The Synthesis and Reactions of Chiral Sulfonium Ylids

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Treatment of (−)-ethylmethylsulfonium phenacylid, (−)-**1**, in THF at room temperature with 15 equiv. of benzoic anhydride, acetic anhydride or 1 equiv. phenyl isocyanate produces the corresponding (−)-ethylmethylsulfonium diacylmethylids, (−)-**5**, (−)-**6**, and (−)-**8**. Treatment of (−)-**1** with dimethyl sulfate in acetone gives (*Z*)-(+)-ethylmethyl-α-methoxy-β-styrylsulfonium methyl sulfate, (+)-**10**. Resolution of (±)-**10** via its DBT salt and conversion to perchlorate gives the corresponding vinyl perchlorates (+)- and (−)-**13**. Under the resolution conditions the ketal perchlorates, (−)- and (+)-ethylmethyl-2,2-dimethoxy-2-phenylethylsulfonium perchlorate, (−)- and (+)-**14**, are also obtained. The rates of racemization at 50° in benzene of **1**, **5**, **6**, and **8** are 39.7, 55.5, 106, and 79.1 × 10^{-5} s^{-1}, respectively. The rates of racemization at 50° in methanol of **10**, **13**, and **14** are 1.93, 2.08, and 5.64 × 10^{-5} s^{-1}. Racemization is proposed to proceed via pyramidal inversion. The synthetic potential of chiral sulfonium ylids is discussed with respect to their ease of racemization.

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Le traitement du phénacylure de (−)-éthylméthylsulfonium, (−)-**1**, à température de la pièce dans le THF, par 15 équiv. d'anhydride benzoïque, d'anhydride acétique ou 1 équiv. d'isocyanate de phényle conduit aux diacylméthylures correspondants, (−)-**5**, (−)-**6** et (−)-**8**. Le traitement de (−)-**1** avec du sulfate de diméthyle dans l'acétone donne le méthylsulfate de (*Z*)-(+)-éthylméthyl α-méthoxy β-styrylsulfonium, (+)-**10**. La résolution du (±)-**10** par son sel de DBT et sa conversion en perchlorate donne les perchlorates de vinyle correspondants (+)- et (−)-**13**. Dans les conditions de résolution on obtient aussi les perchlorates de l'acétal et les perchlorates des (−)- et (+)-éthylméthyldiméthoxy-2,2 phényl-2 éthylsulfonium, (−)- et (+)-**14**. Les taux de racémisation à 50° dans le benzène de **1**, **5**, **6** et **8** sont respectivement de 39.7, 55.5, 106 et 79.1 × 10^{-5} s^{-1}. Les taux de racémisation de **10**, **13** et **14** dans le méthanol à 50 °C sont respectivement de 1.93, 2.08 et 5.64 × 10^{-5} s^{-1}. On suppose que la racémisation s'effectue par une inversion pyramidale. On discute des possibilités de synthèse qu'offrent des ylures chiraux de sulfonium par rapport à leur facilité de racémisation.

[Traduit par le journal]

The first sulfonium ylid, dimethylsulfonium fluorenylid, was prepared by Ingold and Jessop (1) in 1930 by the reaction of its conjugate acid bromide with base. A number of stable sulfonium ylids has been prepared since 1930, the chemical properties of which have been extensively studied and reviewed (2). Although chiral sulfonium salts have been known since 1900 (3), failures in obtaining chiral sulfonium ylids were reported as late as 1966. Nozaki *et al.* (4), for example, obtained racemic methylphenylsulfonium *p*-iodophenacylid upon basic treatment of (−)-*p*-iodophenacylmethylphenylsulfonium picrate. The pyramidal configuration of the sulfur atom in sulfonium ylids, however, had been confirmed by n.m.r. spectroscopy (5–7) and X-ray crystallography studies (8, 9). In 1968, Darwish and Tomilson (10) reported the isolation and facile racemization via pyramidal inversion of (−)-ethylmethylsulfonium phenacylid, (−)-**1**.

