of seal.) Mass balance showed that solvent evaporation was negligible.

(3) In order to account for the heat released by the ultrasonic source the thermostated bath was held at 90 °C. The reaction temperature, which was measured inside the vial with a thermocouple, varied between 92 and 95 °C, but the latter was never exceeded.

(e) Catalyst Recovery and Recycle. The catalyst powder (magnetic stirring) was recovered from the filter cake by 3–4 alternating washings with acetone and water and was dried as usual. (The catalyst was free of potassium ions, which was affirmed by Energy Dispersive Spectrometry.) The particle size was investigated both with a light microscope and by SEM. The percent of active sites remaining in the recovered catalyst was determined by conversions of the catalyst back to its original chloride form,[11] and chloride ion titration was performed in the usual way. The catalytic activity of the recovered catalyst powder was measured by repeating the reaction as described in paragraph a. Catalyst particles bigger than ≈100 μm (as obtained from the reactions with unconventional agitation) were separated from the filter cake by mixing the cake (manually, by means of a spatula) with chloroform. The floating particles were decanted, washed twice with acetone, and dried as usual.

(f) Reaction Kinetics. The reaction conditions were the same as described above (using 15% by weight of A27 catalyst), but samples were taken every hour and analyzed by GC.

Synthetic Applications. (a) Halogen Exchange, Esterification, and Cyanide Displacement Reactions (Reactions 1–9 in Table II). The ractions were performed with A27 resin as catalyst according to the procedure described for formate ion displacement of benzyl chloride. The reaction temperatures and the amount of catalyst (in percent of the organic substrate) are summarized in Table II. Water was added to reactions 2, 6, 8 (20 μL each), and 9 (200 μL). The reactions were followed by GC analysis of samples taken at appropriate time intervals. The dependency of the cyanide displacement of 1-bromooctane on the water content (Table III) was investigated under the same reaction conditions except for the reduced reaction time (25 h) and the variable amount of water added.

(b) Nitrite Displacement. The reaction conditions were the same as those described in paragraph a, except for 0.5 mL of xylene which was added as internal standard (the solvent's volume was reduced to 7.5 mL). The GC integrator was calibrated for 1-bromooctane, 1-nitrooctane, and 1-octyl nitrite.

(c) *p*-Nitroanisole. *p*-Chloronitrobenzene (pCNB, 8 mmol, 1.25 g), sodium methoxide (16 mmol, 0.85 g), A27 (0.8 mmol, 0.3 g), and toluene (8 mL) are magnetically stirred for 4 h at 65 °C. The solids are filterd off and washed twice with toluene. The solvent is evaporated, and the product is dried overnight at 60 °C, 1 mmHg. The solid product (0.93 g, mp 48 °C) contains 98% *p*-nitroanisole (5.9 mmol, yield 74%) and 2% pCNB according to GC analysis.

(d) *N*-Benzylphthalimide. Benzyl chloride (10 mmol, 1.27 g), potassium phthalimide (12 mmol, 2.22 g), A27 (0.5 mmol, 0.17 g), xylene (internal standard, 0.5 mL), and toluene (7.5 mL) are magnetically stirred overnight at 90 °C. A quantitative yield (100%) of *N*-benzylphthalimide is obtained (GC calibration with authentic samples).

(e) Alcohol Oxidations. 2-Octanol (2.5 mmol, 0.352 g), potassium permanganate (7.5 mmol, 1.18 g), A27 (0.3 mmol, 0.10 g), nonane (internal standard, 0.1 g), and toluene (6 mL) were mixed for 20 h at 75 °C. Analysis by GC showed a conversion of 98% and a yield of 90% (according to the peak area ratio of product to standard; additional peaks were not observed).

(f) Michael Addition (Reaction 14). 3-Buten-2-one (10 mmol, 0.7 g), nitroethane (20 mmol, 1.5 g), A27 (0.5 mmol, 0.17 g), potassium fluoride (5 mmol, 0.30 g), toluene (internal standard, 0.3 g), and chlorobenzene (5 mL) were magnetically stirred at room temperature. The reaction solution was analyzed by GC after 2 and 3 h. Potassium fluoride containing 2% water and dried potassium fluoride had the same effect. Less than 2% of the product was obtained when A27 or potassium fluoride was applied alone.

(g) Alkylation of Phenol. Benzyl chloride (3 mmol, 0.38 g), phenol (5 mmol, 0.47 g), A27 (0.3 mmol, 0.10 g), potassium fluoride (2% H_2O, 10 mmol, 0.6 g), dodecane (internal standard, 0.2 g), and toluene (8 mL) were stirred in the standard reaction vial at 85 °C for 30 h. GC analysis was calibrated with benzyl chloride, benzyl phenyl ether, and *o*- and *p*-hydroxydiphenylmethane. Conversions are based on benzyl chloride.

(h) Methylation of 2,4-Pentanedione (Reaction 16/Reaction 17). 2,4-Pentanedione (5 mmol, 0.5 g/1 mmol, 0.10 g), iodomethane (12.5 mmol, 1.78 g/1.25 mmol, 0.178 g), A27 (0.5 mmol, 0.2 g/2.5 mmol, 0.85 g), KF (20 mmol, 1.2 g/4 mmol, 0.24 g), and THF (8 mL/4 mL) were magnestically mixed (at 40 °C/20 °C) for 20 h. Reaction yields were calcualted from GC analysis.

Lewis Acid Induced Nucleophilic Substitution Reaction of β-Nitro Sulfides

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The nitro group of β-nitro sulfides is readily substituted by an allyl or a cyano group or hydrogen on treatment with allyltrimethylsilane, cyanotrimethylsilane, or triethylsilane in the presence of an appropriate Lewis acid. The intramolecular Friedel–Crafts reaction of β-nitro sulfides is also induced by a Lewis acid. Primary and secondary nitro groups as well as tertiary and benzylic nitro groups undergo this substitution reaction. These replacements of the nitro group cannot proceed when the adjacent phenylthio group is absent. Unsymmetrical β-nitro sulfides afford mixtures of two regioisomers. In particular, 1,2-migration of the phenylthio group predominates when the nitro group is located on primary position. This reaction proceeds in a stereospecific way. Stereochemical study reveals that the substitution reaction proceeds via the retention of configuration. These results suggest that episulfonium ions are the intermediates of the reaction. Thus, the β-nitro sulfides–Lewis acid system provides a new method for the generation of episulfonium ions.

