resolution mass spectrum calcd for $C_{23}H_{20}O_4S_2$ 424.080, found 424.079.

2-Hydroxybiphenyl-2′-sulfinic Acid δ-Sultine (7). *o*-Hydroxybiphenyl (1 g, 5.9 mmol) in methylene chloride (5 mL) was added to thionyl chloride (0.47 mL, 6.4 mmol) in methylene chloride (5 mL) at 0 °C under dry argon. Triethylamine (0.82 mL, 5.8 mmol) was added dropwise over a period of 5 min. This mixture was stirred at 0 °C for 15 min and at 25 °C for an additional 15 min before being filtered by suction and subsequent dropwise addition over a 15-min period to a vigorously stirred suspension of aluminum chloride (1.6 g, 12 mmol) in methylene chloride (50 mL at 0 °C under dry argon). The dark green solution was stirred at 0 °C for 1 h and at 25 °C for 12 h. Addition of water (50 mL), filtration, acid wash (30 mL, 3 N), drying (Na_2SO_4), and solvent evaporation led to a red-orange oil (0.85 g) which readily crystallized: mp 92–96 °C. Distillation (Kugelrohr, 180 °C, high vacuum) gave a yellowish oil (0.65 g, 51%), crystallizing as thin prisms: mp 94–97 °C. An analytical sample was prepared by first heating (50–60 °C) under vacuum to drive off a yellow impurity and then recrystallizing the residue from MeOH several times to yield colorless prisms of **7**, mp 95.5–97 °C, indefinitely stable in air: NMR ($CDCl_3$) δ 7.1–8.1 (m); IR ($CHCl_3$) 3070, 3010, 1590, 1474, 1181, 1140, 1125, 1110 cm^{-1}; mass spectrum, *m/e* 216 (M^+, 100), 188 (71), 187 (73), 168 (68), 160 (57), 152 (1.5), 139 (82); high resolution mass spectrum calcd for $C_{12}H_8O_2S$ 216.024, found 216.023.

Anal. Calcd for $C_{12}H_8O_2S$: C, 66.6; H, 3.7; S, 14.8. Found: C, 66.7; H, 3.9; S, 14.7.

Dibenzo-1,2-oxathiin 2,2-Dioxide (8). A mixture of **7** (46 mg, 0.2 mmol), acetic acid (2 mL), and 30% hydrogen peroxide (0.2 mL) was refluxed for 2 h. Cooling and addition of ice caused deposition of small crystals of **8**: 41 mg, 83%; mp 108–110 °C; IR ($CHCl_3$) 1475, 1380, 1180, 870 cm^{-1}; mass spectrum, *m/e* 232 (M^+, 46), 163 (43), 139 (100). Sublimation (90 °C, 0.1 mm) gave an analytical sample: mp 109–111 °C.

Anal. Calcd for $C_{12}H_8O_3S$: C, 62.1; H, 3.5; S, 13.8. Found: C, 62.2; H, 3.5; S, 14.1.

2-Mercapto-2′-hydroxybiphenyl (9). Biphenosultine **7** (200 mg, 0.93 mmol) in anhydrous ether (10 mL) was added dropwise to a slurry of $LiAlH_4$ (100 mg) in ether (10 mL), and this mixture was stirred at 25 °C for 3 h. Aqueous HCl (3 N, 10 mL) was cautiously added, and the ether layer was separated, dried (Na_2SO_4), and evaporated to give crude thiol **9** as a pale yellow oil. Distillation (Kugelrohr, 140 °C, high vacuum) of the crude material gave pure **9** as a colorless oil: 175 mg, 94%; IR ($CHCl_3$) 3542, 3000, 2578, 1582, 1491, 1465, 1330, 1284, 1176 cm^{-1}; NMR ($CDCl_3$) δ 3.0–5.2 (brs, 2 H), 6.90–7.40 (m, 8 H); high-resolution mass spectrum calcd for $C_{12}H_{10}OS$ 202.045, found 202.043.

Anal. Calcd for $C_{12}H_{10}OS$: C, 71.3; H, 5.0; S, 15.8. Found: C, 71.4; H, 5.1; S, 15.7.

