1290, 1260, 1200. 1095, 1040, 1020, 790, 740, 688 cm^{-1}; NMR (CCl_4) δ 3.1 (s, 3 H), 6.8–7.3 and 7.3–7.7 (two m, 8 H), 7.8–8.2 (m, 2 H).

Anal. Calcd for $C_{13}H_{13}NOS$: C, 67.50; H, 5.66; N, 6.05. Found: C, 67.57; H, 5.64; N, 6.10.

S-Butyl-N,S-diphenylsulfoximine. Phenyl N-phenylbenzenesulfonimidate (1.290 g, 4.17 mmol) in approximately 100 mL of anhydrous ether was cooled to 0 °C and butyllithium (15 mL of 1.29 M, 19.42 mmol) was added. The reaction was stirred under nitrogen at 0 °C for 90 min. Water was added slowly to the reaction and it was extracted with benzene. After the solvent was removed, the material was chromatographed on a silica gel column with an ice cold 25% ether–75% carbon tetrachloride mixture employing the "dry column technique" (nylon tubing was used for the column). The product was extracted from the silica gel section by washing it with solvent. The product, obtained as an oil (0.760 g, 67% yield), was shown to be pure by NMR. It was dissolved in a carbon tetrachloride–pentane mixture and cooled. The product crystallized from the solution. Seed crystals were removed. The mother liquor was evaporated and 666 mg of the product was recrystallized from methanol to give 338 mg (mp 47–48 °C). It was then recrystallized from carbon tetrachloride–pentane to yield a sample for analysis (mp 47.5–48.5 °C): IR (KBr) 1600, 1490, 1285, 1260, 1200, 1090, 1035, 1015, 793, 750, 690 cm^{-1}; NMR (CCl_4) δ 0.7–1.1 (nearly a triplet, 3 H), 1.1–2.1 (m, 4 H), 2.9–3.4 (m, 2 H), 6.6–7.3 and 7.3–7.7 (two m, 8 H), 7.7–8.2 (m, 2 H).

Anal. Calcd for $C_{16}H_{19}NOS$: C, 70.29; H, 7.01; N, 5.12. Found: C, 69.90; H, 6.85; N, 5.08. Found: C, 70.17; H, 7.26.

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Registry No.—(+)-(S)-**1**, 33957-73-2; (−)-(R)-**1**, 33993-55-4; (+)-(R)-**2**, 33993-54-3; (+)-(S)-**4**, 33993-53-2; (±)-**4**, 69831-03-4; (+)-(S)-**5**, 33993-56-5; (±)-**5**, 33903-52-5; (−)-(S)-**6**, 18453-46-8; (−)-(S)-**7**, 34513-32-1; (+)-(S)-**8**, 33903-50-3; S-benzyl-N-methyl-S-phenylsulfoximine, 69766-04-7; S-allyl-N-methyl-S-phenylsulfoximine, 69766-05-8; S-cyclopentyl-N-methyl-S-phenylsulfoximine, 69766-06-9; S-methyl-N,S-diphenylsulfoximine, 69766-07-0; S-butyl-N,S-diphenylsulfoximine, 69766-08-1; S-butyl-N-methyl-S-phenylsulfoximine, 69766-09-2; phenyl N-phenylbenzenesulfonimidate, 69766-10-5.

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Preparation and Reactions of N-(p-Tolylsulfonyl)sulfilimines

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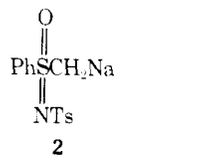
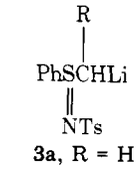
N-(p-Tolylsulfonyl)sulfilimines are prepared in high yield by a phase-transfer-catalyzed process from solid Chloramine-T trihydrate to a solution of a sulfide in dichloromethane. α-Lithio derivatives of N-(p-tolylsulfonyl)-sulfilimines are shown to be useful nucleophilic alkylidene transfer reagents for the conversion of aldehydes and ketones to oxiranes. In the case of benzalacetophenone, 1,2 addition occurred to yield the oxirane. The facile [2,3] sigmatropic rearrangement of allylic sulfilimines to sulfinamides is noted.