Since the nitro group acts as an effective activating group in a carbon–carbon bond formation, aliphatic nitro compounds represent versatile intermediates in organic synthesis.[1] For example, the aldol reaction or the Michael addition reaction using aliphatic nitro compounds proceeds under very mild conditions to form new carbon–carbon bonds. Nitro compounds are also useful in organic syn-

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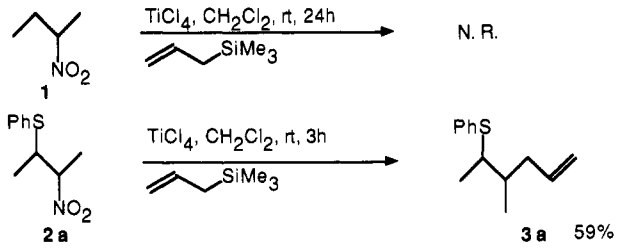
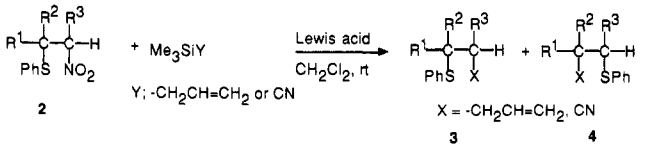
Scheme I

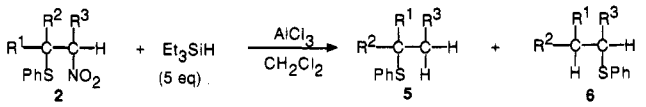


thesis, because many methods are available for the conversion of a nitro group to another functional group such as a keto, an amino, or a cyano group. Recently, we have found that the nitro group is readily replaced by hydrogen on treatment with tributyltin hydride under conditions known to involve free radicals.[2] However, there are a few examples of direct replacement of the nitro group by nucleophiles, since the direct substitution of the nitro group does not proceed under normal S_N2 reaction conditions.[3] The literature reports only two reactions that are representative examples for a direct replacement of a nitro group by a carbon nucleophile: one is a substitution reaction of the nitro group via a single-electron-transfer process ($S_{RN}1$ reaction);[4] the other is a nucleophilic substitution of an allylic nitro compound either catalyzed or not catalyzed by palladium.[5,6] Although unique compounds can be prepared by $S_{RN}1$ reaction, the choices of starting substrates or nucleophiles are very limited. The latter reaction is also limited to allylic nitro compounds. Consequently, a new general method for substitution reaction of the nitro group is of interest. As the nitro group acts as a weak Lewis base, it makes a complex with a Lewis acid. Previously, we reported that an activated nitro groups such as benzyl, allyl, or tertiary nitro group was readily replaced by sulfur or carbon nucleophiles on treatment with Lewis acids.[7,8] Although this reaction is applicable to the activated nitro groups, primary or secondary nitro groups are not replaced under these reaction conditions. We have found that introduction of a vicinal phenylthio group facilitates nucleophilic substitution reaction of primary and secondary nitro groups by carbon nucleophiles under these reaction conditions.[9] In this paper, we report the full experimental details of this reaction. Regio- and stereochemical studies on this reaction suggest that this reaction proceeds via episulfonium ion intermediates. Although the episulfonium ion is a versatile synthetic intermediate, there are relatively few useful methods for generation of episulfonium ion.[10] This system provides a useful method to generate the episulfonium ion.

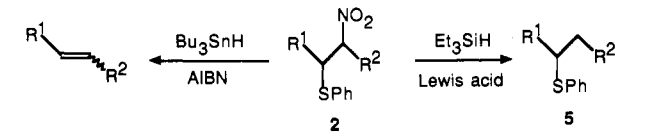
Scheme II



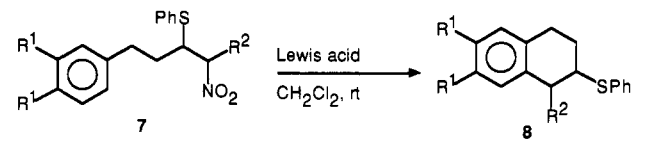
Scheme III



Scheme IV



Scheme V



Results and Discussion

Lewis Acid Induced Substitution of the Nitro Group. Although tertiary nitro groups can be replaced by an allyl group in the presence of allyltrimethylsilane on treatment with Lewis acids,[8] secondary nitro groups are quite inert under this condition. For example, the reaction of 2-nitrobutane (**1**) and $TiCl_4$ resulted in complete recovery of **1** after 24 h. On the other hand, exposure of 2-(phenylthio)-3-nitrobutane (**2a**) to $TiCl_4$ and allyltrimethylsilane provided 4-methyl-5-(phenylthio)-1-hexene (**3a**) in 59% yield (Scheme I). The neighboring group participation of the phenylthio group[11] is crucial for the substitution of the nitro group under these conditions. Lewis acid induced substitution reactions of various substrates **2** led to the results summarized in Table I (Scheme II).

The nitro group of **2** was replaced by allyl or cyano, respectively, in good yield on treatment with an appropriate Lewis acid and either allyltrimethylsilane or cyanotrimethylsilane. $AlCl_3$ effects the replacement of primary nitro groups by an allyl group (runs 7, 9, 12, 14). To complete the reaction, 2 equiv of Lewis acid is necessary. When 1.3 equiv of Lewis acid is used, the starting material still remains after 24 h (run 2). $SnCl_4$ is the best Lewis