Preparation of Unsymmetrical Disulfide Hydrochlorides 1 and 2. The Scm acetate was mixed with methyl *N-tert*-butyloxycarbonyl-L-cysteinate (1 equiv) in methanol/chloroform (1:1) under nitrogen. To this solution was added triethylamine (1 equiv), and the mixture was stirred for 2 h at 25 °C. The solvent was evaporated and the residue was taken up in ethyl acetate, which was then washed with cold citric acid (0.5 M), water, and brine, and dried (Na_2SO_4). After solvent evaporation, the crude oil obtained was purified by preparative layer chromatography on silica (ether). The purified material was then treated with saturated HCl in dioxane at room temperature for 20 min. Freezing and lyophilization gave the hydrochlorides **1** or **2** as white powders.

Compound 1: mp 79–90 °C dec; NMR (DMF-d_7) δ 2.30 (s, 3 H), 3.40 (brd, 2 H), 3.80 (s, 3 H), 4.15 (s, 2 H), 4.40 (m, 1 H), 7.0–7.6 (m, 12 H); IR ($CHCl_3$) 3200–2400, 1746 cm^{-1}.

Compound 2: NMR (DMF-d_7) δ 2.00 (s, 3 H), 3.6 (m, 2 H), 3.7 (s, 3 H), 4.40 (m, 1 H), 7.1–8.2 (m, 10 H); mass spectrum, *m/e* 377 (M^+ − HCl, 0.9), 378 (0.3), 379 (0.2).

Acyl-Transfer Experiments. NMR Method. Hydrochloride **1** or **2** was dissolved in DMF-d_7 and treated with triethylamine (1 equiv) to liberate the free base. The reaction was monitored by NMR spectroscopy (regions δ 1.9–2.5 and 6.8–7.1). Observation was carried out for 5 days at room temperature. Concentrations of amine were typically 0.1 M. At the conclusion of the NMR runs, the solvent was evaporated and the crude mixture was purified by preparative layer chromatography, giving predominantly symmetrical disulfide bearing an intact ester residue. Detection of 5% of amide is possible by this method.

IR Method. Hydrochloride **1** or **2** was deprotonated with aqueous potassium carbonate, and the free amine was extracted and dissolved in acetonitrile, and the solution (0.1 M) was placed in an IR cell. The IR region from ca. 1750 to 1660 cm^{-1} was observed for a period of ca. 5 days.

Acknowledgment. Financial support from the National Institutes of Health (GM 13453-15) is gratefully acknowledged.

Registry No. **1**, 79664-38-3; **1**·HCl, 79664-39-4; **2**, 79664-40-7; **2**·HCl, 79664-41-8; **3**, 79664-42-9; **4**, 79664-43-0; **4** acetate, 79664-44-1; **5a**, 79664-45-2; **5b**, 79664-46-3; **5** (X = Ac, Y = Br), 79664-47-4; **5** (X = H, Y = $SSCO_2Me$), 79664-48-5; **6**, 79664-49-6; **7**, 77123-91-2; **8**, 4371-25-9; **9**, 79664-50-9; *p*-bromotoluene, 106-38-7; 2-(4-methoxyphenyl)cyclohexanone, 37087-68-6; 4-methoxy-4″-methyl-*O*-terphenyl, 79664-51-0; methoxyoxomethanesulfenyl chloride, 26555-40-8; *O*-hydroxybiphenyl, 90-43-7; methyl *N-tert*-butyloxycarbonyl-L-cysteinate, 55757-46-5.

Reaction of a Selenosulfonate with Diazomethane. Unexpected Photochemical Formation of a β-Selenosulfone[1]

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Received September 2, 1981

Insertions of diazo compounds into the Se–Se, Se–CH_2, or Se–X linkage of diselenides,[2] allyl phenyl selenide (with arrangement),[3] or selenenyl halides[3,4] (X = Cl or Br), respectively, have recently been reported. However, similar reactions with other organoselenium compounds have yet to be investigated. In this laboratory, current interest in the chemistry of selenosulfonates[5] (RSO_2SeR) prompted the present study of the reaction of *Se*-phenyl *p*-tolueneselenosulfonate (**1**) with diazomethane.

When a dichloromethane solution of **1** was treated with excess ethereal diazomethane at room temperature in the presence of normal fluorescent laboratory lighting, gradual evolution of nitrogen was observed. The reaction proceeded vigorously when performed near a 100-W incandescent light bulb and the selenosulfonate was consumed within 30 min. Surprisingly, the major product was not one of monoinsertion of methylene into **1** but rather the β-(phenylseleno)ethyl sulfone **2** (Scheme I), isolated in 60% yield. Selenosulfonate **1** also reacted with excess diazomethane at room temperature in the dark, although a longer reaction time was required. Under these conditions, however, none of the previous product **2** was formed. Instead, a mixture of sulfone **3** and sulfinate esters **4** and **5**

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[1] Financial assistance from the Natural Sciences and Engineering Research Council and from the Research Corporation is gratefully acknowledged.

