—0.9, the latter of which was subjected again to TLC (SiO_2, C_6H_6–hexane (2:1)) to give **20** (14%), **21** (6%), and **23** (6%). **19c**: mp 42—43 °C; NMR ($CDCl_3$): δ 0.91 (br t, J=7 Hz, 3H), 1.2—1.9 (m, 4H), 2.22 (s, 6H), 2.86 (br t, J=7 Hz, 2H), 4.87 (s, 1H), and 7.0—8.0 (m, 9H); MS: *m/e* 299 (M^+, 74%), 284 (M^+−Me, 100), 242 (M^+−Bu, 54), and 211 (M^+−SBu+H, 55). Found: C, 76.49; H, 8.47; N, 4.65; S, 10.67%. Calcd for $C_{19}H_{25}NS$: C, 76.20; H, 8.41; N, 4.68; S, 10.71%. **23**: NMR ($CDCl_3$): δ 0.88 (br t, J=7 Hz, 3H), 1.1—1.8 (m, 4H), 2.6—3.0 (m, 2H), 2.89 (s, 3H), 5.1 (br s, 1H), and 6.5—7.6 (m, 4H); IR (neat): 3370 cm^{-1} (NH).

Reaction of ***3d***: DCC (SiO_2, CH_2Cl_2) gave **19d** (13%) as pale yellow viscous oil; NMR ($CDCl_3$): δ 0.75—1.1 (m, 3H), 1.2—1.8 (m, 4H), 2.19 (s, 6H), 2.7—3.0 (m, 2H), 4.79 (s, 1H), and 7.0—7.9 (m, 8H).

Reaction of ***7a***: TLC (SiO_2, CH_2Cl_2) gave **31** (11%) as pale yellow oil; NMR ($CDCl_3$): δ 0.96 (br t, J=7 Hz, 3H), 1.03 (t, J=7 Hz, 3H), 1.3—1.8 (m, 4H), 2.16 (s, 3H), 2.47 (q, J=7 Hz, 2H), 2.7—3.0 (m, 2H), 3.74 (s, 3H), 4.98 (s, 1H), and 6.7—7.9 (m, 8H). HMS: Found: *m/e* 343.1962. Calcd for $C_{21}H_{29}NOS$: 343.1968.

Reaction of ***14*** *with Butyllithium.* *N*-Benzyl-*N*-ethylaniline (5.70 g, 27.0 mmol) was methylated with **4a** (4.38 g, 29.6 mmol) in CH_2Cl_2 (30 ml). After addition of ether, the resulting precipitates were recrystallized from CH_2Cl_2–Et_2O to give **14** (5.82 g, 69%); NMR (DMSO-d_6): δ 1.09 (t, J=7 Hz, 3H), 3.37 (s, 3H), 4.08 (m, 2H), 5.00 (br d, J=2.5 Hz, 2H), and 6.8—7.8 (m, 10H). To **14** (1.06 g, 3.39 mmol) in THF (25 ml) was added BuLi (3.8 mmol) under nitrogen at −50 °C. The products extracted with ether was a mixture of **15** (35%), **16** (6%), and **17** (12%) by glc (column, OV-1, 170 °C). In ether (15 ml), the products were a mixture of **15** (34%), **16** (6%), and **17** (20%).

Preparation of N-*(α-Ethylbenzyl)*-N-*methylaniline (17).* *N*-Benzylideneaniline (5.31 g, 29.3 mmol) in ether (15 ml) was added to EtMgI (31.3 mmol) in ether (50 ml). The mixture was refluxed for 1.5 h and poured into ice and concd HCl (100 ml). After usual work-up, DCC (SiO_2, hexane–CH_2Cl_2 (1.7:1)) of the residue gave *N*-(α-ethylbenzyl)aniline (2.15 g, 35%). The product (2.05 g, 9.70 mmol) was methylated by **4a** (2.10 g, 14.2 mmol) in CH_2Cl_2 (20 ml) under reflux for 1 h. After addition of ether, the resulting precipitates were dissolved in CH_2Cl_2 followed by deprotonation with Et_3N (4.1 ml, 29 mmol). Usual work-up gave **17**, 1.76 g, 80.5% yield, bp 118 °C/0.05 mmHg; NMR ($CDCl_3$): δ 0.97 (t, J=7 Hz, 3H), 1.96 (m, 2H), 2.62 (s, 3H), 4.79 (br t, J=7 Hz, 1H), and 6.5—7.3 (m, 10H). Found: C, 85.20; H, 8.61; N, 6.31%. Calcd for $C_{16}H_{19}N$: C, 85.28; H, 8.50; N, 6.22%.