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Table I. Nucleophilic Substitution of Nitro Groups by X

run	R^1	R^2	R^3	2	X	Lewis acid (equiv)	time, h	products	yield,[a] %	3/4[b]
1	Me	H	Me	2a[c]	$-CH_2CH=CH_2$	$TiCl_4$ (2)	6	**3a**[d]	60	
2	Me	H	Me	**2a**	$-CH_2CH=CH_2$	$TiCl_4$ (1.3)	24	**3a**	44[e]	
3	Me	H	Me	2a[f]	CN	$SnCl_4$ (2)	18	**3b**	60	
4	Ph	H	Ph	**2b**	$-CH_2CH=CH_2$	$AlCl_3$ (2)	0.2	**3c**	45	
5	Me	H	Ph	2c[g]	$-CH_2CH=CH_2$	$TiCl_4$ (2)	1	**3d**[h]	65	100/0
6	Me	H	Ph	2c[f]	CN	$SnCl_4$ (2)	0.1	**3e**	73	100/0
7	Me	Me	H	**2d**	$-CH_2CH=CH_2$	$AlCl_3$ (2)	1	**4f**	72	7/93
8	Me	Me	H	**2d**	CN	$SnCl_4$ (2)	24	**4g**	64	27/73
9	Et	Me	H	**2e**	$-CH_2CH=CH_2$	$AlCl_3$ (2)	1	**4h**	63	16/84
10	Et	Me	H	**2e**	CN	$SnCl_4$ (2)	12	**4i**	61	14/86
11	Me	C_6H_{13}	H	**2f**	CN	$SnCl_4$ (2)	6	**4j**	72	18/82
12	Ph	H	H	**2g**	$-CH_2CH=CH_2$	$AlCl_3$ (2)	1	**4k**	79	6/94
13	H	H	Et	**2h**	$-CH_2CH=CH_2$	$TiCl_4$ (2)	6	**3l + 4l**	52	47/53
14	Me	H	H	**2i**	$-CH_2CH=CH_2$	$AlCl_3$ (2)	6	**3m + 4m**	51	36/64
15	Et	H	Me	2j[f]	$-CH_2CH=CH_2$	$TiCl_4$ (2)	6	**3n + 4n**	55	75/25
16	Me	H	Et	2k[f]	$-CH_2CH=CH_2$	$TiCl_4$ (2)	6	**4n + 3n**	55	25/75

[a] Isolated yield. [b] Determined by GLC. [c] *anti*-**2a**/*syn*-**2a** = 40/60.[i] [d] *anti*-**3a**/*syn*-**3a** = 45/55.[i] [e] 17% of **2a** was recovered. [f] *anti*-**2** was used. [g] *anti*-**2c**/*syn*-**2c** = 34/66.[i] [h] *anti*-**3d**/*syn*-**3d** = 25/75.[i] [i] Determined by HPLC.

Table II. Ionic Denitrohydrogenation of 2

run	R^1	R^2	R^3	2	Lewis acid (equiv)	time, h	products	yield,[a] %
1	Me	H	Me	**2a**	$AlCl_3$ (4.5)	20	**5a**	89
2	Me	H	Ph	**2c**	$AlCl_3$ (2)	0.3	**5b**	80
3	Me	Me	H	**2d**	$AlCl_3$ (2)	1	**6c**	77
4	Et	Me	H	**2e**	$AlCl_3$ (2)	0.5	**6d**	81
5	C_6H_{13}	Me	H	**2f**	$AlCl_3$ (2)	1	**6e**	51
6	$-(CH_2)_4-$		H	**2m**	$AlCl_3$ (4.5)	1	**6f**	76

[a] Isolated yield.

Table III. Intramolecular Friedel–Crafts Reaction of β-Nitro Sulfides 7

run	7	R^1	R^2	Lewis acid (equiv)	time, h	8 (yield, %)[a]
1	**7a**	H	Me	$AlCl_3$ (2)	0.1	**8a** (55)
2	**7a**	H	Me	$TiCl_4$ (2)	0.5	**8a** (70)
3	**7a**	H	Me	$SnCl_4$ (2)	6	**8a** (76)
4	**7a**	H	Me	$BF_3{\cdot}OEt_2$ (2)	24	**8a** (0)[b]
5	**7b**	MeO	Me	$SnCl_4$ (2)	6	**8b** (60)
6	**7c**	MeO	Ph	$SnCl_4$ (2)	6	**8c** (56)
7	**7d**	MeO	$-CH_2CH_2C(=O)CH_3$	$SnCl_4$ (3)	3	**8d** (80)

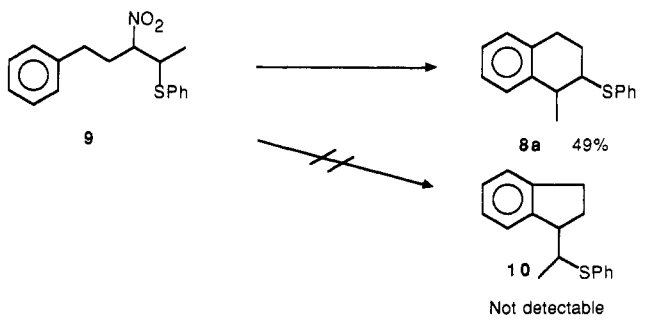
[a] Isolated yield. [b] Complete recovery of **7a**.

acid for replacement of a nitro group by a cyano group, and substitution products are not formed in reactions using $TiCl_4$ and $AlCl_3$.

Unsymmetrical β-nitro sulfides afford mixtures of the two regioisomers **3** and **4**. When the nitro group is primary and the phenylthio group is located on a tertiary or benzyl position, the substitution reaction proceeds with 1,2-migration of the phenylthio group to give **4** as the main product (runs 7–12). When the nitro group and phenylthio group are located on primary and secondary positions (runs 13, 14), the products consist of mixtures of **3** and **4**. The reaction of **2j** and **2k** with allylsilane furnishes a mixture of the same two products (**3n** and **4n**). It is noteworthy that this mixture of **3n** and **4n** is obtained in the same product distribution in spite of different starting substrates (runs 15, 16). The structures of **3l–n** and **4l–n** were confirmed by comparison with authentic samples prepared by other routes. These results suggest episulfonium ions as transient intermediates in the proceeding reactions.

Denitrohydrogenation under Lewis acid conditions led to the results summarized in Table II (Scheme III). $AlCl_3$ was a suitable Lewis acid for ionic denitrohydrogenation by triethylsilane. In several cases, more than 2 equiv of Lewis acid was necessary (runs 1, 6). Although the nitro groups are readily replaced by hydrogen on treatment with tributyltin hydride under radical conditions,[12] the reaction

Scheme VI



of **2** with tin radicals results in the cleavage of the C–N and C–S bonds to give corresponding alkenes. Thus, this ionic denitration reaction compensates for the defects of denitration with tin radicals (Scheme IV).

