moved under reduced pressure, and the residue was stirred in water (25 mL) for 1 h. The solid which resulted was filtered, rinsed with water, dried (air), and analyzed by mass spectrometry and HPLC. See Table IV for results.

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Reaction of Sulfonimidamide Anions with Electrophiles

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The reaction of alkylsulfonimidamides with bases gave corresponding carbanions, which were allowed to react with carbonyl compounds to give (2-hydroxyalkyl)sulfonimidamides in good yields. When benzoic anhydride or chlorotrimethylsilane was treated with these anions, corresponding phenacylsulfonimidamides or (trimethylsilyl)methylsulfonimidamides were obtained. On the other hand, the reaction of methyl *N*-*p*-tosylsulfonimidmorpholide anion with carbonyl compounds afforded epoxides or oxetanes in good yields.

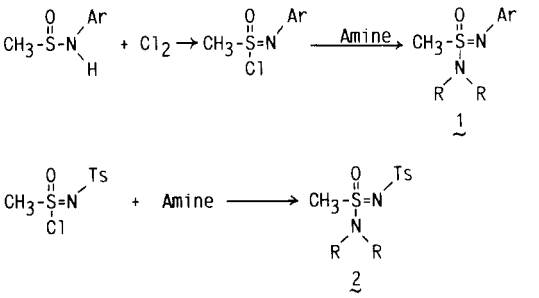
Sulfonamidamides (**1**) and *N*-*p*-tosylsulfonimidamides (**2**), derivatives of sulfonic acid, have been known since their preparation by Levchenco and co-workers in 1963, but very few reports dealing with their reactions have appeared.[1] Only one example mentions the reduction of **1** with aluminum amalgam to give sulfinamides.[2] Previously, we reported the alkylation of alkylsulfonimidamides **1b** to yield corresponding diaminooxosulfonium salts.[3] The reaction of these salts with base afforded corresponding ylides, which were treated with carbonyl compounds to give not only epoxides but also cyclopropyloxosulfonium salts.[4] This anomalous reactivity, in turn, prompted us to investigate the reactions of **1** and **2**. In this paper, we would like to report the reaction of alkylsulfonimidamide anions (**3**) and *N*-*p*-tosylsulfonimidmorpholide anion (**4**) with electrophiles.

Results and Discussion

Sulfonimidamides (**1**) were prepared by the reaction of sulfinamides, chlorine gas, and secondary amines. Compound **2** was prepared by the method described by Johnson et al.[1c] (Scheme I, Table I).

Treatment of **1a** with *n*-BuLi resulted in the formation of corresponding anion (**3a**), which was allowed to react with benzophenone in refluxing ether to give 2-hydroxysulfonimidamide (**5a**) in 62% yield (Scheme II, Table II). However, **1a** was recovered more than 70% when this reaction was carried out at 0 °C. This result showed that the reactivity of the anions **3** toward carbonyl compounds was lower than that of sulfoximide anion (**6**).[1c] We then tried the reaction of **3b** with many kinds of electrophiles. The reaction of **3b** with benzoic anhydride afforded phenacylsulfonimidmorpholine **7a** in 50.5% yield. As shown

Scheme I



Scheme II

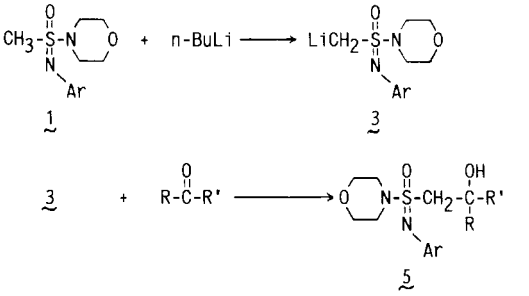


Table I. Preparation of 1 and 2

	R-N-R	Ar	yield, %
1a	morpholide	*p*-Tol	73.0
1b	morpholide	*p*-Br-C_6H_4	69.1
1c	morpholide	*p*-Cl-C_6H_4	53.7
1d	Me, Me	*p*-Cl-C_6H_4	48.7
1e	Me, Ph	*p*-Cl-C_6H_4	32.9
2	morpholide	*p*-Tosyl	92.3

Table II. Preparation of 2-Hydroxysulfonimidmorpholide (5)

