($CDCl_3$) 3.83 (s, 3 H, OCH_3), 3.60 (s, 2 H, CH_2), 2.33 (s, 3 H, SCH_3); IR 2950 (CH), 1740 (C=O), 1682 (C=O), 1483, 1310, 1260. Also prepared by this method were the following. Methyl [(phenylthio)carbonyl]acetate (**6b**): 84% yield; bp 108–110 °C (0.1 mm); NMR ($CDCl_3$) 7.38 (s, 5 H, Ar), 3.70 (s, 3 H, OCH_3), 3.61 (s, 2 H, CH_2); IR (neat) 1740, 1580, 1479, 1010, 715. Methyl [(allylthio)carbonyl]acetate (**6c**): 40% yield; bp 66–67 °C (0.025 mm); NMR ($CDCl_3$) 4.02–4.98 (m, 3 H, vinyl), 3.70 (s, 3 H, OCH_3), 3.60 (s, 2 H, CH_2), 3.55 (d, 2 H, allyl); IR (neat) 1747 (C=O), 1690 (C=O), 1635 (C=C), 1430, 1320. Methyl [(*tert*-butylthio)carbonyl]acetate (**6d**): ~50% yield; bp 55–57 °C (0.25 mm); NMR ($CDCl_3$) 3.69 (s, 3 H, OCH_3), 3.45 (s, 2 H, CH_2), 1.48 (s, 9 H, *tert*-butyl).

General Diazofunctionalization Procedure. Synthesis of Methyl α-Diazo-α-[(methylthio)carbonyl]acetate (7a). The general procedure of Julia et al. was used.[8] To a solution of methyl [(methylthio)carbonyl]acetate (**6a**; 10 g, 0.07 mol) and tosyl azide (13.2 g, 0.07 mol) in 250 mL of anhydrous ether was added dropwise at 0 °C triethylamine (6.8 g, 0.07 mol). The reaction was stirred overnight and worked up by cooling to 0 °C and adding 100 mL of pentane. The precipitate was filtered and the process repeated to recover tosylamide, 17.1 g (91%). The filtrate was concentrated in vacuo to yield a crude yellow crystalline product which was recrystallized from cyclohexane to yield **7a**: 9.4 g (77%); mp 53–55 °C; NMR ($CDCl_3$) 3.83 (s, 3 H, OCH_3), 2.35 (s, 3 H, SCH_3); IR ($CHCl_3$) 2900, 2140 (diazo), 1710 (br, C=O), 1620 (C=N), 1450, 1330, 1130, 955. Anal. Calcd for $C_5H_6N_2O_3S$: C, 34.47; H, 3.47; N, 16.08; S, 18.40. Found: C, 34.41; H, 3.49; N, 16.07; S, 18.33. The following compounds were similarly prepared. **7b**: 70% yield; mp 94–95.5 °C (from cyclohexane); NMR ($CDCl_3$) 7.40 (s, 5 H, Ar), 3.82 (s, 3 H, OCH_3); IR (C_6H_6) 2950 (CH, weak), 2145 (diazo), 1720 (C=O), 1625 (C=N), 1439, 1320 (d), 1120, 740. Anal. Calcd for $C_{10}H_8N_2O_3S$: C, 50.84; H, 3.41; N, 11.85; S, 13.57. Found: C, 50.91; H, 3.51; N, 11.84; S, 13.56. **7c**: 63% yield; bp 79–81 °C (0.005 mm); NMR ($CDCl_3$) 6.20–4.90 (m, vinyl), 3.80 (s, 3 H, OCH_3), 3.58 (d, 2 H, allyl); IR (neat) 2149 (diazo), 1725 (2 C=O), 1625, 1435, 1325, 1130, 900. Anal. Calcd for $C_7H_8N_2O_3S$: C, 41.99; H, 4.02; N, 13.99; S, 16.01. Found: C, 41.90; H, 4.02; N, 13.68; S, 15.99. **7d**: 96% yield; NMR ($CDCl_3$) 3.78 (s, 3 H, OCH_3), 2.50 (s, 9 H, *tert*-butyl); IR (neat) 2960, 2125, (diazo), 1718 (C=O), 1610 (C=N), 1440, 1320, 960.