N-(Tolylsulfonyl)sulfilimines[1] have been prepared most commonly by the reaction of Chloramine-T (the sodium salt of N-chloro-p-toluenesulfonamide) with sulfides in aqueous media, often with methanol or acetone as a cosolvent. The use of aqueous systems sometimes leads to significant formation of byproduct sulfoxides. In some cases, the reactions give poor results due to insolubility of the sulfide in the aqueous medium. We have found phase-transfer catalysts are effective in these reactions. The sulfide and approximately 0.05 mol % of phase-transfer catalyst were dissolved in dichloromethane and Chloramine-T trihydrate was added as a *solid phase*.[2] The reactions were generally complete in 1 to 2 h at ambient temperature (Table I).

Our earlier demonstration of the utility of carbanions derived from N-tosylsulfoximines (e.g., **2**) as nucleophilic alkylidene transfer reagents prompted our examination of the related sulfilimine-stabilized carbanions (e.g., **3**). We found that the lithiated sulfilimines prepared by addition of butyllithium to a dimethyl sulfoxide solution of the sulfilimine were highly satisfactory reagents for the conversion of aldehydes and ketones to oxiranes (eq 1). Subsequent to our first mention of these reagents,[4] the corresponding sodium anions derived from N-tosylsulfilimines have been explored as reagents for carbonyl to oxirane conversions by Tamura and co-workers.[5] Early in our work we found that the rapidly generated lithium reagents consistently gave higher yields than the



2



3a, R = H
b, R = Ph

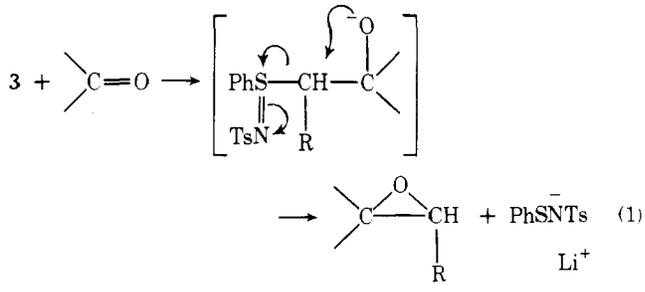


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Table I. Synthesis of Sulfilimines by Phase Transfer of Chloramine-T[b]

$$RSR' + TsNClNa \xrightarrow[CH_2Cl_2]{PTC} RSR' \quad (NTs)$$

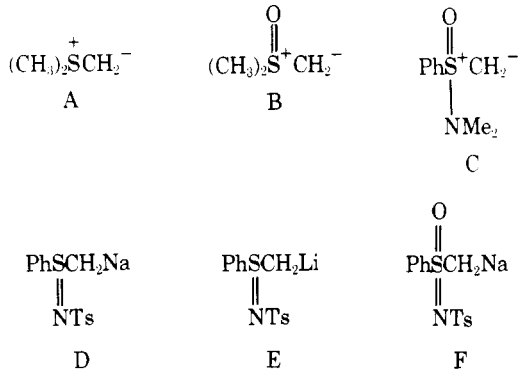
1

sulfilimine 1 R	sulfilimine 1 R′	phase-transfer catalyst[a]	reaction time, h	% yield	mp, °C
Ph	CH_3	none	8	70	129.5–130
		A	1	92	
		B	2	79	
		C	3	89	
Ph	Ph	B	12	73	110–111
n-C_6H_{13}	n-C_6H_{13}	B	1	82	84–85
		C	1	87	
C_2H_5	CH_2CH_2OH	B	0.5	56	85–86
$PhCH_2$	$PhCH_2$	A	1	85	190–191
n-$C_{12}H_{25}$	n-$C_{12}H_{25}$	A	1	55	78–79.5