[2] (a) Petragnani, N.; Schill, G. *Chem. Ber.* **1970**, *103*, 2271. (b) Pellicciari, R.; Curini, M.; Ceccherelli, P.; Fringuelli, R. *J. Chem. Soc., Chem. Commun.* **1979**, 440.

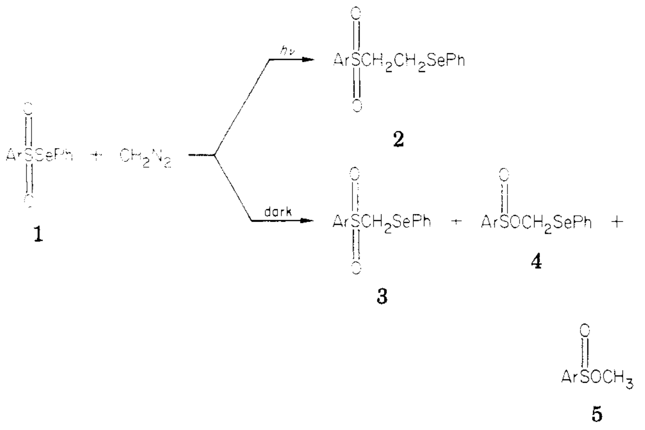
[3] Giddings, P. J.; John, D. I.; Thomas, E. J. *Tetrahedron Lett.* **1980**, 395, 399.

[4] (a) Buckley, D. J.; Kulkowit, S.; McKervey, A. *J. Chem. Soc., Chem. Commun.* **1980**, 506. (b) Petragnani, N.; Rodrigues, R.; Comasseto, J. V. *J. Organomet. Chem.* **1976**, *114*, 281.

[5] (a) Back, T. G.; Collins, S. *Tetrahedron Lett.* **1980**, 2213. (b) *Ibid.* **1980**, 2215. (c) Back, T. G.; Collins, S. *J. Org. Chem.* **1981**, *46*, 3249.

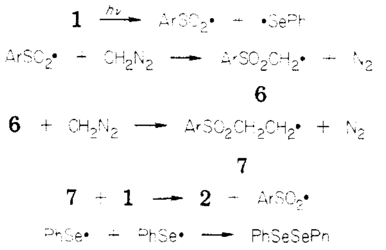
0022-3263/81/1946-5443$01.25/0

Scheme I[a]



[a] Ar = *p*-tolyl.

Scheme II

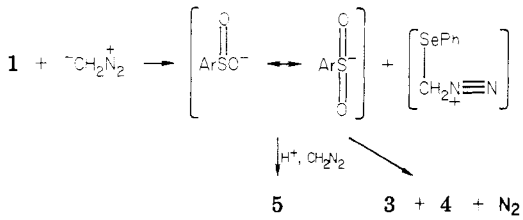


was produced (Scheme I) in respective yields of 21%, 52%, and 27%, along with a small amount of diphenyl diselenide. These compounds were also observed as minor byproducts in the photochemical formation of **2**.

The photochemical transformation does not proceed by a double insertion of methylene into the selenosulfonate via the intermediate α-(phenylseleno) sulfone **3**. This was demonstrated by the failure of an authentic sample of **3** to react with diazomethane under similar conditions. Authentic **3** was prepared in low yield by the sequential treatment of methyl *p*-tolyl sulfone with sodium hydride and benzeneselenenyl chloride.