General Photolysis Procedure. Photolysis of Methyl α-Diazo-α-[(allylthio)carbonyl]acetate (7c). In a typical experiment **7c** (2.0 g, 0.01 mol) was taken up in 800 mL of benzene which had been previously shaken with water. The reaction mixture was irradiated and the course of the reaction followed by the disappearance of the diazo band at 2140 cm^{-1} in the IR. At this concentration the reaction was complete after about 3 h. The benzene was removed under reduced pressure to afford a yellow residue. This residue was taken up in benzene, dried over anhydrous $MgSO_4$, and concentrated again to yield α-(methoxycarbonyl)-α-allylthioacetic acid (**11c**): 1.3 g (~70%); NMR ($CDCl_3$) 10.00 (s, 1 H, COOH), 5.90–4.75 (m, 3 H, vinyl), 4.18 (s, 1 H, CH), 3.58 (s, 3 H, CH_3), 3.18 (d, 2 H, allyl); IR (neat) 3300–3100 (br, COOH), 1745 (C=O), 1627 (C=C), 1427, 1399, 1149, 1002, 917. The following compounds were similarly isolated. **11a**: >90% yield; NMR ($CDCl_3$) 10.00 (s, 1 H, COOH), 4.23 (s, 1 H, CH), 3.77 (s, 3 H, OCH_3), 2.28 (s, 3 H, SCH_3); IR 3400–3300 (br, COOH), 1740 (C=O). **11b**: 85% yield; IR (benzene) 3300–2800 (COOH), 1745–1710 (C=O), 1420, 1270, 1140. **11d** was not isolated. Distillation of the reaction residues resulted in the following observed overall products. **12a**: bp 57–60 °C (14 mm);[9a] NMR ($CDCl_3$) 3.70 (s, 3 H, OCH_3), 3.18 (s, 2 H, CH_2), 2.20 (s, 3 H, SCH_3); IR (neat) 2950 (CH), 1430, 1270, 1130, 1010. **12b**: bp 77–82 °C (0.01 mm);[9b] NMR 7.50–6.90 (m, 5 H, Ar), 3.64 (s, 3 H, OCH_3), 3.62 (s, 2 H, CH_2); IR 2940, 1740 (C=O), 1590, 1440, 745. **12c**: bp 42–43 °C (0.10 mm); NMR ($CDCl_3$) 6.15–4.80 (m, 3 H, vinyl), 3.68 (s, 3 H, OCH_3), 3.20 (d, 2 H, allyl), 3.18 (s, 2 H, CH_2); IR (neat) 2950, 1740 (C=O), 1630 (C=C), 1427, 1275, 1150, 1005, 915. **12d**: bp 30–35 °C (0.1 mm);[9c] NMR ($CDCl_3$) 3.69 (s, 3 H, OCH_3), 3.27 (s, 2 H, CH_2), 1.32 (s, 9 H, *t*-Bu); IR 2960, 1740, 1460, 1435, 1360.

General Procedure. Synthesis of Alternate Possible Photoproduct *S*-Methyl Methoxythioacetate (17a). To a stirred solution of 10.8 g (0.10 mol) of methoxyacetyl chloride and 4.8 g (0.10 mol) of methyl mercaptan in 200 mL of anhydrous ether, under a nitrogen atmosphere, was added dropwise, at 0 °C, 7.5 g (0.10 mol) of pyridine. The reaction mixture was allowed to warm to room temperature and was stirred an additional 2.5 h. The reaction mixture was filtered, and the filtrate was washed with 3% HCl solution (once), 5% $NaHCO_3$ solution (twice), and saturated salt solution (three times). The ether layer was dried (Na_2SO_4) and the ether removed under reduced pressure. The residue was distilled to yield 11.4 g (94%) of *S*-methyl methoxythioacetate (**17a**): bp 27–30 °C (0.05 mm); IR (neat) 2925 (CH), 1685 (C=O), 1440, 1420, 1190, 1125, 1080, 875; NMR ($CDCl_3$) 4.10 (s, 2 H, CH_2), 3.47 (s, 3 H, OCH_3), 2.28 (s, 3 H, SCH_3). *S*-Phenyl methoxythioacetate (**17b**): 90%; bp 86–89 °C (0.20 mm); IR (neat) 2905, 1695 (C=O), 1480, 1440, 1200, 1130, 1070, 910; NMR ($CDCl_3$) 7.33 (s, 5 H, Ar), 4.10 (s, 2 H, CH_2), 3.45 (s, 3 H, OCH_3).