Preparation of N-*Ethyl*-N-*(α-methylbenzyl)aniline (18).* *N*-(α-Methylbenzyl)aniline (42% yield) was prepared from *N*-benzylideneaniline and MeMgI and ethylated with **4b** in a similar manner to that of **17** to afford **18** in 88% yield, bp 115 °C/0.07 mmHg; NMR ($CDCl_3$): δ 1.04 (t, J=7 Hz, 3H), 1.54 (d, J=7 Hz, 3H), 3.19 (q, J=7 Hz, 2H), 5.04 (br q, J=7 Hz, 1H), and 6.5—7.4 (m, 10H). Found: C, 85.17; H, 8.76; N, 6.03%. Calcd for $C_{16}H_{19}N$: C, 85.28; H, 8.50; N, 6.22%.

Reaction of ***27*** *with Butyllithium.* To trimethyl[*o*-(methylthio)phenyl]ammonium tetrafluoroborate (**27**)[28] (298 mg, 1.11 mmol) in ether (15 ml) was added BuLi (1.40 mmol). A similar treatment to that of **7** and submission to TLC (SiO_2, hexane–Et_2O (5:1)) gave **28**, 44.7 mg, 22% yield; NMR ($CDCl_3$): δ 2.25 (s, 6H), 2.42 (s, 3H), 3.45 (s, 2H), and 6.8—7.3 (m, 4H).

Independent Synthesis of ***19c***. *o*-Butylthioaniline was prepared from sodium *o*-aminobenzenethiolate and BuBr in 82.5% yield, bp 87 °C/0.4 mmHg. The aniline was converted into *o*-bromophenyl butyl sulfide by Sandmeyer reaction in 40% yield. The sulfide (1.30 g, 5.32 mmol) was treated with BuLi (5.25 mmol) in ether (10 ml). Benzaldehyde (0.537 g, 5.06 mmol) in ether (10 ml) was added to this solution at −15 °C and the mixture was stirred for 14 h at room temp. After usual work-up, submission to DCC (SiO_2, CCl_4) gave α-(*o*-butylphenyl)benzyl alcohol, 1.26 g, 92% yield. This alcohol (1.17 g, 4.29 mmol) was treated with $SOCl_2$ (0.36 ml) in pyridine (0.39 ml) and ether (15 ml) by a similar method to that described in the literature.[29] Distillation gave butyl *o*-(α-chlorobenzyl)phenyl sulfide, 1.06 g, 85% yield; NMR ($CDCl_3$): δ 0.7—1.0 (m, 3H), 1.2—1.8 (m, 4H), 2.82 (br t, J=7 Hz, 2H), 6.78 (s, 1H), and 7.0—7.6 (m, 9H); MS: *m/e* 290 (M^+). Butyl *o*-(α-chlorobenzyl)-phenyl sulfide (0.85 g, 2.92 mmol) in ether (10 ml) was added at −60 °C to Me_2NLi (6.16 mmol) in ether (15 ml). After stirring for 2 h at room temp and then washing with water, the ethereal layer was subjected to DCC (SiO_2, CCl_4–CH_2Cl_2 (3:1)) to afford **19c** (671 mg, 77%); bp *ca.* 120 °C/0.1 mmHg. The spectral data were in agreement with those of reaction product.