	Ar		R	R′	yield, %
3a	Tol	**5a**	Ph	Ph	61.7
3b	*p*-BrC_6H_4	**5b**	H	Ph	47.8
3b	*p*-BrC_6H_4	**5c**	Ph	Ph	62.7

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Scheme III

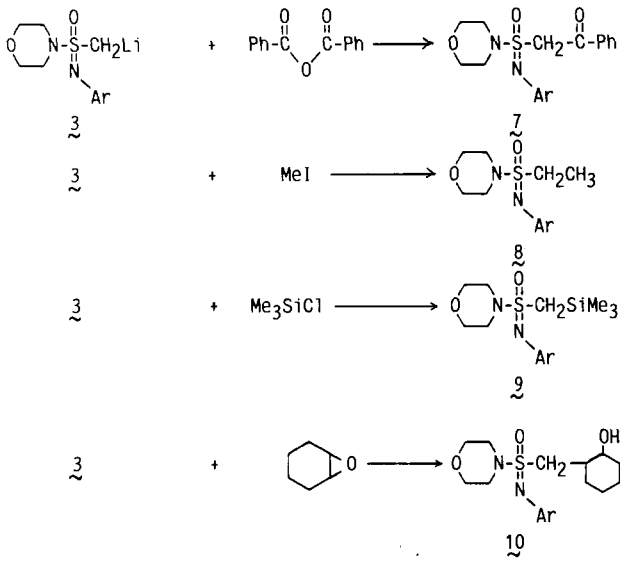


Table III. Reaction of 3 with Electrophiles

compd[a]	reactant	product	yield, %
3c	benzoic anhydride	**7b**	58.5
3b	repeat	**7a**	50.5
3c	methyl iodide	**8**	58.3
3c	trimethylchlorosilane	**9b**	59.7
3b	repeat	**9a**	57.0
3b	cyclohexene oxide	**10**	38.9

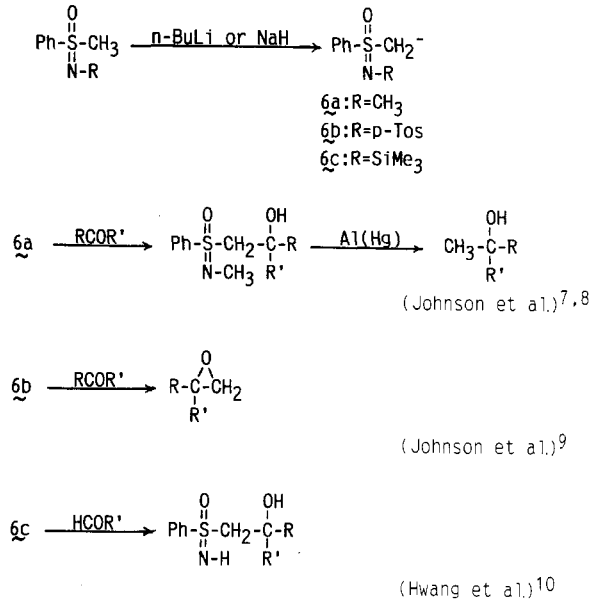
[a] **3b**, Ar = p-BrC_6H_4; **3c**, Ar = p-ClC_6H_4.

in Scheme III, sulfonimidamide derivatives were obtained in moderate yields (Table III).

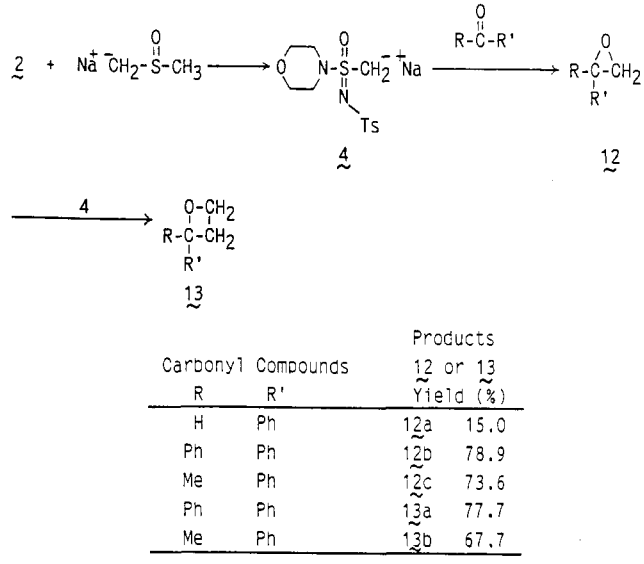
These results were similar to those of the reactions of sulfoximines. Sulfoximide anions (**6**) have been found to react with several electrophiles. Lithiation and alkylation were first described for **6**,[7] and optically active methyl carbinols have been obtained from the reaction of resolved **6** with carbonyl compounds followed by desulfurization.[8] Carbanion alkylations have been reported for *N*-*p*-tosylsulfoximine.[9] Recently, Hwang et al. described the lithiation and alkylation of *N*-(trimethylsilyl)methylphenylsulfoximide.[10] Comparing the above results, the present reaction has a similar tendency toward electrophiles but requires more severe conditions (Scheme IV).