(Carbomethoxy)(methylthio)ketene (10, R = CH_3). A solution of **7a** (174 mg) in 2 mL of anhydrous CH_2Cl_2 or $CDCl_3$ (P_2O_5) was placed in an NMR tube and degassed with argon via a long syringe needle. The tube was outfitted with a septum and a gas release valve and attached to the outside of a standard immersion reactor containing acetone (1-cm path length) and a Pyrex filter sleeve. The unit was submerged in a cooling bath maintained at −5 °C. The course of the irradiation was followed for 5 h by N_2 release and by monitoring the disappearance of the IR band at 1620 cm^{-1} (C=N component of the diazo function). The resulting clear, colorless solution was then subjected to instrumental analysis: IR (CH_2Cl_2) 2950, 2120 (C≡O$^+$), 1720 (C=O), 1580, 1430, 1230; NMR ($CDCl_3$) 3.72 (s, OCH_3), 2.25 (s, SCH_3).

Benzalaniline (**13**, 181 mg) in 1.5 mL of anhydrous solvent was added with agitation to the above solution. The tube was allowed to stand overnight at room temperature. The NMR revealed a spectrum identical with that of β-lactam **14**: IR ($CDCl_3$) 1745 (β-lactam C=O), 1710 (C=O), 1380, 1255; NMR ($CDCl_3$) 7.30–7.00 (m, 10 H, Ar), 5.01 (s, 1 H, β-lactam H), 3.25 (s, 3 H, OCH_3), 2.25 (s, 3 H, SCH_3).

Alternatively, addition of CH_3OH to the photolyzed solution caused the IR band at 2120 cm^{-1} to disappear instantly.

Registry No. 5, 37517-81-0; **6a**, 66301-57-3; **6b**, 72867-13-1; **6c**, 72867-14-2; **6d**, 72867-15-3; **7a**, 66301-56-2; **7b**, 72867-16-4; **7c**, 72867-17-5; **7d**, 72867-18-6; **10** (R = CH_3), 72867-19-7; **11a**, 72867-20-0; **11b**, 72867-21-1; **11c**, 72867-22-2; **12a**, 16630-66-3; **12b**, 17277-58-6; **12c**, 72867-23-3; **12d**, 49827-06-7; **13**, 538-51-2; **14**, 66301-58-4; **17a**, 17640-24-3; **17b**, 72867-24-4; methyl mercaptan, 74-93-1; phenyl mercaptan, 108-98-5; 2-propenyl mercaptan, 870-23-5; *tert*-butyl mercaptan, 16812-19-4.

(9) (a) Reported boiling point of 45–46 °C (11 mm): R. Näf-Müller and B. Willhalm, *Helv. Chim. Acta*, **54**, 1880 (1971). (b) Reported boiling point of 87–90 °C (0.3 mm): R. H. Hiskey and F. I. Carrol, *J. Am. Chem. Soc.*, **83**, 4647 (1961). (c) The compound was mentioned without physical properties. S. Kamata, S. Uylo, N. Haga, and W. Nagata, *Synth. Commun.*, **3**, 265 (1973).

Reactions of Arenesulfenyl Chlorides with Indole. ^{13}C and ^1H Nuclear Magnetic Resonance Spectra of 3-(Arylthio)indoles[1]

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Indole is an ambident nucleophile and is known to react with electrophiles both at nitrogen and at C-3.[2] The position of attack depends on the electrophile used as well as the state of the indole, i.e., whether it reacts as the

(1) (a) This work was supported by the National Science Foundation. (b) Abstracted from the thesis submitted by L.-J.C. in partial fulfillment for the requirements of the M.S. degree, Wayne State University, 1979.

(2) Sundberg, R. S. "The Chemistry of Indoles"; Academic Press: New York, 1970.

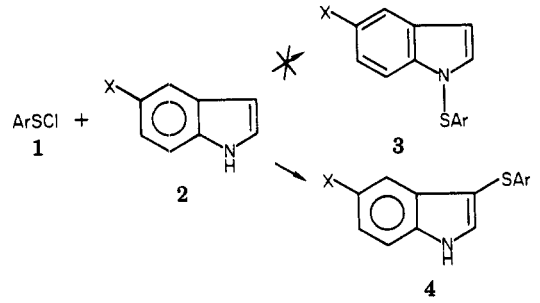
0022-3263/80/1945-1688$01.00/0

Table I

entry	compd[a]	mp, °C	lit. mp, °C	yield, %	IR, cm^{-1}	^1H NMR,[b] δ units	^{13}C NMR,[c] δ units	ref
1	4ag	171-172.5	169-170	59	3360	10.9	100.4	5
			173.5					6a
2	4bg	132-133.5	137-138	55	3350	10.9	99.6	6a
3	4cg	122-123	127.5-128	16	3380	11.0	99.0	6a
4	4ah	237.5-238.5	245-246	65	3380	*d*	103.7	6b
5	4ch	236-237	240-242	70	3360	*d*	102.5	6b
6	4dh	243-244	246-248	55	3370	*d*	102.0	6b
7	4dg	173.5-174.5	177-178	79	3320	11.2	99.8	5
			175-175.5					7