Because of the general utility of ylids as synthetic intermediates, it has been desirable to investigate the synthetic potential of chiral sulfonium ylids as asymmetric transfer agents. In testing the carbonyl and conjugate addition reactions of a chiral sulfonium methylid and the [2,3] sigmatropic rearrangement of a chiral allyl sulfonium salt, Trost and Hammen (11) observed an efficient transfer of asymmetry for the [2,3] sigmatropic rearrangement only. By comparison, several chiral oxosulfonium methylids are efficient asymmetric transfer agents (12). Several factors including temperature and steric effects (13–17), and angular constraint of the

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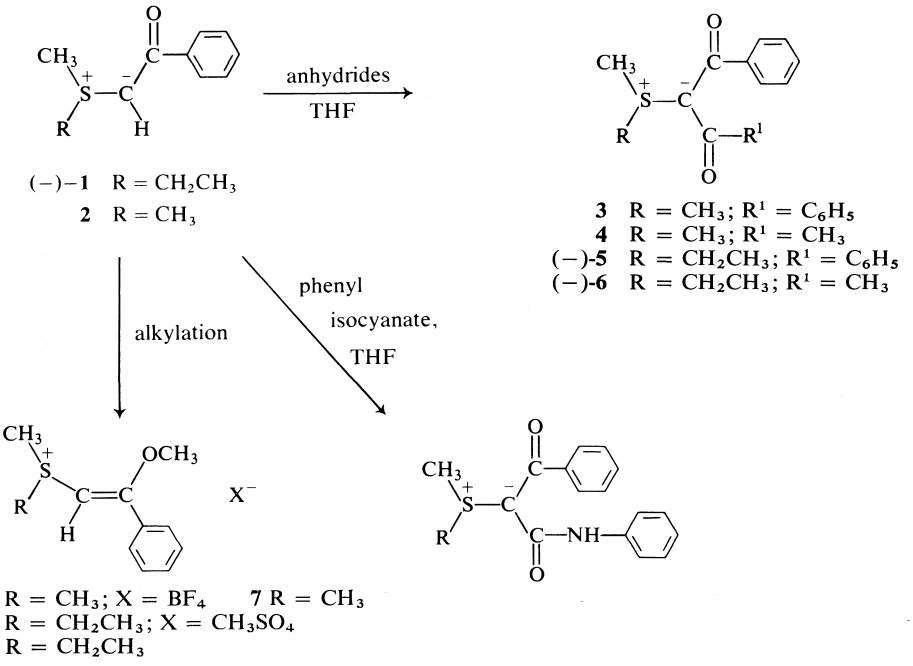


(−)-**1** R = CH_2CH_3
2 R = CH_3

3 R = CH_3; R^1 = C_6H_5
4 R = CH_3; R^1 = CH_3
(−)-**5** R = CH_2CH_3; R^1 = C_6H_5
(−)-**6** R = CH_2CH_3; R^1 = CH_3

9 R = CH_3; X = BF_4 **7** R = CH_3
(+)-**10** R = CH_2CH_3; X = CH_3SO_4
(−)-**8** R = CH_2CH_3

SCHEME 1

sulfonium center (18) affect the rates of pyramidal inversion of sulfonium salts. Presumably, similar factors affect the pyramidal inversion of sulfonium ylids.

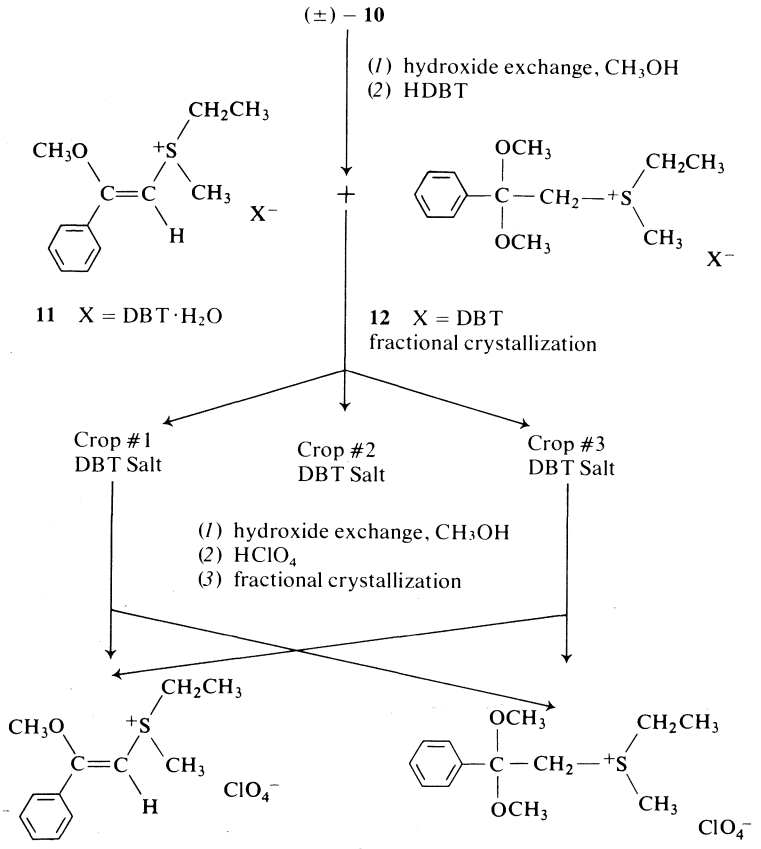
In this article, we describe several reactions of the ylid (−)-**1** in which the stereochemistry of the pyramidal sulfur is largely maintained during the course of each reaction. Kinetic studies of the racemization of the novel sulfonium ylids and salts prepared are reported. From these and a study of a conjugate addition reaction of (−)-**1**, the synthetic potential of chiral sulfonium ylids is discussed in relation to the racemization phenomena.