[a] A = Tributylhexadecylphosphonium bromide; B = Benzyltriethylammonium chloride; C = Adogen 464 (Aldrich Chemical Co.) [trialkyl(C_8–C_{10})methylammonium chloride]. [b] Ts = p-$CH_3C_6H_4SO_2$.

corresponding reagents prepared by the rather slow reaction of the N-tosylsulfilimines with sodium hydride; where there is correspondence the yields reported in this work (Table II) and in that of Tamura seem to confirm this. (We noted that the addition of 1 equiv of diazabicyclooctane to the reaction mixture prior to addition of butyllithium resulted in slight improvements in yield of the oxiranes.) It appears that the anions of N-tosylsulfilimines may not have long-term stability in dimethyl sulfoxide. Excess reagent results in depressed yields of oxiranes, presumably due to attack of the anion on the oxirane.

We anticipated that the complementary regio- and stereoselectivities[6,7] exhibited by sulfonium (A) and oxosulfonium ylides (B and C) in reactions with enones and cyclohexanones would be paralleled by reagents E and F, respec-



tively (Table III). In an earlier study[6] we demonstrated that simple sulfonium ylides (e.g., A) add irreversibly to carbonyls, whereas the addition of the more stable oxosulfonium ylides (e.g., B and C) to carbonyl groups is readily reversible. In like manner, we suspected that the anions derived from the less acidic[8] N-tosylsulfilimines would add irreversibly to carbonyl groups and result in kinetically controlled products, whereas the anions derived from the more acidic N-tosylsulfoximines would add to carbonyls in a reversible fashion and result in thermodynamically controlled products. The results shown in Table III are in accord with these predictions.

We envisioned a synthesis of chrysanthemic acid based on the conjugate addition of the anion derived from **5** (R = Ph) to mesityl oxide. We rationalized that the additional stability

Table II. Preparation of Oxiranes

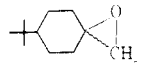
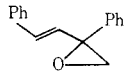
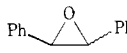
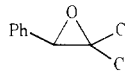
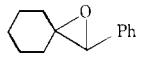
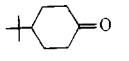
anion	carbonyl compound	product	% yield
3a	PhCHO		100
3a			88
3a			71
3a	PhCH=CH-COPh		71
3a			71
3b	PhCHO		100
3b	CH_3COCH_3		86
3b			76

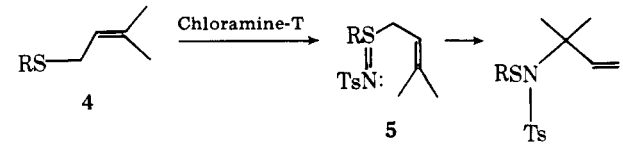
Table III. Stereo- and Regioselectivity of Nucleophilic Methylene Transfer Reagents

substrate	reagent	products: oxirane	products: cyclopropane
PhCH=CH-COPh	A[a]	100	
	B[a]		100
	C[b]		100
	E	100	
	F[c]		100

substrate	reagent	(E)-oxirane	(Z)-oxirane
	A[a]	83	17
	B[a]		100
	C[b]		100
	D[d]	~33	~67
	E[e]	~50	~50
	F[c]		100

[a] Reference 7. [b] C. R. Johnson, M. Haake, C. W. Schroeck, *J. Am. Chem. Soc.*, **92**, 6594 (1970). [c] Reference 3. [d] Reference 5b. [e] Ratio determined as described in ref 7.

of the carbanion due to the allylic system would facilitate cyclopropane formation (thermodynamic control). Allylsulfilimines are known to undergo [2,3] sigmatropic rearrangements to sulfinamides at moderate temperatures.[1] Our hope that the presence of *gem*-dimethyl groups on the vinyl terminus would block the rearrangement of **5** to **6** was not real-



ized. The product of reaction of sulfide **4** (R = Ph) with Chloramine-T under the conditions described above was entirely sulfinamide **6** (R = Ph). Apparently the presence of the S-aryl group facilitates the sigmatropic shift; when the corresponding S-methyl sulfide (**4**, R = CH_3) was treated with Chloramine-T the product obtained was a mixture of sulfilimine **5** (R = CH_3) and sulfinamide **6** (R = CH_3).