[a] In ref 6a and 6b the corresponding sulfenamide structures 3 were assigned. In ref 5 and 7 the diaryl sulfide structures 4 were assigned. [b] Chemical shift of the N-H resonance. [c] Chemical shift of the indole C-3 resonance. [d] The broad N-H resonance could not be observed at the low concentration (1%) at which the spectrum was measured.

neutral species or is metalated. Alkylations with alkyl halides generally favor attack at carbon, while preferential acylation at nitrogen is the rule. Thus, the reaction of indoles (2) with arenesulfenyl halides (1) could conceivably



a, Ar = 2-$(NO_2)C_6H_4$ g, X = H
b, Ar = 3-$(NO_2)C_6H_4$ h, X = NO_2
c, Ar = 4-$(NO_2)C_6H_4$
d, Ar = 2,4-$(NO_2)_2C_6H_4$

give rise to either sulfenamides (3) or isomeric 3-(arylthio)indoles (4).

The literature on this subject was ambiguous when our work in this area was initiated. Jardin and Brown[3] suggested that 3-(ethylthio)indole was present in the mixture of products from the reaction of indolylmagnesium bromide and ethanesulfenyl chloride, although it could not be isolated. Wieland and co-workers[4] also observed reaction at carbon in the reaction of 3-phenylindole with methanesulfenyl chloride which gave rise to 2-(methylthio)-3-phenylindole.

Fontana et al. reported formation of diaryl sulfides **4ag** and **4dg** from reaction of the corresponding sulfenyl chlorides with indole in ethyl ether or chloroform.[5]

On the other hand, Tulecki and Szulc in two recent papers[6] indicated that the reaction of a series of nitrobenzenesulfenyl chlorides (**1a–c**) with indole **2g** in refluxing benzene (or **1a,c,d** with 5-nitroindole **2h**) afforded the sulfenamides **3**. Because of our interest in determining the barriers to torsion about the N-S bond in sulfenylindoles, we have carried out the reactions previously reported[6] and now report that the products obtained are the isomeric sulfides **4**.

Reaction of indoles **2** with the appropriate sulfenyl chlorides in refluxing benzene and recrystallization of the resulting products from aqueous ethanol (or glacial acetic acid for **4ch**) afforded crystalline products in moderate yield whose melting points accorded fairly well with, but were slightly lower than, those reported previously (Table I, entries 1–6). We also carried out the reaction of indole with 2,4-dinitrobenzenesulfenyl chloride (Table I, entry 7). All these compounds exhibited infrared absorptions attributable to N–H stretching vibration, although in most cases they were broad and often of low intensity.

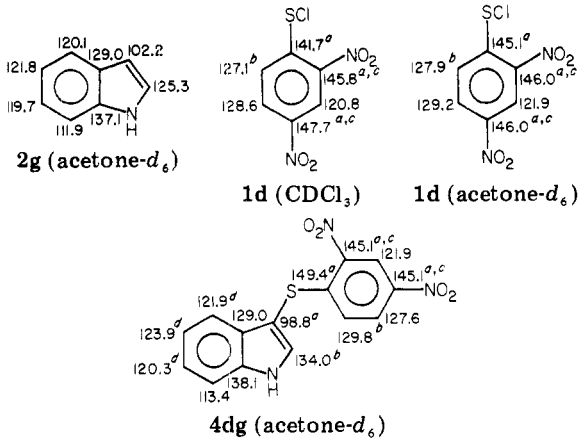
The definitive assignment of the structures of these compounds as diaryl sulfides **4**, rather than sulfenamides **3**, could be made on the basis of their ^1H and ^{13}C NMR spectra. Compound **4dg**, which was not prepared by the Polish workers, but which had been previously prepared from indole-3-thiol and 2,4-dinitrochlorobenzene[7] (Table I, entry 7), serves as an example.