Synthesis and Reactions

The treatments of the achiral analog of (−)-**1**, dimethylsulfonium phenacylid, **2**, with acylating and alkylating agents have afforded various sulfonium compounds as depicted in Scheme 1 (19–21). The synthesis of (−)-**5** and (−)-**6** from (−)-**1** illustrates one solution to the problem associated with racemization of starting material. (−)-**1** racemizes with $t_{\frac{1}{2}}$ *ca.* $5\frac{1}{2}$ h at 25° in CH_2Cl_2 (10). Benzoylation of **2** with equimolar benzoic anhydride is reported to require a reaction time of 43 h (21). Even if (−)-**5** were to racemize at the same rate as (−)-**1**, it would have been impossible to isolate (−)-**5** in the reaction time reported. However, a kinetic study of the loss of optical activity of a THF solution of (−)-**1** containing 15 equiv. of benzoic anhydride at 25° indicated the benzoylation reaction time could be reduced to *ca.* 50 min. The rate of loss of optical activity did not become first order until after 50 min which suggested that before this time (−)-**1** was reacting to give a product of different optical rotatory power than itself. Therefore, by quenching the acylation reactions after 1 h, the chiral ylids (−)-**5** and (−)-**6** were obtained. The synthesis of (−)-**8** required no such modification as the reaction of (−)-**1** with equimolar phenyl isocyanate is complete within 15 min.

Alkylation of (−)-**1** with excess dimethyl sulfate in acetone for 30 min at room temperature afforded (*Z*)-(+)-ethylmethyl-α-methoxy-β-styrylsulfonium methyl sulfate, (+)-**10**. The alkylation of **2** with trimethyloxonium tetrafluoroborate has been reported to yield a *Z*:*E* isomeric mixture of the vinyl sulfonium salt **9** in a ratio of 94:6 (22). The assignment of the *Z* configuration to (+)-**10** is based on analogy to that of the major product of this alkylation reaction.

Because considerable quantities of (+)-**10** were required for racemization studies, a more



SCHEME 2

efficient synthesis was attempted by direct resolution. Upon elution of a methanolic solution of (±)-**10** through a Dowex 1-X8 hydroxide exchange column and neutralization of the eluate with (2*R*,3*R*)-2,3-dibenzoyltartaric acid monohydrate (HDBT), a diastereomeric salt mixture of the corresponding DBT·H_2O salt, **11**, was obtained. In addition to **11**, variable amounts of the ketal sulfonium salt, ethylmethyl-2,2-dimethoxy-2-phenylethylsulfonium hydrogen (2*R*,3*R*)-2,3-dibenzoyltartrate **12**, were also obtained. The complex mixtures of vinyl and ketal sulfonium DBT salts were resolved by fractional crystallization and conversion to the corresponding perchlorate salts, **13** and **14**, as outlined in Scheme 2. Unfortunately, the experimental conditions could not be established such that either DBT salt could be obtained predictably. Recently, Stirling and co-workers (23) have reported the base-catalyzed addition of methanol across the double bonds of analogous vinyl sulfonium salts.

Carbonyl stabilized sulfonium ylids are considerably less nucleophilic than simple alkylids. Thus, **1** decomposed to phenacylmethyl sulfide (10) rather than undergoing the carbonyl addition reaction with cyclohexanone or benzaldehyde. Treatment of **1** with equimolar chalcone in benzene for 17 h at 25° yielded the expected *dl*- and *meso*-cyclopropanes (19). Under the same conditions, (–)-**1** also provided the *dl*- and *meso*-cyclopropanes. The enantiomeric purity of this reacting ylid would have been considerably reduced prior to the cyclopropanation. Therefore, we diverted our attention to studies of more reactive chiral sulfonium ylids. In this

TABLE 1. Rates of racemization of some sulfonium ylids[a]