N-*p*-tosylsulfonimidamides **2** were prepared by two groups.[1c,d] However, there is no report on the reaction of **2**. Johnson and co-workers reported that the reaction of *N*-*p*-tosylsulfoximide anion with carbonyl compounds gave epoxides in good yields.[8] We first tried the reaction of **2** with bases and carbonyl compounds. Treatment of **2** with dimsyl sodium resulted in the formation of corresponding anion **4**, which was allowed to react with benzophenone to give corresponding epoxide (**12**). Since Welch et al. prepared 2,2-disubstituted oxetanes by the reaction of *N*-*p*-tosylsulfoximide anion with ketones,[5] we also tried the reaction of excess amount of **4** with carbonyl compounds. Treatment of 4 equiv of **4** with benzophenone afforded 2,2-diphenyloxetane (**13a**) in 76.0 % yield. As shown in Scheme V, oxetanes were obtained in moderate yields.

Scheme IV



Scheme V



Carbonyl Compounds R	R'	Products 12 or 13 Yield (%)	
H	Ph	12a	15.0
Ph	Ph	12b	78.9
Me	Ph	12c	73.6
Ph	Ph	13a	77.7
Me	Ph	13b	67.7

Compounds **3** and **4** have been virtually ignored in reactions probably due to their lack of reactivity and difficulty of synthesis.

In summary, the reaction of sulfonimides (**1** and **2**) with bases gave corresponding carbanions (**3** and **4**). The reaction of **3** with carbonyl compounds gave corresponding alcohols in good yields. When benzoic anhydride or chlorotrimethylsilane were treated with **3**, the obtained products were corresponding phenacyl or trimethylsilyl derivatives, respectively. On the other hand, the reaction of **4** with carbonyl compounds afforded epoxides or oxetanes in good yields.

Experimental Section

General Methods. Melting points were uncorrected. ^1H NMR spectra were determined with a JEOL PMX-60 spectrometer or a FX-200 spectrometer. IR spectra were determined with a Hitachi IR-345 spectrophotometer. Analytical GLC was performed on a Yanagimoto G-3800 instrument with a flame ionization detector and a capillary glass column filled with OV 101. Helium was the carries gas at 50 mL/min.

Materials. *N*-*p*-tolylmethanesulfinamide was prepared from methanesulfinyl chloride, *p*-toluidine, and triethylamine (mp

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114–115 °C, lit.[11] mp 115–116 °C). *N*-(*p*-Chlorophenyl)-methanesulfinamide (mp 73.0–74.0 °C) and *N*-(*p*-bromophenyl)methanesulfinamide (mp 102.7–103.5 °C) were prepared in a similar manner.