The ^1H NMR spectrum of indole features a characteristic resonance for H-3 at δ 6.5 which lies well upfield of the other resonances which appear as a complex absorption centered at δ 7.32.[8-10] The strong upfield shift observed is in accord with the postulation of significant π density at C-3 as suggested by the typical canonical structures associated with the vinyl amine portion of the indole system (RNH—CH=CHR ↔ RNH^+=$CHCH^-$—R). The resonance of the proton on nitrogen is also isolated and appears well downfield from the aromatic protons as a broad singlet at ca. δ 10.1. The spectrum of **4dg** prepared by reaction of indole with 2,4-dinitrobenzenesulfenyl chloride (Table I, entry 7) lacks the upfield resonance characteristic of H-3 and features a broad resonance at δ 11.2 which can be ascribed to an N–H proton. This resonance is shifted downfield relative to that in indole itself, seemingly as the result of substitution at C-3. The spectra of the other indole derivatives listed in Table I also lacked upfield resonances in the region expected for H-3. The spectra of the derivatives of indole **4ag**, **4bg**, and **4cg** also exhibited resonances characteristic of N–H protons with chemical shifts intermediate between that of indole and that of **4dg** (Table I). Because of solubility problems, the spectra of the 5-nitroindole derivatives **4ah**, **4ch**, and **4dh** were measured at much lower concentrations at which the broad N–H resonance could not be observed.

The ^{13}C NMR spectra also provide evidence for the assignment of the diaryl sulfide structure. The chemical shift assignments for **4dg** were made using the assignments in indole and 2,4-dinitrobenzenesulfenyl chloride as guides (Scheme I). The assignments given for indole were made by Parker and Roberts[11] using off resonance decoupling

(3) Jardin, R. V.; Brown, R. K. *Can. J. Chem.* **1965**, *43*, 1298.
(4) Wieland, T.; Weiberg, O.; Fischer, E.; Hörlein, G. *Justus Liebigs Ann. Chem.* **1954**, *587*, 146.
(5) Fontana, A.; Marchiori, F.; Rocchi, R.; Pajetta, P. *Gazz. Chim. Ital.* **1966**, *96*, 1301.
(6) (a) Tulecki, J.; Szulc, C. *Ann. Pharm. (Poznan)* **1969**, *7*, 3. (b) Tulecki, J.; Szulc, C. *Ibid.* **1973**, *10*, 3.
(7) Grant, M. S.; Snyder, H. R. *J. Am. Chem. Soc.* **1960**, *82*, 2742.
(8) Cohen, L. A.; Duly, J. W.; Kny, H.; Witkop, B. *J. Am. Chem. Soc.* **1960**, *82*, 2184.
(9) Reinecke, M. G.; Johnson, H. W., Jr.; Sebastian, J. F. *Tetrahedron Lett.* **1963**, 1183.
(10) Reinecke, M. G.; Johnson, H. W., Jr.; Sebastian, J. F. *J. Am. Chem. Soc.* **1969**, *91*, 3817.
(11) Parker, R. G.; Roberts, J. D. *J. Org. Chem.* **1970**, *35*, 996.

Scheme I



2g (acetone-d_6) 1d ($CDCl_3$) 1d (acetone-d_6)

4dg (acetone-d_6)

[a] Nondecoupled spectrum indicated no $^1J_{CH}$ (quaternary carbon). [b] Nondecoupled spectrum indicated no $^3J_{CCCH}$. [c] Signal of doubled intensity. [d] The assignments of C-4, C-5, and C-6 in the indole ring are uncertain.

and comparisons with spectra of substituted compounds. As indicated in Scheme I, the C-3 carbon atom exhibits an upfield shift paralleling that of the attached hydrogen in the ^{1}H NMR spectrum. The adjacent atom C-2 is shifted to low field. The C-2 and C-3 resonances represent the highest and lowest field resonances of the protonated carbon atoms in indole. The assignments of the resonances in 2,4-dinitrobenzenesulfenyl chloride were made by assuming additivity in substituent effects, the known[12] substituent parameters for nitro (*i*, +20; *o*, −4.8; *m*, +0.9, *p*, 5.8), and substituent parameters for SCl (*i*, +10.8; *o*, −2.0; *m*, +0.7; *p*, −0.8), derived from spectra of nitrobenzenesulfenyl chlorides **1b**, **1c**, and **1d** (in deuteriochloroform). The resonances in acetone-d_6 are fairly similar to those measured in deuteriochloroform except for C-1. Identification of quaternary carbon atoms was accomplished by measuring nondecoupled spectra in which they appeared as singlets. Two carbon atoms in **4dg**, viz., C-2 in the indole ring and C-6 in the nitrobenzene ring, were distinguished in the nondecoupled spectra since they appeared as doublets (due to coupling with the attached protons) but did not exhibit coupling to a meta proton (^3J) which was observed in other resonances.