Compound	[Ylid]	Temperature (°C)	$10^5 k_{rac}$ (s^{-1})	$\Delta H^{\ddagger}$ (kcal/mol)	$\Delta S^{\ddagger}$ (e.u.)
(−)-**5**	0.0463	50	55.5 ±1.3	23.9±0.5	0.4±1.5
	0.0232	50	57.7 ±1.1		
	0.0463[b]	25	2.27±0.07		
(−)-**6**	0.0325	50	106 ±2	23.7±0.3	0.1±0.9
	0.066	50	107 ±2		
	0.0325	25	4.40±0.07		
(−)-**8**	0.0232	50	79.1 ±0.3	23.9±0.2	1.1±0.6
	0.0232	25	3.20±0.04		
(−)-**1**[c]	0.018	50	39.7 ±0.2	23.6±0.2	−1.1±0.5
	0.021	25	1.67±0.01		

[a]546 nm; Method I unless otherwise specified; benzene.
[b]546 nm; Method II; benzene.
[c]References 10 and 27.

connection, our observations with chiral benzyl sulfonium salts[3] parallel those recently reported by Trost and Hammen for chiral allyl sulfonium salts.

Kinetic Studies

The rates of loss of optical activity, k_α, of the chiral sulfonium ylids and salts prepared were studied by following the disappearance of optical activity with time. A Perkin-Elmer Model 141 Polarimeter was used with incident light of wavelength 546 and 365 nm as required. Reaction solutions were heated either in thermostated polarimeter cells (Method I) or in sealed ampoules immersed in constant temperature oil baths (Method II). Rotations were obtained directly from the digital readout of the instrument with infinity measurements taken after 10 half-lives of reaction. Reactions were usually followed to *ca.* 85% completion. As the n.m.r. spectra of the evaporation residues obtained after 10 half-lives of loss of optical activity were superimposable upon those for racemic materials, k_{dec} for these ylids and salts were estimated to be very much smaller than k_α. Therefore, to an excellent approximation, $k_{rac} = k_\alpha$.

Table 1 summarizes the racemization rate constants for the sulfonium ylids and Table 2, those for the salts. The values for (−)-**1** and (−)-ethylmethylphenacylsulfonium perchlorate, (−)-**15**, are included for comparison. The estimation of errors in the enthalpy and entropy of activation was calculated from the average deviation of the rate constants using the method described by Wiberg (24). Though the average deviations for the salts are high, it was not practical to endeavour to reduce them because of the low specific rotations of the salts and the difficulties in the resolutions.

Discussion

In 1967, Nozaki *et al.* (7) reported an n.m.r. spectral study of dimethylsulfonium diacetylmethylid. This compound exhibited magnetic equivalence of the two *C*-methyl groups at room temperature. At −60°, the *C*-methyl signal split into a 1:1 doublet with the coalescence temperature being *ca.* −25°. However, no change was observed for the *S*-methyl signal. Nozaki also observed that the *C*-methyl signal of **4** was broadened on cooling to −60°. Of the processes postulated to account for these observations, hindered rotation around the ylid bond and inversion of configuration at the sulfur atom, both of which would be slowed down upon cooling, were considered most likely. In favoring the latter interpretation, these authors calculated the half-life of pyramidal inversion to be *ca.* 0.02 s at −25°. We have recorded a broadening of the *C*-methyl signal of (−)-**6** identical to that reported for the related ylid **4**. In view of the isolation and kinetic study of the related optically active diacylmethylids, the kinetic process observed in the temperature dependent n.m.r. appears related to hindered rotation about the ylid bond. Furthermore, the steric and electronic effects of a diacylmethylid substituent *vs.* those of a phenacylid are not so great as would be

[3]Asymmetric induction in the Sommelet rearrangement of chiral sulfonium salts. Stewart J. Campbell and D. Darwish. In preparation.

TABLE 2. Rates of racemization of some ethylmethylsulfonium salts*

Compound	[Salt]	Temperature (°C)	$10^5 k_{rac}$ (s^{-1})	$\Delta H^{\ddagger}$ (kcal/mol)	$\Delta S^{\ddagger}$ (e.u.)
(+)-**10**	0.127†	70	29.7 ±1.5†	29.5±0.5	11 ±1.6
	0.163	50	1.93 ±0.06		
(+)-**13**	0.078†	70	32.8 ±2.0†	29.8±1.8	12 ±5.7
	0.072	50	2.08 ±0.17		
(+)-**14**	0.111	50	5.61 ±0.14		
	0.077	50	5.64 ±0.02	25.5±0.5	0.8±2.6
	0.074†	25	0.187±0.010		
(−)-**15**‡	0.020†	70	5.58 ±0.18	29.0±0.5	4.4±0.6
	0.020†	50	0.373±0.006		

*365 nm; Method I unless otherwise specified; methanol.
†365 nm; Method II; methanol.
‡References 13 and 27.

implied from the earlier results of Nozaki *et al.* and Darwish and Tomilson.