Preparation of Sulfonimidamide (1a). To a solution of 16.9 g (0.1 mol) of *N*-*p*-tolylmethanesulfinamide in dichloromethane (200 mL) cooled to −50 °C was added 8 mL of chlorine. After being stirred for 1 h, the resulting solution was warmed up to room temperature and concentrated to 100 mL. This solution was added to a solution of morpholine (20.0 g, 0.23 mol) in dichloromethane at −10 °C. After being stirred for 3 h, the reaction mixture was washed with water and dried over $MgSO_4$ and evaporated to give pale brown crystals. Recrystallization from ethanol gave colorless crystals of **1a** (18.6 g, 73.0%): mp 109.5–110.0 °C; ^1H NMR ($CDCl_3$) δ 2.23 (s, 3 H, tol-CH_3), 2.89 (s, 3 H, SCH_3), 3.05–3.30 (m, 4 H, NCH_2), 3.50–3.75 (m, 4 H, OCH_2), 6.90 (s, 4 H, Ar); ^{13}C NMR ($CDCl_3$) δ 20.69 (tol-CH_3), 36.67 (SCH_2), 46.70 (NCH_2), 66.42 (OCH_2), 123.24, 129.58, 129.56, 131.32; IR (KBr, cm^{-1}) 3025, 2970, 2925, 2905, 2865, 1599, 1503, 1452, 1320, 1282, 1259, 1221, 1210, 1108, 1080, 1049, 952, 932, 905. Anal. Calcd for $C_{12}H_{18}N_2O_2S$: C, 56.67; H, 7.08; N, 11.02. Found: C, 56.56; H, 7.12; N, 10.83. Other sulfonimidamides were prepared in a similar manner. **1b**: mp 129.1–129.5 °C; yield 69.1%; ^1H NMR ($CDCl_3$) δ 3.00 (s, 1 H, SCH_3), 3.17–3.33 (m, 4 H, NCH_2), 3.63–3.88 (m, 4 H, OCH_2), 7.00–7.42 (4 H, Ar); ^{13}C NMR ($CDCl_3$) δ 36.62 (SCH_3), 46.59 (NCH_2), 66.31 (OCH_2), 114.58, 124.93, 131.86, 142.97. Anal. Calcd for $C_{11}H_{15}BrN_2O_2S$: C, 41.38; H, 4.70; N, 8.78. Found: C, 41.13; H, 4.76; N, 8.49. **1c**: mp 109–110 °C; yield 53.7%; ^1H NMR ($CDCl_3$) δ 2.95 (s, 3 H, SCH_3), 3.1–3.28 (m, 4 H, NCH_2), 3.58–3.73 (m, 4 H, OCH_2), 6.93–7.28 (2 H, Ar); ^{13}C NMR ($CDCl_3$) δ 36.51 (SCH_3), 46.54 (NCH_2), 66.26 (OCH_2), 124.38, 126.88. Anal. Calcd for $C_{11}H_{15}ClN_2O_2S$: C, 48.10; H, 5.46; N, 10.20. Found: C, 47.80; H, 5.17; N, 10.20. **1d**: mp 118.0–119.0 °C; yield 48.7%; ^1H NMR ($CDCl_3$) δ 2.82 (S, 6 H, NCH_3), 2.91 (s, 3 H, SCH_3), 6.96–7.21 (4 H, Ar); ^{13}C NMR ($CDCl_3$) δ 35.65 (SCH_3), 38.30 (NCH_3), 124.49, 126.71, 128.83, 142.90 (Ar); IR (KBr, cm^{-1}) 3009, 2941, 2975, 2890, 1599, 1496, 1462, 1418, 1349, 1318, 1264, 1218, 1118, 1108, 1049, 1020, 980, 952. Anal. Calcd for $C_9H_{13}ClN_2OS$: C, 46.35; H, 5.58; N, 12.02. Found: C, 46.47; H, 5.56; N, 11.74. **1e**: mp 85.0–86.0 °C; yield 32.9%; ^1H NMR ($CDCl_3$) δ 3.02 (s, 3 H, SCH_3), 3.23 (s, 3 H, NCH_3), 7.08 (s, 5 H, N-Ar), 7.22 (s, 4 H, *p*-Cl-Ar). Anal. Calcd for $C_{14}H_{15}ClN_2OS$: C, 57.01; H, 5.09; N, 9.50. Found: C, 56.95; H, 5.08; N, 9.51.