In comparing the chemical shifts of **4dg** to those in the starting materials **1d** and **2g**, we note that the resonance at highest field is that corresponding to C-3 in the indole ring which is shifted upfield relative to that in the parent indole. This is true for all of the derivatives 4. The presence of a substituent at C-3 was substantiated by the appearance of this resonance as a singlet in the nondecoupled spectrum. This was similarily true for the ^{13}C spectra of the other compounds 4. The highest field resonances, assigned to C-3 in the indole system, appeared as singlets in the nondecoupled spectra (Table I).

Metalation of indole can change the relative reactivity at nitrogen and C-3. The indolyl anion should exhibit enhanced reactivity at nitrogen. While magnesium might be expected to be highly associated, and hence less reactive at nitrogen, the sodium salt should be less coordinated especially in polar solvents. In an effort to increase the propensity for reaction at nitrogen, we carried out reactions of **1d** with indole under several sets of reaction conditions with various bases before addition of the sulfenyl chloride: (a) triethylamine (solvent benzene), (b) formation of the sodium salt by treatment with sodium hydride [solvent tetrahydrofuran (THF)], (c) formation of the lithium salt by treatment with *n*-butyllithium (solvent ether–THF), and (d) formation of the silver salt by precipitation following addition of sodium hydroxide and silver nitrate (solvent benzene). However, all four sets of reaction conditions led to formation of the same product, sulfide **4dg**. These types of reaction conditions, especially the reaction of the sodium salt in THF conditions, are more favorable for reaction at nitrogen than those used by the Polish,[6] Canadian,[3] or Italian[5] workers and comparable conditions do lead to N-substitution in alkylation reactions. Either reaction at carbon is very favorable in reactions with sulfenyl chlorides, or the sulfenamide **3** is unstable under the reaction conditions and is converted into the diaryl sulfide **4**.

Experimental Section

The ^{1}H NMR spectra were measured on a Varian T-60A spectrometer. The ^{13}C NMR spectra were measured at 15.04 MHz on a JNM-FX 60 spectrometer on 10% w/v solutions where solubility permitted (i.e., for all compounds except **4ah**, **4ch**, and **4dh** for which 1% w/v solutions were used). Chemical shifts, expressed in δ units relative to internal Me_4Si, were obtained from noise-decoupled spectra. Except as indicated, noise decoupling of protons was carried out and 8192 data points were collected over a spectral width of 4 kHz. Infrared spectra were measured on a Perkin-Elmer 267 grating spectrophotometer. Melting points were determined on a Thomas-Hoover apparatus and are uncorrected.

Indole, 5-nitroindole, 2-nitrobenzenesulfenyl chloride, and 2,4-dinitrobenzenesulfenyl chloride were obtained commercially. The 3-nitro- and 4-nitrobenzenesulfenyl chlorides, **1b** and **1c**, were prepared by treatment of the nitrothiophenols with chlorine:[12] **1b**, bp 120 °C (1.0 mm) [lit.[13] bp 140 °C (5 mm)]; **1c**, mp 50–52 °C [lit.[12] mp 52 °C].

3-[(2,4-Dinitrophenyl)thio]indole (4dg). Reaction 1: No Base.[6] A solution of 2,4-dinitrobenzenesulfenyl chloride (2.34 g, 10 mmol) in 50 mL of dry benzene was added dropwise to 1.17 g (10 mmol) of indole in 50 mL of dry benzene. After addition the reaction mixture was heated at reflux for 3 h. The solution was concentrated to one-fourth of the initial volume and allowed to stand at 5 °C for 24 h. The crystals which formed were collected and purified by recrystallization from ethanol; yield 79%.

Reaction 2: Triethylamine as Base. A solution of the sulfenyl chloride (10 mmol) in 20 mL of dry benzene was added dropwise to a solution of 10 mmol of indole and 10 mmol of triethylamine in 50 mL of benzene. After reaction for 5 h at room temperature, the reaction mixture was filtered to remove the amine hydrochloride and the organic solvent was removed in vacuo. The pure product was obtained by chromatography on silica gel (hexane–ethyl acetate, 9:1) and recrystallization from tetrahydrofuran–ethanol; yield 55%.