It is known that selenosulfonates undergo a facile photolytic cleavage of the Se–SO_2 bond, as recently demonstrated by Gancarz and Kice.[6] The stepwise reaction of the sulfonyl radicals thus produced with two molecules of diazomethane (Scheme II) would form α- and β-sulfonyl radicals **6** and **7**, respectively. The latter species have been previously generated by the addition of sulfonyl radicals to olefins and are known[5c,6] to react with **1** to afford β-(phenylseleno) sulfones. Thus, the formation of **7** in the present reaction would be expected to produce **2** in the same manner. It is interesting to note that the mechanism in Scheme II requires the α-sulfonyl radical **6** to react preferentially with diazomethane and its β-sulfonyl counterpart to react preferentially with diazomethane and its β-sulfonyl counterpart to react preferentially with selenosulfonate **1**. This contrasting behavior in **6** and **7** is attributed to their different electrophilic or nucleophilic characters. Thus, intermediate **6**, where the electron-withdrawing sulfonyl group is attached directly to the radical center, is electrophilic in nature and reacts most favorably with nucleophilic species such as diazomethane. On the other hand, the sulfonyl group is remote from the radical center in **7**, and so this species displays more nucleophilic character and reacts preferentially with electrophilic substrates such as selenosulfonate **1**.[7] The possibility that product formation arises from the coupling of **6** with the α-phenylseleno radical **8** (in turn formed from PhSe· and diazomethane) appears less probable as the expected symmetrical coupling products **9** and **10** were not observed.

Scheme III



$\mathrm{PhSeCH_2}\cdot$	$\mathrm{PhSeCH_2CH_2SePh}$	$\mathrm{ArSO_2CH_2CH_2SO_2Ar}$
8	9	10

A plausible mechanism for the dark reaction is depicted in Scheme III. The formation of both sulfone **3** and sulfinate ester **4** supports the intermediacy of the ambident sulfinate anion, in turn formed by displacement from **1** by diazomethane. Furthermore, the reaction of the sulfinate anion, probably in the form of its conjugate acid, with diazomethane accounts for the remaining product **5**.[8]

These experiments thus indicate that the reaction of selenosulfonate **1** with diazomethane may follow either a dark, ionic pathway leading mainly to monoinsertion products or a photochemical route resulting in the unusual formation of β-(phenylseleno) sulfone **2**.

Experimental Section

Melting points were determined on an A. H. Thomas hot-stage apparatus. IR and ^1H NMR spectra were obtained on Perkin-Elmer 467 and Hitachi Perkin-Elmer R24B instruments, respectively. All NMR spectra were taken at 60 MHz in $CDCl_3$ solution and are reported in parts per million downfield from tetramethylsilane as internal standard. Mass spectra were obtained on a Varian MAT CH5 spectrometer. GC–mass spectra and elemental analyses were kindly provided by Dr. R. Yamdagni and Mr. L. Malek. Preparative TLC was performed on Analtech 20 × 20 cm glass plates coated with 1 mm of silica gel GF. Selenosulfonate **1** was prepared according to a method reported previously.[5a] All other reagents were either purchased from commercial sources or prepared by standard procedures.

Photochemical Reaction of Selenosulfonate 1 with Diazomethane. Selenosulfonate **1** (205 mg, 0.66 mmol) was dissolved in 1 mL of dichloromethane in a water-cooled Pyrex reaction vessel. Ethereal diazomethane was added in portions while the solution was irradiated with a 100-W incandescent lamp. Vigorous gas evolution was observed. After 30 min, a white precipitate had formed and TLC indicated no remaining selenosulfonate. The precipitate was filtered and a second crop was obtained by concentration of the filtrate, affording a total of 135 mg (60%) of 1-(phenylseleno)-2-(*p*-toluenesulfonyl)ethane (**2**): mp 132–133 °C; IR (Nujol) 1303, 1143 cm^{-1}; NMR δ 7.70 (d, $J = 9$ Hz, 2 H), 7.5–7.1 (complex, 7 H), 3.6–2.8 (m, 4 H), 2.43 (s, 3 H); mass spectrum, *m/e* 340 (M^+, ^{80}Se), 338 (M^+, ^{78}Se). Anal. Calcd for $C_{15}H_{16}O_2SSe$: C, 53.09; H, 4.75; S, 9.45. Found: C, 53.14; H, 4.71; S, 9.87. The mother liquor was evaporated in vacuo to afford a mixture containing mostly products **3**, **4**, and **5** (NMR), as well as diphenyl diselenide (TLC).

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(6) Gancarz, R. A.; Kice, J. L. *Tetrahedron Lett.*, **1980**, 4155.

(7) From a frontier orbital description, **6** has a low-energy SOMO and interacts favorably with species having a high-energy HOMO (e.g., diazomethane), while **7** has a high-energy SOMO and so interacts well with molecules possessing a low-energy LUMO (e.g., **1**). For an excellent discussion of the reactivity of electrophilic and nucleophilic radicals, see: Fleming, I. in "Frontier Orbitals and Organic Chemical Reactions", Wiley: New York, 1976; Chapter 5, pp 182–186.