Experimental Section

General Method of Preparation of Sulfilimines by Phase Transfer of Chloramine-T. To a 200-mL round-bottom flask equipped with a condenser and magnetic stirrer were added 100 mL of dichloromethane, 0.05 mol of sulfide, and approximately 0.0025

mol of phase-transfer catalyst. Solid Chloramine-T trihydrate (15.5 g, 0.0055 mol) was slowly added with stirring and cooling with a water bath. After addition was complete the water bath was removed; stirring was continued until the reaction was complete (usually 1–2 h) as ascertained by occasional monitoring by a thin-layer chromatography. The reaction mixture was washed with 200 mL of cold 5% aqueous sodium hydroxide followed by two washes with 200-mL portions of water. The dichloromethane layer was dried over anhydrous magnesium sulfate, filtered, and concentrated. The crude sulfilimine was recrystallized from methanol–water (9:1).

General Procedure for Preparation of Oxiranes. The *N*-(*p*-tolylsulfonyl)sulfilimine (3 mmol) was dissolved in 10 mL of dimethyl sulfoxide in a dry nitrogen atmosphere. After addition of 1 equiv of butyllithium in hexane the mixture was magnetically stirred for 10 min at room temperature, and the aldehyde or ketone (3.0 mmol) was added with a syringe. The reaction mixture, after stirring at ambient temperature for 18–20 h, was poured into 10% aqueous sodium chloride. The product was obtained by several extractions with hydrocarbon solvent, washing the combined extracts with water, drying over anhydrous sodium carbonate, and short-path distillation.

Reaction of Chloramine-T with 3-Methyl-1-(phenylthio)-2-butene (4, R = Ph). Sulfide **4** (R = Ph), bp 120–122 °C (6 mm), prepared in 93% yield by alkylation of sodium benzenethiolate with 1-bromo-3-methyl-2-butene in ethanol, was subjected to the general procedure given above for reaction of Chloramine-T with sulfides at both ambient temperature and 0 °C. In each case an oil was obtained in 63 and 53% yield, respectively, which was identified as *N*-(1,1-dimethyl-2-propenyl)-*N*-(phenylthio)-*p*-toluenesulfonamide (**6**, R = Ph): ^{1}H NMR ($CDCl_3$) δ 1.5 (6, s), 2.3 (3, s) 4.8–6.3 (3, vinyl multiplet), 7–8 (9, Ar).

Reaction of Chloramine-T with 3-Methyl-1-(methylthio)-2-butene (4, R = CH_3). Sulfide **4** (R = CH_3), bp 79–81 °C (77 mm), was treated with Chloramine-T according to the general procedure. The crude product was washed with ether to give the sulfilimine **5** (R = CH_3) (40%): mp 73.5–75 °C; ^{1}H NMR ($CDCl_3$) δ 1.68 and 1.72 (6, 2 s), 2.38 (3, s), 2.58 (3, s), 3.54 (2, d), 5.02 (1, t), 7–8 (4, AB quartet). These crystals were stored for several months in the refrigerator without noticeable deterioration.

Evaporation of the ether extract and chromatography of the residue gave, as an oil, the rearranged product *N*-(1,1-dimethyl-2-propenyl)-*N*-(methylthio)-*p*-toluenesulfonamide (**6**, R = CH_3) (19%); ^{1}H NMR ($CDCl_3$) δ 1.57 (6, s), 2.42 (6, s, ArMe and SMe), 4.9–6.4 (3, vinyl multiplet), 7–8 (4, AB quartet).

Acknowledgment. This work was supported by a grant from the National Science Foundation.