Reaction 3: Sodium Hydroxide/Silver Nitrate as Base.[14] Aqueous sodium hydroxide (10 mL, 1 N) was added to an ice-cold solution of indole (10 mmol) in 20 mL of methanol and allowed to stir for 2 h. Aqueous alcoholic silver nitrate (10 mmol in 3 mL of water and 10 mL of methanol) was added dropwise to the solution and allowed to stir for 30 min. The precipitated silver salt was removed by filtration and dried in vacuo ($CaCl_2$).

A solution of the sulfenyl chloride (3.5 mmol) in 10 mL of benzene was added to a suspension of 4 mmol of the silver salt in 30 mL of benzene and allowed to stir at room temperature for 48 h. The precipitate was removed by filtration and the solvent removed in vacuo. The product was obtained by chromatography (hexane–ethyl acetate, 9:1).

Reaction 4: Butyllithium as Base.[15] Equimolar amounts of *n*-butyllithium and indole were allowed to stir for 1 h in sodium-dried ether. A solution of the sulfenyl chloride (1.1 equiv)

(12) Hubacher, M. H. "Organic Syntheses"; Wiley: New York, 1963; Collect. Vol. II, p 455.

(13) Montanari, F. *Gazz. Chim. Ital.* **1956**, *86*, 406.
(14) Raban, M.; Yamamoto, G. *J. Org. Chem.* **1977**, *42*, 2549.
(15) Raban, M.; Carlson, E. M. *Isr. J. Chem.* **1977**, *15*, 106.

in dry THF was added dropwise to the lithium salt. After the solution was stirred for 5 h the precipitate was removed by filtration and the solvent evaporated in vacuo. The pure product was obtained by chromatography and recrystallization.

Reaction 5: Sodium Hydride as Base. Indole (1 equiv) in dry ether was added to 1.5 equiv of sodium hydride and the mixture allowed to stir for 1 h to form a suspension of the sodium salt. The sulfenyl chloride (1.1 equiv) in dry THF was added dropwise. After stirring for 5 h, the reaction mixture was filtered and the solvent evaporated in vacuo. The product was obtained by chromatography and crystallization.

The other nitrophenylthioindoles **4** were prepared using reaction 1. The products were obtained by recrystallization from ethanol, except for **4ch** which was recrystallized from glacial acetic acid.

Registry No. **1a**, 7669-54-7; **1b**, 37692-14-1; **1c**, 937-32-6; **1d**, 528-76-7; **2g**, 120-72-9; **2h**, 6146-52-7; **4ag**, 72496-78-7; **4bg**, 72496-79-8; **4cg**, 72496-80-1; **4ah**, 72496-81-2; **4ch**, 72496-82-3; **4dh**, 72496-83-4; **4dg**, 72496-84-5.

Fragmentation Reactions of Ylides. 8. Reaction of 2-Alkyloxaziridines with Episulfide and Evidence for the Formation of Thionitrosoalkanes

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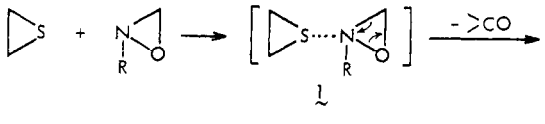
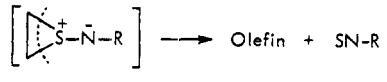
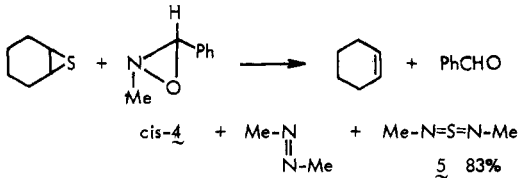
Recently, we found an interesting fragmentation reaction[1] of the oxaziridine ring with nucleophilic reagents in which these reagents exclusively attacked the nitrogen atom of the three-membered oxaziridine ring followed by a fragmentation reaction to form ylides. We also have reported previously on a cheletropic reaction of the ylide derived from the reaction of cyclohexene sulfide and carbene.[2] These findings taken together suggest the possibility that the reaction of episulfide and oxaziridine might occur by a cheletropic reaction to give olefin and the previously unknown thionitrosoalkane **3**.[3] With this in mind, we have studied the reaction of episulfides and 2-alkyloxaziridines and report here our results.