Preparation of *N*-(*p*-Tolylsulfonyl)methanesulfonimidmorpholide (2). To a solution of morpholine (13.1 g, 0.15 mol) in dichloromethane (100 mL) was added this solution of *N*-(*p*-tolylsulfonyl)methanesulfonimidoyl chloride (20.5 g, 0.07 mol) in dichloromethane (80 mL) at −10 °C. After being stirred for 1 h, the reaction mixture was washed with water and dried over $MgSO_4$, evaporated to give *N*-tosylsulfonimidamide **2** (27.90 g, 58.5%, colorless crystals). **2**: mp 113.2–114.0 °C; yield 50.0%; ^1H NMR ($CDCl_3$) δ 2.42 (s, 3 H, tol-Me), 3.05 (s, 3 H, SMe), 3.17–3.37 (m, 4 H, NCH_2), 3.67–3.82 (m, 4 H, OCH_2), 7.17–7.87 (4 H, Ar); ^{13}C NMR ($CDCl_3$) δ 21.51 (Ar-Me), 38.89 (SCH_3), 46.27 (NCH_2), 66.20 (OCH_2), 126.82, 129.37, 140.69, 143.02. Anal. Calcd for $C_{12}H_{18}N_2O_4S_2$: C, 45.27; H, 5.70; N, 8.80. Found: C, 44.87; H, 5.68; N, 8.6.

Preparation of 2-Hydroxy-2-phenyl-*N*-(*p*-bromophenyl)ethanesulfonimidmorpholide. (5b) A 250-mL, three-necked, round-bottomed flask equipped with a magnetic stirring bar was charged with **1b** (1.28 g, 4 mmol) and ether (50 mL). To this solution was added *n*-BuLi (7.7 mL, 10% w/v in hexane, 12.0 mmol) in ether (50 mL) via syringe over 5 min under nitrogen atmosphere. After addition was complete, the reaction mixture was refluxed and benzaldehyde (1.27 g, 12.0 mmol) in ether (30 mL) was added dropwise. After being refluxed for 25 h, the reaction mixture was washed with water (3 × 50 mL) and brine (2 × 50 mL), dried over $MgSO_4$, and filtered. The filtrate was evaporated under reduced pressure to give pale brown oil, which was chromatographed through silica gel by elution with hexane, dichloromethane, and ethyl acetate. The desired alcohol **6** was obtained as a diastereoisomer's mixture by evaporation of the dichloromethane eluate, which was crystallized upon standing (0.71 g, 1.7 mmol, 41.8%). Recrystallization with methanol gave a diastereoisomer of **5b** (0.47 g, 1.1 mmol): mp 127.5–128.3 °C; ^1H NMR ($CDCl_3$) δ 3.26, 3.28 (d, 2 H, SCH_2), 3.13–3.32 (m, 4 H, NCH_2), 3.44–3.57 (m, 4 H, OCH_2), 4.77–4.85 (d, 1 H, OH), 5.05–5.27 (m, 1 H, CH), 6.85–7.35 (m, 9 H, Ar); ^{13}C NMR ($CDCl_3$) δ 46.64 (NCH_2), 59.43 (OHCH), 66.47 (OCH_2), 68.96 (SCH_2), 115.06, 124.98, 125.73, 128.81, 133.13, 141.02, 142.37, (Ar); IR (KBr, cm^{-1}) 3425, 3051, 3023, 2955, 2914, 2850, 2249, 2051, 1950, 1882, 1735, 1582, 1479, 1445, 1389, 1330, 1305, 1259, 1200, 1175, 1110, 1070, 1130, 1005, 950. Anal. Calcd for $C_{18}H_{21}BrN_2O_3S$: C, 50.83; H, 4.98; N, 6.59. Found: C, 50.98; H, 4.96; N, 6.59. Compounds **5a** and **5c** were prepared in a similar manner. **5a**: pale yellow oil; ^1H NMR ($CDCl_3$) δ 2.18 (s, 3 H, Ar), 2.85–2.98 (m, 4 H, NCH_2), 3.22–3.41 (m, 4 H, OCH_2), 3.79, 3.85 (d, 2 H, SCH_2), 6.89–7.56 (14 H, Ar); ^{13}C NMR ($CDCl_3$) δ 20.71 (Ar CH_3), 46.06 (NCH_2), 59.71 (COH), 66.16 (OCH_2), 75.91 (SCH_2), 123.21, 125.81, 126.40, 126.56, 127.27, 127.43, 128.03, 128.41, 129.65, 139.62, 144.50, 144.24, 145.80 (Ar). Anal. Calcd for $C_{25}H_{28}N_2O_3S$: C, 68.78; H, 6.46. Found: C, 68.39; H, 6.31. **5c**: mp 121.8–122.5 °C; ^1H NMR ($CDCl_3$) δ 3.87, 3.90 (d, 2 H, SCH_2), 7.17–7.61 (14 H); ^{13}C NMR ($CDCl_3$) δ 46.05 (NCH_2), 59.70 (COH), 66.09 (OCH_2), 75.95 (SCH_2), 115.39, 124.92, 125.68, 126.28, 126.50, 127.36, 127.53, 128.07, 128.34, 128.45, 131.97, 141.50, 144.05, 145.40 (Ar). Anal. Calcd for $C_{24}H_{25}BrN_2O_3S$: C, 57.47; H, 5.02; N, 5.59. Found: C, 57.36; H, 4.97; N, 5.51.