Registry No.—**1** (R = Ph; R′ = Me), 10330-22-0; **1** (R = Ph; R′ = Ph), 13150-76-0; **1** (R = *n*-C_6H_{13}; R′ = *n*-C_6H_{13}), 69745-50-2; **1** (R = Et, R′ = CH_2CH_2OH), 69745-51-3; **1** (R = $PhCH_2$, R′ = $PhCH_2$), 3249-66-9; **1** (R = *n*-$C_{12}H_{25}$, R′ = *n*-$C_{12}H_{25}$), 69745-52-4; **3a**, 69745-53-5; **3b**, 69745-54-6; **4** (R = Ph), 10276-04-7; **4** (R = Me), 5897-45-0; **5** (R = Me), 69745-55-7; **6** (R = Ph), 69745-56-8; **6** (R = Me), 69745-57-9; A, 6814-64-8; B, 5367-24-8; C, 30004-64-9; D, 69745-58-0; F, 29835-23-2; PhCHO, 100-52-7; cyclohexanone, 108-94-1; 4-*tert*-butylcyclohexanone, 98-53-3; PhCH=CHCOPh, 94-41-7; CH_3COCH_3, 67-64-1; phenyloxirane, 96-09-3; 1-oxaspiro[2.5]octane, 185-70-6; *cis*-6-*tert*-butyl-1-oxaspiro[2.5]octane, 7787-78-2; *trans*-6-*tert*-butyl-1-oxaspiro[2.5]octane, 18881-26-0; (*E*)-2-(benzylidenemethyl)-2-phenyloxirane, 69745-59-1; 2,3-diphenyloxirane, 17619-97-5; 2,2-dimethyl-3-phenyloxirane, 10152-58-6; 2-phenyl-1-oxaspiro[2.5]octane, 37545-92-9; sodium benzenethiolate, 930-69-8; 1-bromo-3-methyl-2-butene, 870-63-3; methyl phenyl sulfide, 100-68-5; diphenyl sulfide, 139-66-2; dihexyl sulfide, 6294-31-1; 2-(ethylthio)ethanol, 110-77-0; dibenzyl sulfide, 538-74-9; didodecyl sulfide, 43-9.

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Synthetic Application of Methyl(phenylthio)ketene. Synthesis of Vicinal-Substituted Cyclopentene Derivatives

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Received January 3, 1979

Methyl(phenylthio)ketene (**1**) reacts with olefins to yield α-*endo*-(phenylthio)cyclobutanones **3**, which are converted into α-methylenecyclobutanones **5**. On the other hand, the reaction of the ketene **1** with imines gives a mixture of *cis*- and *trans*-α-(phenylthio)azetidin-2-ones (**7** and **8**). α-Methyleneazetidin-2-one **10a** was obtained similarly from *cis*-α-(phenylthio)azetidin-2-one **7a**. The reaction of the cyclopentadiene adduct, 7-methyl-7-(phenylthio)bicyclo[3.2.0]-2-hepten-6-one (**3a**), with various nucleophiles was investigated. The synthetic evaluation and the stereochemistry of the products are discussed.

There has recently been considerable interest in synthetic applications of modified ketenes such as monohalo-,[2] dihalo-,[3] and dithioketenes[4] because ketenes can serve as one of the most powerful and regioselective reagents for vicinal alkylation of the C–C double bond. On the other hand, in connection with syntheses of natural products, many methods for introduction of α,β-unsaturated carbonyl units have been developed.[5] From these points of view, methyleneketene ($H_2C{=}C{=}C{=}O$) is expected to have great synthetic utility. However, with the exception of the flash vacuum pyrolysis of the cyclopentadiene adduct of 2,2-dimethyl-5-methylene-1,3-dioxane-4,6-dione,[6] methyleneketene has not been detected.

In our preliminary paper,[7] we reported a versatile synthetic reagent, methyl(phenylthio)ketene (**1**), which can be regarded as the synthetic equivalent of methyleneketene. We now wish to report the detailed results and further investigation of the reactions and applications of **1**.

Cycloaddition Reactions of 1 with Olefins 2 and with Imines 6. In the presence of excess cyclopentadiene (**2a**) at −15 °C, the ketene **1** generated in situ by dehydrochlorination of α-(phenylthio)propanoyl chloride with triethylamine af-

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