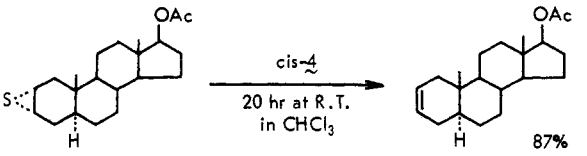


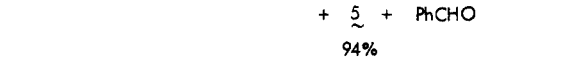


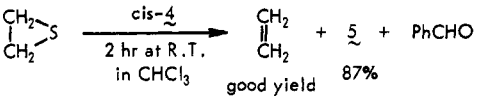
2 **3**

In chloroform solution, cyclohexene cis or trans smoothly in the reaction with a double molar amount of *cis*-2-methyl-3-phenyloxaziridine (*cis*-**4**) at room temperature and gave quantitative yields of cyclohexene and benzaldehyde, 83% of dimethylsulfur diimide (**5**), and a small amount of azomethane. Compound **5** was identified by comparison with an authentic sample.[4] Similar results were observed with ethylene sulfide and a steroidal episulfide.

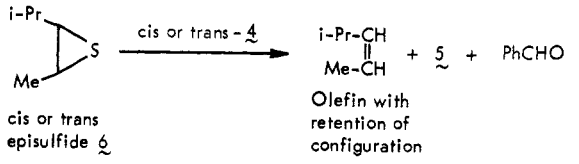




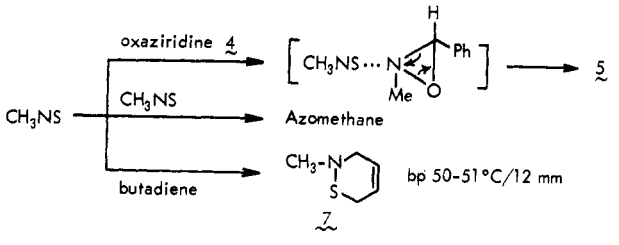




In the reaction of cis or trans isomers of 4-methyl-2-pentene sulfide **6** with *cis*- or *trans*-**4** in chloroform at room temperature, we observed the formation of cis or trans olefin having the same configuration as the starting episulfide in a yield of 80–50%[5] and found that the stereochemical reaction course was completely independent of the configuration of oxaziridines.



In these reactions, compound **5** and azomethane were presumed to arise by reactions of CH_3NS formed in an initial step of the reaction with the second mole of oxaziridine or thionitrosomethane. Evidence for the formation of thionitrosomethane was obtained by isolation of 2-methyl-3,6-dihydro-1,2-thiazine (**7**) when the reaction of



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cyclohexene sulfide and *cis*- or *trans*-**4** was carried out in the presence of butadiene. The yields of thiazine **7**, sulfur diimide **5**, and azomethane depended on the rate ratio of the competition reaction of thionitrosomethane with butadiene, oxaziridines, and another molecule of thionitrosomethane, respectively. Generally, in the desulfurization reaction of episulfide, *trans*-**4** usually gave a better yield of thiazine **7** than *cis*-**4**. This suggested that thionitrosomethane reacted with another molecule of *cis*-**4** more favorably than with *trans*-**4** due to less steric hindrance.

In a similar reaction using *trans*-2-ethyl- or *trans*-2-isopropyl-3-phenyloxaziridine, we obtained 2-ethyl- or 2-isopropyl-3,6-dihydro-1,2-thiazine. Attempted preparation of the *tert*-butyl derivative of thiazine failed due to the very low reactivity of 2-*tert*-butyl-3-phenyl-

(1) Y. Hata and M. Watanabe, *J. Am. Chem. Soc.*, **101**, 6671 (1979).
(2) Y. Hata and M. Watanabe, *J. Am. Chem. Soc.*, **97**, 2553 (1975).
(3) Thionitrosobenzenes were assumed to be reactive intermediates in the decomposition of *N,N*-thiodianiline: P. Tavs, *Angew. Chem., Int. Ed. Engl.*, **5**, 1048 (1966); F. A. Davis and E. B. Skibo, *J. Org. Chem*, **41**, 1333 (1976).
(4) R. Appel and J. Kohnke, *Chem. Ber.*, **104**, 2648 (1971).
(5) Greater than 99% retention by VPC.

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