Intramolecular Friedel–Crafts reaction also proceeds from β-nitro sulfides containing an aromatic ring in the side chain as summarized in Table III (Scheme V). $AlCl_3$, $TiCl_4$, and $SnCl_4$ are effective for this cyclization (runs 1–3). However, $BF_3{\cdot}OEt_2$ is not suitable for this reaction (run 4). The nitro group can be replaced after it has served as an activating group for carbon–carbon bond formation. For example, **8d** was readily produced by the Michael addition reaction and subsequent intramolecular cyclization reaction. Treatment of **9** with $SnCl_4$ gave **8a** exclusively, where 1,2-migration of phenylthio group occurred.

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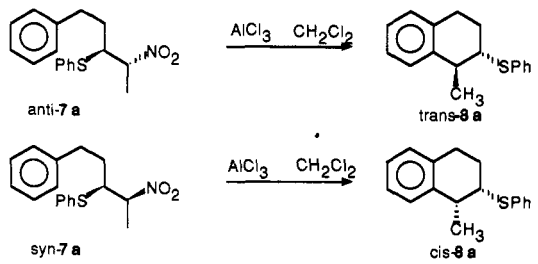
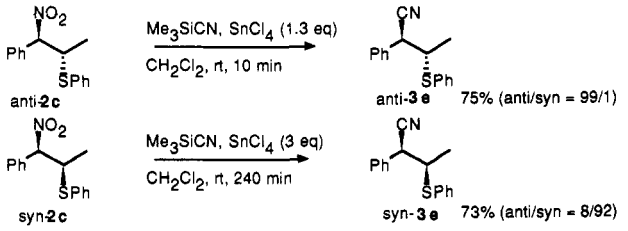
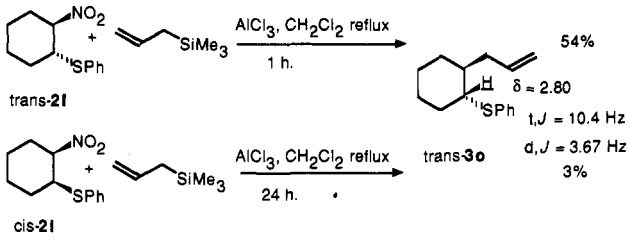
Scheme VII



Scheme VIII



Scheme IX

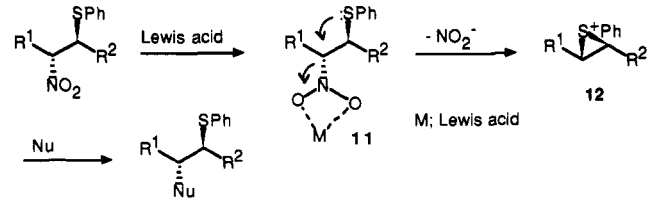


The absence of the indane derivative **10** also supports episulfonium intermediates (Scheme VI).

Stereochemistry of the Reaction. The intramolecular Friedel–Crafts reaction proceeds stereospecifically as illustrated by the conversion of *anti*-**7a**[13,16] to *trans*-**8a**. Cyclization of mixture of *anti*- and *syn*-**7a** (50:50) is also carried out in the same way to give *cis*- and *trans*-**8a**, whose ratio is 42/58 by GLC analysis. Thus, cyclization of *syn*-**7a** also furnishes *cis*-**8a** stereospecifically (Scheme VII). In support of the stereochemical assignments of **8a**, the quasi-equatorial methyl group of the *trans*-**8a** (δ = 1.40) is deshielded relative to *cis*-**8a** (δ = 1.29).[10g] Thus, the reaction proceeds with retention of configuration.

The cyano substitution reaction proceeds stereospecifically as shown in Scheme VIII. The reaction of *anti*-**2c** gives *anti*-**3e** and *syn*-**2c** gives *syn*-**3e**. The stereospecificity from *syn*-**2c** (92/8) was slightly lower than from *anti*-**2c** (>99/1), where some isomerization occurred. It is noteworthy that *anti*-**2c** is more reactive than *syn*-**2c**. The reaction of *anti*-**2c** is completed within 10 min to give *anti*-**3e** exclusively, while the reaction *syn*-**2c** proceeds so slowly that starting *syn*-**2c** remains after 2 h. Excess amounts of $SnCl_4$ and 4 h are necessary to consume all of *syn*-**2c**. The reactivity of *anti*-**2c** appears to be about 20 times higher than that of *syn*-**2c** in comparison with both reaction time (Scheme VIII). The difference in the reactivity as a function of stereochemistry is also observed in the case of substitution of cyclic β-nitro sulfide (Scheme IX). For example, *trans*-1-nitro-2-(phenylthio)cyclohexane (*trans*-**21**) reacts with allyltrimethylsilane in the presence of $AlCl_3$ to give 1-allyl-2-(phenylthio)cyclohexane (**3o**) in 54% yield. This reaction is complete within 1 h, and ^1H NMR and GLC analysis indicate that **3o** is a single isomer. The signal of the proton at α-position to phenylthio group (H^2) appears at δ = 2.80 as double triplets, with coupling constants of 10.4 Hz (t) and 3.67 Hz (d). This result indicates that both H^1 and H^2 are axial. Thus, the structure of **3o** appears to be trans. On the other hand, *cis*-**2l** is very unreactive under the same conditions, and the formation of **3o** is very slow. Only 3% of **3o** is isolated after 24 h. Differing reactivity depending on the stereochemistry of starting materials is also observed in the solvolysis reaction of *trans*- and *cis*-1-chloro-2-(phenylthio)cyclohexane.[14] Thus, these results suggest strongly that the reaction proceeds via episulfonium ion intermediates.

Scheme X



Scheme XI

The mechanistic course of this reaction is shown in Scheme X. A Lewis acid attacks the nitro group to give the complex **11**. The adjacent phenylthio group assists the cleavage of the carbon–nitrogen bond to form an episulfonium ion intermediate **12**. This assistance of the phenylthio group takes place from the backside of the carbon–nitrogen bond in an S_N2-like process. According to this assumption, anti-β-nitro sulfides afford trans-episulfonium ions and syn isomers afford cis-episulfonum ions stereospecifically. If an antiperiplanar conformation between the phenylthio group and the nitro group can be achieved in starting β-nitro sulfides, the reaction proceeds very rapidly. On the other hand, if it is difficult to attain this conformation, the reaction rate is retarded. For example, the antiperiplanar conformation is achieved in *trans*-**2l**, whereas there is always a gauche conformation for *cis*-**2l**. Thus, *trans*-**2l** readily forms an episulfonium ion intermediate, while this is impossible for *cis*-**2l**. This phenomenon is also observed in acyclic cases such as nitrosulfide **2c**. ^1H NMR studies on *anti*- and *syn*-**2c** are consistent with the conformations in Scheme XI, because the larger coupling constants (J_{12}) indicate a dihedral angle of H^1 and H^2 close to 180°. Consequently, the preferred conformation of the phenylthio group and the nitro group should be "anti" in *anti*-**2c** and "gauche" in *syn*-**2c**. The large difference of reactivity between *anti*- and *syn*-**2c** may be explained in this way. The reaction is completed by nucleophilic attack on the episulfonium intermediates. This step should occur with inversion in an S_N2-type process. That is, we obtain a net retention of configuration via a double inversion.