Preparation of 1-Benzoyl-*N*-(*p*-chlorophenyl)methanesulfonimidmorpholide (7b). To a solution of **1c** (0.77 g, 2.8 mmol) in ether (50 mL) was added dropwise a solution of *n*-BuLi (5.7 mL, 10% w/v, 9.0 mmol) in ether (50 mL) at room temperature. After the mixture was refluxed for 1 h, a solution of benzoic anhydride (2.03 g, 9.0 mmol) in ether (50 mL) was added to this reaction mixture. After being refluxed for 24 h, the resulting suspension was washed with water (3 × 50 mL), dried over $MgSO_4$, and evaporated to give a reddish brown oil. This oil was chromatographed over SiO_2 by elution with hexane–dichloromethane (1:1) to give desired **7b** (0.62 g, 1.65 mmol, 59.0%): mp 116.1–117.0 °C; ^1H NMR ($CDCl_3$) δ 3.10–3.60 (m, 8 H, morpholine), 4.67 (s, 2 H, SMe), 6.75–8.10 (9 H, Ar); IR (KBr, cm^{-1}) 3050, 3028, 3000, 2902, 2855, 1675, 1592, 1489, 1448, 1418, 1398, 1325, 1242, 1218, 1118, 1079, 1050, 1008, 928. Anal. Calcd for $C_{18}H_{19}ClN_2O_3S$: C, 57.06; H, 5.05; N, 7.39. Found: C, 56.82; H, 5.01; N, 7.28.

***N*-(*p*-Bromophenyl)ethanesulfonimidmorpholide (8).** To a solution of **1b** (1.92 g, 6 mmol) in ether (50 mL) was added a solution of *n*-BuLi (4.6 mL, 10% w/v, 7.2 mmol) at room temperature. After being stirred for 30 min, the reaction mixture was refluxed and a solution of methyl iodide (1.02 g, 7.2 mmol) in ether (50 mL) was added. After being refluxed for 18 h, the reaction mixture was washed with water (3 × 50 mL), dried over $MgSO_4$, and filtered. The filtrate was evaporated to give a brown oil, which was chromatographed on SiO_2 by elution with hexane–dichloromethane (1:1) to give desired **8** (1.16 g, 3.48 mmol): mp 70.0–70.5 °C; yield 58.3%; ^1H NMR ($CDCl_3$) δ 1.43 (t, 3 H, CH_3), 3.10 (q, 2 H, SCH_2), 3.13–3.30 (m, 4 H, NCH_2), 3.50–3.68 (m, 4 H, OCH_2), 6.88–7.38 (4 H, Ar); ^{13}C NMR ($CDCl_3$) δ 7.49 (CH_3), 45.57 (SCH_2), 46.22 (NCH_2), 66.16 (OCH_2), 113.94, 124.62, 131.44, 143.03. Anal. Calcd for $C_{12}H_{17}BrN_2O_2S$: C, 43.64; H, 5.41; N, 8.01. Found: C, 43.27; H, 5.10; N, 8.41.