Pyramidal inversion of sulfonium salts has been shown to be subject to steric acceleration. For example, substitution of a phenyl for an ethyl substituent in several aryl sulfonium salts results in *ca.* 10-fold increases in the rates of racemization (16). A rate acceleration from substitution of a phenyl for an ethyl substituent probably accounts for the failure to obtain chiral methylphenylsulfonium *p*-iodophenacylid (4).

The slower rate of racemization of (+)-**10** compared with that for (−)-**1** is expected from changes in the electronegativities of the sulfur substituents (25). To explain the fact that the salt (−)-**15** racemized 200 times slower than the ylid (−)-**1** in methanol, it was assumed the greater electronegativity of the phenacyl substituent relative to that of the phenacylid favored a less planar ground state in the salt (10). Thus, a higher activation energy for the racemization of the salt was expected. Similarly, the β-styryl substituent of **10** would be more electronegative than the phenacylid substituent of **1** and (+)-**10** would racemize slower than (−)-**1**. The 15-fold rate enhancement upon ketalization of the phenacyl substituent of (−)-**15** may be due to the reduced electronegativity of the ketal substituent relative to that of the phenacyl substituent and to the increased steric size of the ketal substituent.

The ease racemization and reduced reactivity of the ylid (−)-**1** contributed to the failure to observe significant optical activity in the product of the conjugate addition reaction. As shown by Trost and Hammen (11), extensive racemization may be avoided by operating at low temperatures, however the chemical reactivity of the ylid must be considered. Enantiomeric stability of an ylid may be improved by minimizing steric interactions of the sulfonium substituents. Nevertheless, chiral sulfonium ylids will serve as useful asymmetric transfer agents only if significant free energy differences between diastereomeric transition states exist.

Experimental

All melting points (uncorrected) were obtained using a Hershberg-type melting point apparatus with a set of Anschutz thermometers. Nuclear magnetic resonance spectra were recorded on Varian Analytical n.m.r. Spectrometers, Models A-60 and A-56-60. Chemical shifts are reported in δ units from internal TMS. Infrared spectra were recorded on a Perkin-Elmer Grating Infrared Spectrometer, Model 421. Optical rotations were obtained using a Perkin-Elmer Polarimeter, Model 141. Synthetic procedures and physical constants, except specific rotation, were identical for racemic and chiral compounds.

*(—)-Ethylmethylsulfonium Phenacylid ((—)-**1**)*

(±)-**1** was obtained by treatment with 5% NaOH of the crude product from reaction of phenacyl bromide with ethyl methyl sulfide in acetone and extraction of the mixture with $CHCl_3$. The racemic ylid was treated with equimolar HDBT (26) in methanol to provide the corresponding crude diastereomeric tartrates after evaporation of the solvent. (—)-Ethylmethylphenacylsulfonium hydrogen (2*R*,3*R*)-2,3-dibenzoyltartrate, $[\alpha]_{589}^{r.t.}$ −90.2° (*c* 0.56, methanol) (reported $[\alpha]_{589}^{r.t.}$ −88.2° (*c* 0.44, methanol) (27) was obtained after three to five fractional crystallizations at 5° of the crude dissolved in minimum amounts of methanol at room temperature. (−)-**1**, $[\alpha]_{589}^{r.t.}$ −216° (*c* 0.42, benzene) (lit. (10) $[\alpha]_{589}^{r.t.}$ −137° (*c* 0.49, benzene)) was prepared directly from the resolved tartrate by treatment with 5% NaOH at 0°. Extraction of the crude ylid with cold $CHCl_3$, a rapid and efficient evaporation of the solvent, and recrystallization of the residual oil from benzene – Skellysolve B at −10° provided ylid of high specific rotation. In synthetic experiments, (−)-**1**, with $[\alpha]_{589}^{r.t.}$ *ca.* −180° was used as the

final recrystallizations of the resolution were extremely tedious. Other physical data for (−)-**1** were identical with those reported elsewhere (10).

The precautions indicated in isolating (−)-**1** with high optical rotation were rigorously followed in isolating the new diacylmethylids.