Nucleophiles attack the more substituted site of the episulfonium ions more preferentially than the less sub-

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stituted site. In particular, nucleophilic attack occurs predominantly at tertiary and benzylic sites. These tendencies are also observed in other episulfonium ions (Table I, runs 4–12).[10]

As various kinds of β-nitro sulfides are readily available, these reactions provides a new method for generation of episulfonium ions and a general method for replacement of the nitro group by carbon nucleophiles or hydrogen.

Experimental Section

Melting points were uncorrected. ^{1}H NMR spectra were recorded on JEOL-FX-400 spectrometer at 400 MHz, Hitachi R-250-H spectrometer at 250 MHz, JEOL-PS-100 spectrometer at 100 MHz, or Hitachi R-600 spectrometer at 60 MHz. The solvent used was $CDCl_3$ with internal tetramethylsilane as the standard. Infrared spectra were recorded on a Hitachi 215 spectrometer. High-resolution mass spectra were recorded on a JEOL-DX-300/JMA-3100 mass spectrometer at 70 eV (EI). High-performance liquid chromatography (HPLC) analyses were carried out on TSK gel ODS-80 (4.6 mm i.d. × 15 cm, Tosoh Co. Ltd.) with Tosoh Model CCPE pump and UV-8000 UV detector. GLC analyses were performed on a 2.6 mm i.d. × 2 m column filled with silicone DC-550 with Shimadzu GC-8A. β-Nitro sulfides **2**, **7**, and **9** were prepared from corresponding nitroolefins[15] and thiophenol according to the literature.[16] Pure *syn*-**2c** was prepared by recrystallization of a mixture of *syn*-**2c** and *anti*-**2c** from hexane. Allyltrimethylsilane, cyanotrimethylsilane, and triethylsilane were purchased from Shin'etsu Chemical Co. Ltd. CH_2Cl_2 was distilled over calcium hydride before use.

Nucleophilic Substitution of 2. The following procedure for the preparation of **3a** is representative. Under an argon atmosphere, $TiCl_4$ (0.26 mL, 2.37 mmol) was added to a mixture of **2a** (0.21 g, 1.00 mmol, anti/syn = 40/60) and allyltrimethylsilane (0.57 g, 5.00 mmol) in CH_2Cl_2 (5 mL) at 0 °C, and the resulting solution was stirred for 6 h at ambient temperature. The reaction mixture was poured into ice–water, and the aqueous layer was extracted with CH_2Cl_2 (3×). The combined organic layer was washed with brine and dried over anhydrous Na_2SO_4. Filtration followed by concentration gave a crude product, which was subjected to column chromatography (silica gel/hexane–ethyl acetate 20:1) to give **3a** (0.12 g) as a mixture of diastereomers in 60% yield. The anti/syn ratio of this **3a** was 45/55 (HPLC).

4-Methyl-5-(phenylthio)-1-hexene: colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ of *anti*-**3a** 1.00 (d, J = 5 Hz, 3 H), 1.28 (d, J = 7 Hz, 3 H), δ of *syn*-**3a** 0.99 (d, J = 5 Hz, 3 H), 1.21 (d, J = 5 Hz, 3 H); the following signals were observed in both isomers: 1.60–2.20 (m, 2 H), 2.35–2.60 (m, 1 H), 3.20–3.50 (m, 1 H), 5.00–5.24 (m, 2 H), 5.60–6.04 (m, 1 H), 7.24–7.56 (m, 5 H); IR 1580, 1640 cm^{-1}; MS, m/z (M^+) calcd for $C_{13}H_{18}S$ 206.1129, found 206.1118. Other **3** and **4** were prepared in the same way. The ratios of **3**/**4** were determined by GLC. Physical and spectral data are summarized.

***anti*-2-Methyl-3-(phenylthio)butyronitrile (*anti*-3b)**: colorless liquid; ^{1}H NMR (100 MHz, $CDCl_3$) δ 1.36 (d, J = 8 Hz, 3 H), 1.43 (d, J = 6 Hz, 3 H), 2.80 (q, d, J = 6 Hz, 8 Hz, 1 H), 3.20 (q, d, J = 6 Hz, 8 Hz, 1 H), 7.30–8.56 (m, 5 H); IR 2250 cm^{-1}; MS, m/z (M^+) calcd for $C_{11}H_{13}NS$ 191.0769, found 191.0790.

4,5-Diphenyl-5-(phenylthio)-1-pentene (3c): mp 80–81 °C; ^{1}H NMR (100 MHz, $CDCl_3$) δ 2.44 (t, J = 7 Hz, 2 H), 3.05–3.30 (m, 1 H), 4.40 (d, J = 8 Hz, 1 H), 4.70–4.90 (m, 2 H), 5.28–5.70 (m, 1 H), 7.06–7.36 (m, 15 H); IR 1580, 1640 cm^{-1}; MS, m/z (M^+) calcd for $C_{23}H_{22}S$ 330.1441, found 330.1427.

3-Phenyl-4-(phenylthio)-1-hexene (3d): colorless liquid; ^{1}H NMR (100 MHz, $CDCl_3$) δ of *anti*-**3d** 1.21 (d, J = 6 Hz, 3 H), 3.42 (q, J = 11 Hz, 1 H); δ of *syn*-**3d** 1.06 (d, J = 6 Hz, 3 H), 3.46 (q, J = 5 Hz, 1 H); the following signals were observed in both isomers 2.40–3.00 (m, 3 H), 4.80–5.10 (m, 2 H), 5.40–5.75 (m, 1 H), 7.12–7.46 (m, 10 H); IR 1580, 1640 cm^{-1}; MS, m/z (M^+) calcd for $C_{18}H_{20}S$ 268.1285, found 268.1281; anti/syn = 25/75 (HPLC).