(8) The formation of methyl esters from sulfinic acids and diazomethane has been reported: Meek, J. S.; Fowler, J. S. *J. Org. Chem.* **1968**, *33*, 3422.

When the irradiation was repeated in chloroform instead of dichloromethane, the reaction gave similar results to those reported above.

Dark Reaction of Selenosulfonate 1 with Diazomethane. Selenosulfonate **1** (156 mg, 0.50 mmol) was dissolved in 2 mL of dichloromethane and excess ethereal diazomethane was added. The reaction mixture was allowed to stand for 17 h at room temperature in an apparatus completely wrapped in aluminum foil to exclude light. After removal of volatile material in vacuo, NMR analysis of the resulting oil indicated the presence of three components with signals at δ 5.52 (d, J = 10 Hz) and 5.18 (d, J = 10 Hz), δ 4.24 (s) and 3.44 (s), attributed to **4** (CH_2), **3** (CH_2), and **5** (OCH_3), respectively, as well as the expected aromatic and aryl methyl resonances. The integrated intensities of these signals provided yields of 21%, 52%, and 27% for **3**, **4** and **5**, respectively. A 110-mg portion of this mixture was separated by preparative TLC in 25% ethyl acetate–hexane to afford, in increasing order of R_f, 26 mg of the α-(phenylseleno) sulfone **3**, identical (TLC, IR, NMR) with an authentic sample (vide infra), 60 mg of a mixture of sulfinate esters **4** and **5**, and 15 mg of diphenyl diselenide, identical (TLC, IR, NMR) with an authentic sample. The mixture of **4** and **5** could not be further separated. The presence of **5** was confirmed by comparing the mixture with an authentic sample (IR, NMR, GC–mass spectra); that of **4** was inferred from the NMR spectrum.[9] Finally, the mixture of **4** and **5** gave a mass spectrum showing m/e 326 and 324 at probe temperatures over 100 °C (M^+ of **4**, ^{80}Se and ^{78}Se, respectively) and m/e 170 (M^+ of **5**) at room temperature.

(Phenylseleno)methyl *p*-Tolyl Sulfone (3). Methyl *p*-tolyl sulfone (170 mg, 1.00 mmol) and sodium hydride (30 mg, 1.25 mmol) were refluxed 1 h in 5 mL of toluene under nitrogen. The mixture was then added to a solution of benzeneselenenyl chloride (239 mg, 1.25 mmol) in 5 mL of toluene. After being stirred for 30 min at room temperature, the solution was washed with water (2×), dried over anhydrous $MgSO_4$, and evaporated to dryness under vacuum. The residue was separated by preparative TLC in 25% ethyl acetate–hexane to afford 91 mg (28%) of the title compound: mp 79–81 °C; IR (film of melted product) 1317, 1303, 1145 cm^{-1}; NMR δ 7.70 (d, J = 9 Hz, 2 H), 7.5–7.0 (complex, 7 H), 4.24 (s, 2 H), 2.40 (s, 3 H); mass spectrum, m/e 326 (M^+, ^{80}Se), 324 (M^+, ^{78}Se). Anal. Calcd for $C_{14}H_{14}O_2SSe$: C, 51.69; H, 4.34; S, 9.86. Found: C, 51.79; H, 4.33; S, 10.14.

Attempted Reaction of Sulfone 3 with Diazomethane. Sulfone **3**, prepared in the preceding procedure, was dissolved in 1 mL of dichloromethane. Excess ethereal diazomethane was added and the solution was irradiated as in the case of selenosulfonate **1**. After 1 h, volatile material was removed in vacuo and the remaining residue consisted of unchanged **3** (melting point, NMR).

Registry No. **1**, 68819-94-3; **2**, 79665-09-1; **3**, 79665-10-4; **4**, 79665-11-5; **5**, 672-78-6; methyl *p*-tolyl sulfone, 3185-99-7; benzeneselenyl chloride, 5707-04-0.

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(9) The AB quartet observed for the diastereotopic methylene protons in **4** closely resembles those in similar sulfinate esters such as benzyl *p*-toluenesulfinate: Wilt, J. W.; Wagner, W. J. *Chem. Ind.* (*London*) **1964**, 1389.