References

1) J. L. Richards and D. S. Tarbell, *J. Org. Chem.*, **35**, 2079 (1970).
2) H. Minato, K. Yamaguchi, and M. Kobayashi, *Chem. Lett.*, **1975**, 991.
3) C. R. Johnson, E. R. Janiga, and M. Haake, *J. Am. Chem. Soc.*, **90**, 3890 (1968).
4) J. W. Masico, Jr., G. O. Morton, and L. Goldman, *J. Org. Chem.*, **42**, 2164 (1977).
5) K. Akiba, Y. Ohara, and N. Inamoto, *Heterocycles*, **6**, 13 (1977).
6) M. Hori, T. Kataoka, H. Shimizu, and Y. Imai, *Chem. Pharm. Bull. (Tokyo)*, **25**, 1482 (1977).
7) S. H. Pine, *Org. React.*, **18**, 403 (1970); *J. Chem. Educ.*, **48**, 99 (1971).
8) For review see: Y. Ohara and K. Akiba, *Kagaku No Ryoiki*, **33**, 843 (1979).
9) a) T. S. Johnstone and T. S. Stevens, *J. Chem. Soc.*, **1930**, 2107; b) J. H. Brewster and M. W. Kline, *J. Am. Chem. Soc.*, **74**, 5179 (1952); c) U. Schöllkopf, U. Ludwig, G. Ostermann, and M. Patsch, *Tetrahedron Lett.*, **1969**, 2619, 3415.
10) A. Campbell, A. H. J. Houston, and J. Kenyon, *J. Chem. Soc.*, **1949**, 93; B. J. Millard and T. S. Stevens, *ibid.*, **1963**, 3397.
11) U. E. Baldwin, W. F. Erickson, R. E. Hackler, and R. M. Scott, *Chem. Commun.*, **1970**, 576; A. R. Lepley, *ibid.*, **1969**, 1460.
12) M. J. S. Dewar and C. A. Ramsden, *J. Chem. Soc., Perkin Trans. 1*, **1974**, 1839.
13) Preliminary reports: K. Akiba, Y. Ohara, and N. Inamoto, *Heterocycles*, **11**, 231 (1978); Y. Ohara, K. Akiba, and N. Inamoto, *ibid.*, **13**, 289 (1979).
14) J. W. Henderson, *Chem. Soc. Rev.*, **2**, 397 (1973).
15) P. T. Lansbury, V. A. Pattison, J. D. Sidler, and J. B. Bieber, *J. Am. Chem. Soc.*, **88**, 78 (1966); H. Schäfer, U. Schöllkopf, and D. Walter, *Tetrahedron Lett.*, **1968**, 2809.
16) U. Schöllkopf, *Angew. Chem., Int. Ed. Engl.*, **9**, 763 (1970).
17) M. Hisaoka, K. Akiba, and Inamoto, *Bull. Chem. Soc. Jpn.*, **48**, 3274 (1975).
18) K. Goda, R. Okazaki, K. Akiba, and N. Inamoto, *Bull. Chem. Soc. Jpn.*, **51**, 260 (1978).
19) T. J. Curphey, *Org. Synth.*, **51**, 142 (1971).
20) H. Meerwein, *Org. Synth.*, Coll. Vol. V, 1080 (1973).
21) J. Metzger, H. Lanire, E. J. Vincent, and R. Dennilauler, *J. Chim. Phys.*, **60**, 944 (1963).
22) A. I. Kiprianov and V. A. Portnyagina, *Zh. Obshch. Khim.*, **25**, 2257 (1955); *Chem. Abstr.*, **50**, 9378[b] (1956).
23) K. Akiba, T. Kawamura, M. Hisaoka, and N. Inamoto, *Bull. Chem. Soc. Jpn.*, **48**, 3262 (1975).
24) Preliminary report: K. Akiba, Y. Ohara, M. Hisaoka, and N. Inamoto, *Heterocycles*, **3**, 567 (1975).

25) K. Baker and H. E. Fierz-David, *Helv. Chim. Acta*, **33**, 2011 (1950).
26) K. Akiba, H. Shiraishi, and N. Inamoto, *Bull. Chem. Soc. Jpn.*, **52**, 156 (1979).
27) A. I. Kiprianov and Ya. Shtets, *Zh. Obshch. Khim.*, **33**, 3519 (1963); *Chem. Abstr.*, **60**, 10839^{f} (1964).
28) Y. Ohara, K. Akiba, and N. Inamoto, unpublished result.
29) D. W. Meek, G. Dyer, and M. O. Workman, *Inorg. Synth.*, **16**, 168 (1976).