*(−)-Ethylmethylsulfonium Dibenzoylmethylid ((−)-**5**)*

Benzoic anhydride (20.3 g, 91 mmol) and (−)-**1** (1.16 g, 5.97 mmol) were dissolved in 15 ml THF. The solution was stirred for 1 h at room temperature, diluted with chloroform, and extracted with dilute NaOH several times. The combined aqueous layers were extracted with $CHCl_3$. The organic layers were washed with water, dried over $MgSO_4$ and concentrated. The residual oil was recrystallized from $CHCl_3$ – Skellysolve B to yield (−)-**5** (1.132 g, 3.80 mmol, 63.4%), m.p. 153–154°; $[\alpha]_{546}^{r.t.}$ −31.9° (*c* 1.38, benzene); n.m.r. ($CDCl_3$), δ 7.02 (m, 10H), 3.92 (m, 1H), 3.24 (m, 1H), 2.95 (s, 3H), 1.34 (t, J = 7.0 Hz, 3H); i.r. (Nujol), 1570, 1545, 1015, 955 cm^{-1}.

Anal. Calcd. for $C_{18}H_{18}O_2S$: C, 72.45; H, 6.08; S, 10.74. Found: C, 72.26, 72.48; H, 6.23, 5.89; S, 10.85, 10.67.

*(−)-Ethylmethylsulfonium Acetylbenzoylmethylid ((−)-**6**)*

Acetic anhydride (10 ml, 106 mmol) and (−)-**1** (1.26 g, 6.47 mmol) were dissolved in 10 ml THF. The solution was stirred for 45 min at room temperature diluted with 100 ml 10% NaOH and the resulting mixture stirred for 20 min at 0°. Extraction of the mixture with CH_2Cl_2, drying and concentration of the extracts and crystallization of the residual oil from benzene – Skellysolve B provided (−)-**6** (1.31 g, 5.55 mmol, 85%), m.p. 98–99°; $[\alpha]_{546}^{r.t.}$ −30.8° (*c* 0.77, benzene); n.m.r. ($CDCl_3$), δ 7.33 (s, 5H), 3.81 (m, 1H), 3.06 (m, 1H), 2.86 (s, 3H), 2.14 (s, 3H), 1.24 (t, J = 7.0 Hz, 3H); i.r. (Nujol), 1605, 1560, 1020, 960, 710 cm^{-1}.

Anal. Calcd. for $C_{13}H_{16}O_2S$: C, 66.07; H, 6.82; S, 13.57. Found: C, 65.69, 66.10; H, 6.83, 6.76; S, 13.50, 13.44.

*(−)-Ethylmethylsulfonium Benzoyl-(N-phenylcarbamoylmethylid) ((−)-**8**)*

Phenyl isocyanate (1.3 g, 10.9 mmol) and (−)-**1** (2.09 g, 10.8 mmol) were dissolved in 25 ml THF, and the solution stirred for 15 min at room temperature. The solvent was removed and the residual oil crystallized from $CHCl_3$ – Skellysolve B to yield (−)-**8** (3.03 g, 9.67 mmol, 89.6%), m.p. 171–172°; $[\alpha]_{546}^{r.t.}$ −39.9° (*c* 0.73, benzene); n.m.r. ($CDCl_3$), δ 12.32 (s, 1H), 7.34 (m, 10H), 3.97 (m, 1H), 3.09 (m, 1H), 2.89 (s, 3H), 1.20 (t, J = 7.0 Hz, 3H); i.r. (Nujol), 2200–4000, 1635, 1595, 1520, 1055 cm^{-1}.

Anal. Calcd. for $C_{18}H_{19}NO_2S$: C, 68.98; H, 6.11; N, 4.47; S, 10.23. Found: C, 68.79, 69.11; H, 6.37, 6.20; N, 4.42, 4.45; S, 10.49, 10.38.

*(Z)-(+)-Ethylmethyl-α-methoxy-β-styrylsulfonium Methyl Sulfate ((+)-**10**)*

Dimethyl sulfate (2.2 g, 17.5 mmol) and (−)-**1** (2.2 g, 11.3 mmol) were dissolved in 30 ml acetone, and the solution stirred for 30 min at room temperature. Ether was added to the cloud point and the mixture cooled at −5° to yield (+)-**10**, m.p. 103°; $[\alpha]_{365}^{r.t.}$ +3.94° (*c* 5.2, methanol); n.m.r. ($CDCl_3$), δ 7.51 (s, 5H), 6.00 (s, 1H), 3.74 (s, 1H), 3.62 (s, 3H), 3.62 (q, J = 7.0 Hz, 2H), 3.13 (s, 3H), 1.42 (t, J = 7.0 Hz, 3H); i.r. ($CHCl_3$), 2990, 1608, 1572, 1490, 1452, 1210, 610, 575 cm^{-1}.