***anti*-2-Phenyl-3-(phenylthio)butyronitrile (*anti*-3e)**: colorless liquid; ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.34 (d, J = 6.6 Hz, 3 H), 3.46 (d, q, J = 4.3 Hz, 7.0 Hz, 1 H), 4.04 (d, J = 4 Hz, 1 H), 7.20–7.60 (m, 10 H); IR 2250 cm^{-1}; MS, m/z (M^+) calcd for $C_{16}H_{15}NS$ 253.0925, found 253.0909.

***syn*-2-Phenyl-3-(phenylthio)butyronitrile (*syn*-3e)**: liquid; ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.28 (d, J = 7 Hz, 3 H), 3.59 (m, J = 7 Hz, 1 H), 3.93 (d, J = 6.4 Hz, 1 H), 7.30–7.40 (m, 10 H); IR 2250 cm^{-1}.

The following compounds (**4h–k**) were obtained as major products.

4,4-Dimethyl-5-(phenylthio)-1-pentene (4f): liquid; ^{1}H NMR (100 MHz, $CDCl_3$) δ 1.00 (s, 6 H), 2.08 (d, J = 6 Hz, 2 H), 2.84 (s, 2 H), 4.90–5.05 (m, 1 H), 5.10 (m, 1 H), 5.60–6.00 (m, 1 H), 7.10–7.36 (m, 5 H); IR 1580, 1640 cm^{-1}; MS, m/z (M^+) calcd for $C_{13}H_{18}S$ 206.1129, found 206.1174.

2,2-Dimethyl-3-(phenylthio)propionitrile (4g): liquid; ^{1}H NMR (100 MHz, $CDCl_3$) δ 1.42 (s, 6 H), 3.11 (s, 2 H), 7.18–7.50 (m, 5 H); IR 2250 cm^{-1}; MS, m/z (M^+) calcd for $C_{11}H_{13}NS$ 191.0769, found 191.0771.

4-Methyl-4-[(phenylthio)methyl]-1-hexene (4h): liquid; ^{1}H NMR (100 MHz, $CDCl_3$) δ 0.80 (t, J = 7 Hz, 3 H), 0.96 (s, 3 H), 1.38 (q, J = 7 Hz, 2 H), 2.11 (d, J = 7 Hz, 2 H), 2.85 (s, 2 H), 4.90–5.20 (m, 2 H), 5.60–6.00 (m, 1 H), 7.12–7.38 (m, 5 H); IR 1580, 1640 cm^{-1}; MS, m/z (M^+) calcd for $C_{14}H_{20}S$ 220.1286, found 220.1301.

2-Methyl-2-[(phenylthio)methyl]butyronitrile (4i): liquid; ^{1}H NMR (100 MHz, $CDCl_3$) δ 1.01 (t, J = 6 Hz, 3 H), 1.36 (s, 3 H), 1.50–1.96 (m, 2 H), 3.12 (s, 2 H), 7.18–7.62 (m, 5 H); IR 2250 cm^{-1}; MS, m/z (M^+) calcd for $C_{12}H_{15}NS$ 205.0925, found 205.0974.

2-Methyl-2-[(phenylthio)methyl]octanonitrile (4j): liquid; ^{1}H NMR (100 MHz, $CDCl_3$) δ 0.88 (t, J = 6 Hz, 3 H), 1.20–1.80 (m, 10 H), 1.36 (s, 3 H), 3.15 (s, 2 H), 7.22–7.55 (m, 5 H); IR 2250 cm^{-1}; MS, m/z (M^+) calcd for $C_{16}H_{23}N\,S$ 261.1551, found 261.1464.

4-Phenyl-5-(phenylthio)-1-pentene (4k): liquid; ^{1}H NMR (100 MHz, $CDCl_3$) δ 2.54 (t, J = 6 Hz, 2 H), 2.72–3.04 (m, 1 H), 3.17 (d, J = 6 Hz, 1 H), 3.18 (d, J = 8 Hz, 1 H), 4.95 (d, J = 11 Hz, 1 H), 4.98 (d, J = 16 Hz, 1 H), 5.40–5.84 (m, 1 H), 7.10–7.36 (m, 10 H); IR 1580, 1640 cm^{-1}; MS, m/z (M^+) calcd for $C_{17}H_{18}S$ 254.1129, found 254.1121.

The nucleophilic substitution of **2h** and **2i** gave a mixture of **3** and **4**, which could not be separated from each other. Their ratios were determined by GLC. The structures of **3l**, **4l**, **3m**, and **4m** were confirmed by comparison with authentic samples that were made by another route.

4-[(Phenylthio)methyl]-1-hexene (3l): liquid; ^{1}H NMR (100 MHz, $CDCl_3$) δ 0.89 (t, J = 6 Hz, 3 H), 1.24–1.75 (m, 3 H), 2.20 (t, J = 6 Hz, 2 H), 2.89 (d, J = 6 Hz, 2 H), 5.02 (d, J = 16 Hz, 1 H), 5.03 (d, J = 8 Hz, 1 H), 5.45–6.01 (m, 1 H), 7.13–7.37 (m, 5 H); IR 1580, 1640 cm^{-1}; MS, m/z (M^+) calcd for $C_{13}H_{18}S$ 206.1129, found 206.1074.

5-(Phenylthio)-1-heptene (4l): liquid; ^{1}H NMR (100 MHz, $CDCl_3$) δ 1.01 (t, J = 7 Hz, 3 H), 1.41–1.83 (m, 4 H), 2.07–2.42 (m, 2 H), 3.05 (m, J = 7 Hz, 1 H), 4.96 (d, J = 12 Hz, 1 H), 5.00 (d, J = 17 Hz, 1 H), 5.50–6.06 (m, 1 H), 7.16–7.44 (m, 5 H).

5-(Phenylthio)-1-hexene (3m): liquid; ^{1}H NMR (100 MHz, $CDCl_3$) δ 1.28 (d, J = 6 Hz, 3 H), 1.50–1.81 (m, 2 H), 2.23 (q, J = 7 Hz, 2 H), 3.21 (m, J = 7 Hz, 1 H), 4.85–5.18 (m, 2 H), 5.48–6.15 (m, 1 H), 7.16–7.48 (m, 5 H); MS, m/z (M^+) calcd for $C_{12}H_{16}S$ 192.0973, found 192.0908.