1-(Trimethylsilyl)-*N*-(*p*-bromophenyl)methanesulfonimidmorpholide (9a). To a solution of **1b** (9.05 g, 33 mmol) in ether (200 mL) was added a solution of *n*-BuLi (25 mL, 10% w/v, 39 mmol) at room temperature. After being stirred for 30 min, the reaction mixture was refluxed and a solution of chlorotrimethylsilane (4.02 g, 39 mmol) in ether (50 mL) was added. After being refluxed for 18 h, the reaction mixture was washed with water (3 × 60 mL), dried over $MgSO_4$, and filtered. The filtrate was evaporated to give a brown oil, which was chromatographed on SiO_2 by elution with hexane and dichloromethane. The desired trimethylsilylated sulfonimidamide was obtained from the dichloromethane eluate. **9a** (6.51 g, 17.8 mol, 57.0%): mp 59.0–60.0 °C; ^1H NMR ($CDCl_3$) δ 1.83–2.60 (m, 2 H, SCH_2), 2.77–2.97 (m, 4 H, NCH_2), 3.23–3.47 (m, 4 H, OCH_2), 6.65–6.95 (m, 4 H, Ar); ^{13}C NMR ($CDCl_3$) δ 1.90 (CH_3), 38.42 (SCH_2), 47.39 (NCH_2), 67.09 (OCH_2), 116.92, 125.11, 127.15, 129.49, 129.79 (Ar); IR (KBr, cm^{-1}) 2955, 2898, 2857, 1590, 1482, 1451, 1362, 1300, 1258, 1215, 1177, 1141, 1115, 1071, 1042, 1018, 930. Anal. Calcd for $C_{14}H_{23}BrN_2O_2SSi$: C, 42.63; H, 5.75. Found: C, 42.98; H, 5.88.

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1-(2-Hydroxycyclohexyl)-*N*-(*p*-bromophenyl)methanesulfonimidmorpholide (10). To a solution of **1b** (1.28 g, 4 mmol) in ether (50 mL) was added a solution of *n*-BuLi (5.1 mL, 10% w/v, 8 mmol) at room temperature. After being stirred for 30 min, the reaction mixture was refluxed and a solution of cyclohexene oxide (0.78 g, 8 mmol) in ether (50 mL) was added. After being refluxed for 20 h, the reaction mixture was washed with water (3 × 50 mL), dried over $MgSO_4$, and filtered. The filtrate was evaporated to give a brown oil, which was chromatographed on silica gel by elution with dichloromethane–ethyl acetate (9:1) to give desired **10** (0.65 g, 1.56 mmol, 38.9%, pale brown oil): ^1H NMR ($CDCl_3$) δ 1.10–2.23 (m, 9 H, cyclohexyl), 3.13–3.37 (m, NCH_2), 3.50–3.73 (m, 4 H, OCH_2), 6.85–7.35 (4 H, Ar); ^{13}C NMR ($CDCl_3$) δ 24.60, 25.62, 31.69, 35.48, 42.15, 72.81 (cyclohexyl), 53.80 (SCH_2), 46.54 (NCH_2), 66.42 (OCH_2), 124.81, 131.86, 142.80, 167.45 (Ar). Anal. Calcd for $C_{17}H_{25}BrN_2O_3S$: C, 48.57; H, 5.56. Found: C, 48.94; H, 5.99.

Preparation of 1,1-Diphenylethylene Oxide (12b). To a solution of dimsyl sodium (prepared from 0.16 g of NaH; 4.0 mmol) in DMSO (100 mL) was added **2** (1.25 g, 3.9 mmol) portionwise at 50 °C for 30 min. After the mixture was stirred for 2 h at room temperature, a solution of benzophenone (0.35 g, 1.95 mmol) in DMSO (20 mL) was added dropwise at room temperature. After being stirred for 3 days, the reaction mixture was poured into water (100 mL) and extracted with hexane (3 × 30 mL). The combined extract was dried over $MgSO_4$ and evaporated to give **12b** (0.30 g, 1.53 mmol, 78.9%). Other epoxides were prepared in a similar manner. **12a**: bp 56–60 °C (2 mmHg) [lit.[12] bp 67–68 °C (8 mmHg)]. **12b**: bp 92–93 °C (0.011 mmHg). **12c**; bp 30.2 °C (0.009 mmHg) [lit. bp 70 °C/ (8 mmHg)].