Anal. Calcd. for $C_{13}H_{20}O_5S_2$: C, 48.73; H, 6.29; S, 20.01. Found: C, 48.60, 48.95; H, 6.18, 6.23; S, 20.26, 20.28.

*Resolution of (±)-**10***

The difficulties encountered in this resolution are illustrated by the nonreproducibility of the following three experiments.

Experiment 1: (±)-**10** (2.75 g, 8.58 mmol) was dissolved in a minimum amount of CH_3OH, and the solution eluted through a Dowex 1–X8 hydroxide exchange column into a flask containing HDBT (3.15 g, 8.48 mmol). The solution was concentrated to *ca.* 50 ml, ether added to the cloud point and the mixture cooled at 5° to yield **11** (1.39 g, 2.46 mmol), m.p. 114°; $[\alpha]_{589}^{r.t.}$ −78.2° (*c* 0.60, methanol); n.m.r. (DMSO-d_6), δ 8.00–7.10 (m, 15H), 6.08 (s, 1H), 5.70 (s, 2H), 3.76 (s, 3H), 3.43 (q, J = 7.0 Hz, 2H), 3.03 (s, 3H), 1.30 (t, J = 7.0 Hz, 3H); i.r. (Nujol), 3500, 1715, 1645, 1625, 1600, 1255, 1110, 715 cm^{-1}.

Anal. Calcd. for $C_{30}H_{32}O_{10}S$: C, 61.63; H, 5.52; S, 5.48. Found: C, 61.75, 61.40; H, 5.51, 5.54; S, 5.54, 5.74.

Experiment 2: (±)-**10** (5.50 g, 17.2 mmol) was treated in a similar manner with equimolar HDBT to yield **12** (6.6 g, 11.0 mmol), m.p. 129°; $[\alpha]_{589}^{r.t.}$ −75.6° (*c* 0.45, methanol); n.m.r. (DMSO-d_6), δ 8.08–7.17 (m, 15H), 5.64 (s, 2H), 4.05 (s, 2H), 3.26 (q, J = 7.0 Hz, 2H), 3.20 (s, 6H), 2.73 (s, 3H), 1.22 (t, J = 7.0 Hz, 3H); i.r. (Nujol), 1728, 1670, 1600, 1585, 1260, 710 cm^{-1}.

Anal. Calcd. for $C_{31}H_{34}O_{10}S$: C, 62.20; H, 5.72; S, 5.36. Found: C, 62.51, 62.41; H, 5.74, 5.63; S, 5.35, 5.57.

Experiment 3: (±)-**10** (4.68 g, 14.6 mmol) was treated in a similar manner with equimolar HDBT to yield 2.67 g of a 3:2 mixture (by n.m.r.) of **11**:**12**, m.p. 114–120°.

In each of the above three experiments, a second crop of material was obtained by the addition of more ether and the cooling of the resulting mixture at 5°. After filtering the second crop, the mother liquor was concentrated to near dryness and excess ether added. After cooling, the supernatant was decanted leaving a tacky white semi-solid which solidified to a hard cake under reduced pressure.

Conversion of DBT Salts to Perchlorate Salts

A methanolic solution of 2.67 g of a 3:2 mixture of **11**:**12** (first crop) was eluted through an hydroxide exchange column into a flask containing 70% $HClO_4$ (0.72 g, 5.04 mmol). The resulting solution was neutralized by the addition of dilute sodium methoxide, reduced in volume and ether added to the cloud point. The mixture was cooled at 5° to precipitate (−)-**13** (0.361 g, 1.17 mmol), m.p. 115°; $[\alpha]_{365}^{r.t.}$ −8.80° (*c* 0.72, methanol); n.m.r. (DMSO-d_6), δ 7.56 (s, 5H), 6.02 (s, 1H), 3.79 (s, 3H), 3.43 (q, J = 7.0 Hz, 2H), 3.04 (s, 3H), 1.36 (t, J = 7.0 Hz, 3H); i.r. ($CHCl_3$), 1610, 1570, 1490, 1080, 1000, 970 cm^{-1}. Excess ether was added to the mother liquor to precipitate after cooling (+)-**14** (0.621 g, 1.82 mmol), m.p. 65°; $[\alpha]_{365}^{r.t.}$ +4.75° (*c* 0.64, methanol); n.m.r. (DMSO-d_6), δ 7.55 (s, 5H), 4.03 (s, 2H), 3.24 (q, J = 7.0 Hz, 2H), 3.28 (s, 6H), 2.72 (s, 3H), 1.73 (t, J = 7.0 Hz, 3H); i.r. ($CHCl_3$), 2840, 1490, 1450, 1420, 1285, 1090, 703,

622 cm^{-1}. The conversion of a sample of pure **11** (first crop) to its perchlorate gave only (+)-**14**.