4-[(Phenylthio)methyl]-1-pentene (4m): liquid; ^{1}H NMR (100 MHz, $CDCl_3$) δ 1.02 (d, J = 6.2 Hz, 3 H), 1.75 (m, 1 H), 1.96–2.30 (m, 2 H), 2.79 (d, J = 5.5 Hz, 1 H), 2.90 (d, J = 4.3 Hz, 1 H), 5.02 (d, J = 13.8 Hz, 1 H), 5.03 (d, J = 9.4 Hz, 1 H), 5.46–6.13 (m, 1 H), 7.11–7.43 (m, 5 H).

The reaction of *anti*-**2j** (or *anti*-**2k**) with allylsilane and $TiCl_4$ gave a mixture of **3n** and **4n**. Their ratio was determined by GLC. These two mixtures showed identical ^{1}H NMR spectra and the same retention time on GLC analyses. ^{1}H NMR (250 MHz, $CDCl_3$) δ for **3n** 3.04 (ddd, J = 3.0 Hz, J = 6.0 Hz, J = 7.9 Hz, 1 H); δ for **4n** 3.42 (dq, J = 3.6 Hz, 7.0 Hz, 1 H); the following signals were observed in both isomers: 0.98 (q, 6 H), 1.37–2.08 (m, 5 H), 2.33–2.48 (m, 1 H), 4.94–5.17 (m, 2 H), 5.64–5.94 (m, 1 H), 7.15–7.43 (m, 5 H); IR 1580, 1640 cm^{-1}; MS, m/z (M^+) calcd for $C_{14}H_{20}S$ 220.1286, found 220.1270. The ratio of **3n**/**4n** from *anti*-**2j** was 75/25 (GLC) and 76/24 (^{1}H NMR at δ = 3.04 and δ = 3.42) and from *anti*-**2k** was 76/24 (GLC).

Ionic Denitrohydrogenation of 2. The following procedure for the preparation of **5a** is representative. Under argon atmosphere, $AlCl_3$ (0.58 g, 4.5 mmol) was added to a mixture of **2a** (0.21 g, 1.00 mmol) and triethylsilane (0.35 g, 3 mmol) in CH_2Cl_2 (5

mL) at ambient temperature, and the resulting solution was stirred for 4 h. The reaction mixture was poured into ice–water, and the aqueous layer was extracted with CH_2Cl_2 three times. The combined organic layer was washed with brine and dried over anhydrous Na_2SO_4. Filtration followed by concentration gave a crude product, which was subjected to column chromatography (silica gel/hexane–ethyl acetate 20:1) to give **5a** (0.13 g) in 76% yield.

2-(Phenylthio)butane (5a): liquid; ^1H NMR (100 MHz, $CDCl_3$) δ 1.02 (t, J = 6 Hz, 3 H), 1.29 (d, J = 6 Hz, 3 H), 1.34–1.82 (m, 2 H), 3.20 (m, J = 6 Hz, 1 H), 7.20–7.50 (m, 5 H).

1-Phenyl-2-(phenylthio)propane (5b): liquid; ^1H NMR (100 MHz, $CDCl_3$) δ 1.27 (d, J = 6 Hz, 3 H), 2.60 (ABX, J = 8 Hz, 14 Hz, 1 H), 3.02 (ABX, J = 5 Hz, 14 Hz, 1 H), 3.24–3.68 (m, 1 H), 7.04–7.72 (m, 10 H); MS, m/z (M^+) calcd for $C_{15}H_{16}S$ 228.0973, found 228.0972.

2-Methyl-1-(phenylthio)propane (6c): liquid; ^1H NMR (100 MHz, $CDCl_3$) δ 1.02 (d, J = 7 Hz, 6 H), 1.86 (m, J = 6 Hz, 1 H), 2.79 (d, J = 7 Hz, 2 H), 6.96–7.68 (m, 5 H).

2-Methyl-1-(phenylthio)butane (6d): liquid; ^1H NMR (100 MHz, $CDCl_3$) δ 1.00 (t, J = 7 Hz, 6 H), 1.48–2.00 (m, 3 H), 2.82 (dd, J = 8 Hz, 12 Hz, 1 H), 2.94 (dd, J = 6 Hz, 12 Hz, 1 H), 7.16–7.44 (m, 5 H); MS, m/z (M^+) 180.

2-Methyl-1-(phenylthio)octane (6e): liquid; ^1H NMR (100 MHz, $CDCl_3$) δ 1.00–1.90 (m, 17 H), 2.56–3.04 (m, 2 H), 7.54–7.74 (m, 5 H); MS, m/z (M^+) calcd for $C_{15}H_{24}S$ 236.1599, found 236.1594.

[(Phenylthio)methyl]cyclopentane (6f): liquid; ^1H NMR (100 MHz, $CDCl_3$) δ 0.66–2.24 (m, 11 H), 2.71 (d, J = 6 Hz, 2 H), 7.00–7.38 (m, 5 H).

Intramolecular Friedel–Crafts Reaction of 7. The following procedure for the preparation of **8a** is representative. Under argon atmosphere, $SnCl_4$ (0.28 mL, 2.40 mmol) was added to a solution of **7a** (0.31 g, 1.03 mmol) in CH_2Cl_2 (5 mL), and the resulting solution was stirred for 6 h at ambient temperature. The reaction mixture was poured into ice–water, and the aqueous layer was extracted with CH_2Cl_2 three times. The combined organic layer was washed with brine and dried over anhydrous Na_2SO_4. Filtration followed by concentration gave a crude product, which was subjected to column chromatography (silica gel/hexane–ethyl acetate 20:1) to give **8a** (0.20 g) in 76% yield as colorless liquid. The ratio of *trans*-**8a**/*cis*-**8a** was found to be 58/42 (from *anti*-**7a**/*syn*-**7a** = 51/49) or 95/5 (from *anti*-**7a**/*syn*-**7a** = 88/12) by GLC analyses.