Preparation of 2,2-Diphenyloxetane (13a). To a solution of dimsyl sodium (prepared from 0.44 g of NaH, 18.4 mmol) in DMSO (100 mL) was added **2** (5.86 g, 18.4 mmol) in DMSO (100 mmol) at 50 °C for 30 min. After the mixture was stirred for 2 h at 50 °C, a solution of benzophenone (0.78 g, 4.28 mmol) in DMSO (20 mL) was added dropwise at 50 °C. After being stirred for 3 days, the reaction mixture was poured into water (100 mL) and extracted with hexane (3 × 30 mL). The combined extract was dried over $MgSO_4$ and evaporated to give 2,2-diphenyloxetane **13a** (0.7 g, 3.3 mmol, 77.7%). The yield was estimated by GLC. **13b** was prepared in a similar manner. **13a**: bp 111–115 °C (0.013 mmHg) [lit.[13] bp 109–112 °C (0.013 mmHg)], **13b**: bp 31–35 °C (0.009 mmHg) [lit. bp 30–35 °C (0.008 mmHg)].

Registry No. **1a**, 76867-83-9; **1b**, 115204-35-8; **1c**, 115204-36-9; **1d**, 115204-37-0; **1e**, 115204-38-1; **2**, 93938-04-6; **5a**, 115204-39-2; **5b**, 115204-40-5; **5c**, 115204-41-6; **7a**, 115204-42-7; **7b**, 115204-43-8; **8**, 115204-44-9; **9a**, 115204-45-0; **9b**, 115204-46-1; **10**, 115204-47-2; **12a**, 96-09-3; **12b**, 882-59-7; **12c**, 2085-88-3; **13a**, 884-73-1; **13b**, 19352-10-4; *p*-$MeC_6H_4NHS(=O)Me$, 19977-37-8; *p*-$BrC_6H_4NHS(=O)Me$, 115204-48-3; *p*-$ClC_6H_4NHS(=O)Me$, 69726-88-1; Me_2NH, 124-40-3; MeNHPh, 100-61-8; MeS(=O)(Cl)=NTs, 28614-56-4; PhCHO, 100-52-7; PhCOPh, 119-61-9; PhCOOCOPh, 93-97-0; Me_3SiCl, 75-77-4; MeCOPh, 98-86-2; morpholine, 110-91-8; cyclohexene oxide, 286-20-4.

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Photochemistry of Cyclopropene Derivatives. Intramolecular Hydrogen Transfer Reaction of Some 1-(Alkyl-substituted)cyclopropenes

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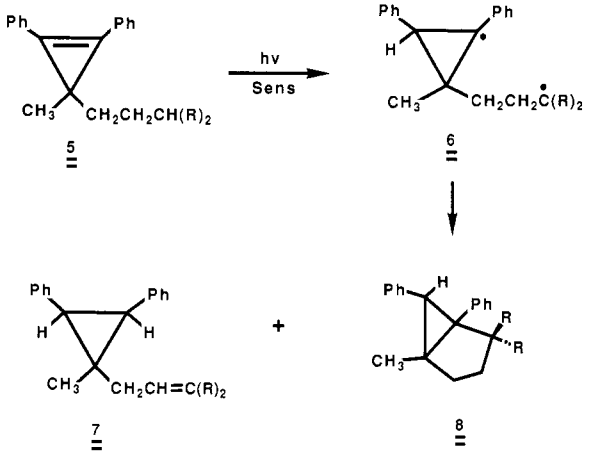
The photochemical behavior of a number of 1-(alkyl-substituted)cyclopropenes that contain a hydrogen atom in the γ or δ position of the side chain has been studied in mechanistic detail. The triplet state, generated by sensitization techniques, undergoes hydrogen atom abstraction by a mechanism analogous to the Norrish type II process of carbonyl compounds. The quantum yield for the triplet-state hydrogen transfer reaction decreased substantially with deuterium substitution. The value of the isotope effect ($k_H/k_D \sim 3.0$) correlated well with related results in the literature indicating an early transition state for hydrogen transfer. The high regioselectivity of hydrogen transfer can be attributed to the stereoelectronic requirements for abstraction as well as the fact that the resulting diradical produced allows for maximum delocalization of the radical centers.

Intramolecular hydrogen transfer reactions of excited states have been the subject of intense research activity since their first discovery by Norrish in 1937.[1] Most studies have centered on the photochemistry of ketones possessing γ-hydrogens.[2-7] In contrast to carbonyl compounds, examples of hydrogen abstraction in the direct and sensitized photolysis of olefins are less common.[8-27]

Scheme I



Considering the wealth of photochemistry exhibited by alkenes,[28] a systematic study of the hydrogen transfer

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