In a similar manner, a 1.77 g quantity of a 2:1 mixture of **11**:**12** (third crop) was converted to the less soluble (+)-**13**, m.p. 114°; $[\alpha]_{365}^{r.t.}$ +8.84° (*c* 0.84, methanol) and the more soluble (−)-**14**, m.p. 55°; $[\alpha]_{365}^{r.t.}$ −5.16° (*c* 1.14, methanol).

Conjugate Addition Reaction of (−)-1

(−)-**1** (1.16 g, 6 mmol) and chalcone (1.25 g, 6 mmole) were stirred in 20 ml benzene for 17 h at room temperature. The solvent was removed and the residual oil crystallized from benzene–pentane. The precipitate was collected and recrystallized from cyclohexane to yield 0.14 g (1.26 mmol, 21%) of the *meso*-cyclopropane, m.p. 149° (19). The original mother liquor was concentrated and the residual oil crystallized from cyclohexane to yield 0.49 g (1.5 mmole, 25%) of the *dl*-cyclopropane, m.p. 114°, $[\alpha]_{589}^{25} \sim 0$.

1. C. K. Ingold and J. A. Jessop. J. Chem. Soc. 713 (1930).
2. A. W. Johnson. Ylid chemistry. Academic Press, New York, N.Y. 1966.
3. W. J. Pope and S. J. Peachey. J. Chem. Soc. 1072 (1900).
4. H. Nozaki, M. Takaku, and K. Kondo. Tetrahedron. **22**, 2145 (1966).
5. K. W. Ratts. Tetrahedron Lett. 4707 (1966).
6. A. Hochrainer and W. Silan. Monatsh. Chem. **97**, 1477 (1966).
7. H. Nozaki, D. Tunemoto, K. Nakamura, K. Watanabe, M. Takaku, and K. Kondo. Tetrahedron. **23**, 4279 (1967).
8. A. F. Cook and J. C. Moffat. J. Am. Chem. Soc. **90**, 740 (1968).
9. J. P. Schaefer and L. L. Reed. J. Am. Chem. Soc. **94**, 908 (1972).
10. D. Darwish and R. L. Tomilson. J. Am. Chem. Soc. **90**, 5938 (1968).
11. B. M. Trost and R. F. Hammen. J. Am. Chem. Soc. **95**, 962 (1973).
12. C. R. Johnson and C. W. Schroeck. J. Am. Chem. Soc. **95**, 7418 (1973).
13. D. Darwish and G. Tourigny. J. Am. Chem. Soc. **88**, 4303 (1966).
14. D. Darwish, S. H. Hui, and R. Tomilson. J. Am. Chem. Soc. **90**, 5631 (1968).
15. D. Darwish. Mech. Reactions Sulfur Compd. **3**, 33 (1968).
16. D. Darwish and C. E. Scott. Can. J. Chem. **51**, 3647 (1973).
17. B. C. Menon and D. Darwish. Tetrahedron Lett. 4119 (1973).
18. B. M. Trost, W. L. Schinski, and I. B. Mantz. J. Am. Chem. Soc. **91**, 4320 (1969).
19. B. M. Trost. J. Am. Chem. Soc. **89**, 138 (1967).
20. K. W. Ratts and A. N. Yao. J. Org. Chem. **31**, 1185 (1966).
21. A. W. Johnson and R. T. Amel. J. Org. Chem. **34**, 1240 (1969).
22. S. H. Smallcombe, R. J. Holland, R. H. Fish, and M. C. Caserio. Tetrahedron Lett. 5987 (1968).
23. J. W. Batty, P. D. Howes, and C. J. M. Stirling. J. Chem. Soc. Perkin I, 59 (1973).
24. K. B. Wiberg. Physical organic chemistry. Wiley, New York. 1964. p. 378.
25. A. Rauk, L. C. Allen, and K. Mislow. Angew. Chem. Int. Ed., **9**, 400 (1970).
26. C. L. Butler and L. H. Cretcher. J. Am. Chem. Soc. **55**, 2605 (1933).
27. R. L. Tomilson. Master's Thesis. University of Alberta, Edmonton, Alberta. 1968.