1-Methyl-2-(phenylthio)-1,2,3,4-tetrahydronaphthalene (8a): ^1H NMR (100 MHz, $CDCl_3$) δ for *trans*-**8a** 1.40 (d, J = 7 Hz, 3 H), 3.23–3.50 (m, 1 H); δ for *cis*-**8a** 1.27 (d, J = 7 Hz, 3 H for *cis*-**8a**), 3.60 (m, 1 H for *cis*-**8a**); the following signals were observed in both isomers: 1.63–2.38 (m, 2 H), 2.48–3.20 (m, 3 H), 7.04–7.50 (m, 9 H); MS, m/z (M^+) calcd for $C_{17}H_{18}S$ 254.1129, found 254.1152.

Other **8** were prepared in the same way. Physical and spectral data are summarized.

6,7-Dimethoxy-1-methyl-2-(phenylthio)-1,2,3,4-tetrahydronaphthalene (8b): liquid; ^1H NMR (100 MHz, $CDCl_3$) δ for *trans*-**8b** 1.39 (d, J = 7 Hz, 3 H); δ for *cis*-**8b** 1.27 (d, J = 7 Hz, 3 H); the following signals were observed in both isomers: 1.65–2.32 (m, 2 H), 2.50–3.18 (m, 3 H), 3.28–4.05 (m, 1 H), 3.87 (s, 6 H), 6.55 (s, 1 H), 6.61 (s, 1 H), 7.00–7.50 (m, 5 H); IR 1260, 1520 cm^{-1}; MS, m/z (M^+) calcd for $C_{19}H_{22}O_2S$ 314.1340, found 314.1291; trans/cis = 48/52 (HPLC).

***trans*-6,7-Dimethoxy-1-phenyl-2-(phenylthio)-1,2,3,4-tetrahydronaphthalene (*trans*-8c)**: yellow liquid. These *trans*- and *cis*-**8c** were separated by column chromatography; ^1H NMR (100 MHz, $CDCl_3$) δ 1.65–2.20 (m, 2 H), 2.70–3.10 (m, 2 H), 3.60–3.80 (m, 1 H), 3.66 (s, 3 H), 3.86 (s, 3 H), 4.14 (d, J = 4 Hz, 1 H), 6.26 (s, 1 H), 6.60 (s, 1 H), 6.94–7.42 (m, 10 H); IR 1260, 1500 cm^{-1}.

***cis*-6,7-Dimethoxy-1-phenyl-2-(phenylthio)-1,2,3,4-tetrahydronaphthalene (*cis*-8c)**: yellow liquid; ^1H NMR (100 MHz, $CDCl_3$) δ 1.84–2.10 (m, 2 H), 2.80–3.00 (m, 2 H), 3.60–3.80 (m, 1 H), 3.66 (s, 3 H), 3.86 (s, 3 H), 4.40 (d, J = 3 Hz, 1 H), 6.36 (s, 1 H), 6.60 (s, 1 H), 7.00–7.36 (m, 10 H); IR 1260, 1500 cm^{-1}; MS, m/z (M^+) calcd for $C_{24}H_{24}O_2S$ 376.1497, found 376.1513.

6,7-Dimethoxy-1-(3′-oxobutyl)-2-(phenylthio)-1,2,3,4-tetrahydronaphthalene (8d): yellow liquid; 1H NMR (100 MHz, $CDCl_3$) δ 2.08 (s, 3 H), 2.36–3.05 (m, 10 H), 3.82 (s), 3.90 (s), 3.96 (s), 6.84 (s, 1 H), 7.00 (s, 1 H), 7.05–7.44 (m, 5 H); IR 1260, 1510, 1710 cm^{-1}; MS, m/z (M^+) calcd for $C_{22}H_{26}O_3S$ 370.1603, found 370.1601.

Reaction of 9 with Lewis Acid. To a solution of **9** (0.17 g, 0.56 mmol) in CH_2Cl_2 (5 mL) was added $SnCl_4$ (0.16 mL, 1.37 mmol), and the resulting solution was stirred for 6 h at room temperature. The usual workup followed by column chromatography gave **8a** (0.07 g) in 49% yield.

Reaction of 21 with $AlCl_3$ and Allyltrimethylsilane. A mixture of *trans*-**21** (434 mg, 1.83 mmol), allyltrimethylsilane (995 mg, 8.72 mmol), and powdered $AlCl_3$ (564 mg, 4.23 mmol) in 10 mL of CH_2Cl_2 was refluxed for 1 h. The reaction mixture was poured into ice–water, and the aqueous layer was extracted with CH_2Cl_2 three times. The combined organic layer was washed with brine and dried over anhydrous Na_2SO_4. Filtration followed by concentration gave a crude product, which was subjected to column chromatography (silica gel/hexane–ethyl acetate 20:1) to give *trans*-**3o** (230 mg) in 54% yield as colorless liquid: ^1H NMR (250 MHz, $CDCl_3$) δ 1.05–2.15 (m, 10 H), 2.63–2.70 (m, 1 H), 2.80 (dt, J = 3.67 Hz, 10.4 Hz, 1 H), 5.03 (d, J = 8.5 Hz, 1 H), 5.06 (d, J = 18 Hz, 1 H), 5.71–5.88 (m, 1 H), 7.15–7.47 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 25.51, 26.47, 31.81, 34.33, 38.60, 41.63, 52.08, 116.48, 126.71, 128.73, 132.47, 136.45; MS, m/z (M^+) calcd for $C_{15}H_{20}S$ 232.1286, found 232.1208.

Methoxy(phenylthio)(trimethylsilyl)methane as a One-Carbon Homologation Reagent: Efficient 1,4-Addition of a Formyl or a Carboxy Anion Equivalent to Cyclic α-Enones Concomitant with in Situ α-Alkylation

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Efficient 1,4-addition of a formyl and carboxy anion equivalent is realized by use of [methoxy(phenylthio)(trimethylsilyl)methyl]lithium. Of further synthetic value is consecutive α-alkylation by in situ trapping of intermediary enolates with various alkyl halides. The reaction proceeds highly regioselectively, thus no α'-isomers are formed, and highly stereoselectively, thus trans α,β-dialkylation products of more than 95% purity are formed. The unique selectivity is ascribed to chelation by the proximate methoxy group to the lithium. The new method is applied to sarkomycin synthesis.

Introduction

The 1,4-addition of acyl anion equivalents to α,β-unsaturated systems has received extensive attention on account of facile accessibility to 1,4-dicarbonyl compounds. In particular, sulfur-stabilized reagents played a central role in this field.[1] Nevertheless, there appeared a limited

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