Synthesis of Adamantane Derivatives. 56. Reaction of 1-Adamantyl Chloride with Trimethylsilyl Pseudohalide

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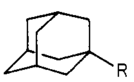
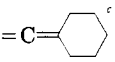
It is well documented that α- and β-unsaturated organosilanes are useful synthons as mild and stable nucleophiles, acting formally as the corresponding organometallics.[1] Their selective reactivity originating from the less electropositive nature of silicon sometimes gives advantages over other metals under the right conditions. Substitution at the adamantane bridgehead is a typical example. While nucleophilic attack of alkali organometallics at the bridgehead is severely restricted due to the intrinsic structure of adamantane, displacement under electrophilic conditions is easily realized with unsaturated organosilanes; we have reported that allylsilane and its analogues are reactive with 1-adamantyl chloride (**1**, Chart I) in the presence of Lewis acids.[2] In continuation of synthetic studies of adamantane derivatives we attempted the titanium tetrachloride catalyzed reactions of **1** with reagents represented as $Me_3SiX{\equiv}Y$ and $-X{=}Y{=}Z$ (X, Y, Z = C, N, O, or S). The reactions of these reagents with a typical tertiary alkyl halide are not precedented, although those with carbonyl functions are reported frequently. In fact, it was found that trimethylsilyl pseudohalide reacted smoothly. Notably, ambident cyanide **2** and isothiocyanate **6** showed nucleophilic behavior at the nitrogen and sulfur ends, respectively.

Chart I



1, R = Cl
3, R = NC
4, R = NHCHO
7, R = SCN
8, R = NCS
9, R = Br
12, R = NCO
13, R = NHCONH-*t*-Bu
14, R = N(Me)CN
16, R = N_3

Me_3SiR

2, R = CN
5, R = CH=C=CH_2 [a]
6, R = NCS
10, R = NCO
11, R = N=C=NMe [b]
15, R = N_3
17, R = N=C=  [c]
18, R = CHN_2 [d]

[a] G. Merault, P. Bourgeois, and J. Dunogues, *C. R. Hebd. Seances Acad. Sci., Ser. C*, 274, 1857 (1972). The reagent obtained by this procedure is contaminated with a small amount of propargylsilane. See ref 4 for the preparation of pure 5. [b] I. Ruppert, *Tetrahedron Lett.*, 1987 (1977). [c] *tert*-Butyldimethylsilyl group was used in this case: D. S. Watt, *Synth. Commun.*, 4, 127 (1974). [d] D. Seyferth, A. W. Dow, H. Menzel, and T. C. Flood, *J. Am. Chem. Soc.*, 90, 1080 (1968).

As for the reaction with $Me_3X{\equiv}Y$, we already have reported the system where X and Y are carbons.[2] Another possible combination is the case of trimethylsilyl cyanide (**2**). Treatment of **2** with an equal amount of titanium tetrachloride and **1** in methylene chloride at 0 °C for 150 min gave the isonitrile **3** in 78% yield after liberation from the complex with pyridine. Decomposition with water resulted in the formation of the formamide **4** (61%) together with **3** (12%). An interesting feature is that the adamantyl cation attacked **2** at nitrogen to give the product **3** directly, whereas the reaction of a heteroatom-stabilized carbonium ion with **2** is reported to lead to the formation of nitrile derivatives.[3]

The reactions of (trimethylsilyl)cumulens toward **1** were next studied. Attempted reaction of **5**, a prototype of

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(1) (a) T. H. Chan and I. Fleming, *Synthesis*, 761 (1979). (b) I. Fleming in "Comprehensive Organic Chemistry", Vol. 3, D. N. Jone, Ed., Pergamon Press, Oxford, 1979, Part 13.

(2) T. Sasaki, A. Usuki, and M. Ohno, *J. Org. Chem.*, **45**, 3559 (1980).

(3) V. Asher, C. Becu, M. J. O. Antenius, and R. Callens, *Tetrahedron Lett.*, **22**, 141 (1981). We have also observed that the $AlCl_3$-catalyzed reaction of **16** with **2** was mediated by azahomoadamantyl cation, affording 3-cyano-4-azahomoadamantane: T. Sasaki, S. Eguchi, and T. Okano, *J. Org. Chem.*, in press. See also the case of oxirane: W. Lidy and W. Sundermeyer, *Tetrahedron Lett.*, 1449 (1973).

0022-3263/81/1946-5445$01.25/0