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Reaction of 3-[2′-Tetrahydropyranyl(furanyl)thio]indole with Silver Ion

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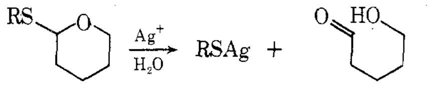
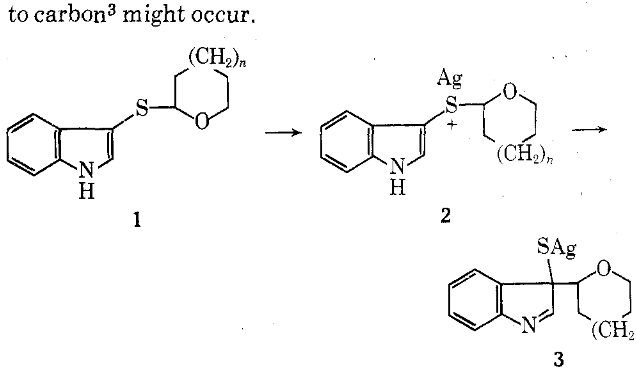
When 3-(2′-tetrahydropyranylthio)indole is treated with 1 equiv of silver ion in aqueous methanol, the silver salt of 3-thioindole and 5-hydroxyvaleraldehyde are produced quantitatively. If the reaction is carried out in an aprotic solvent (toluene, tetrahydrofuran), rearrangements occur to produce low yields of products in which the cyclic ether moiety is bonded to N-1 or C-2 of the indole nucleus. The reactions are envisaged as involving collapse of an initially formed adduct, in which silver ion is bound to sulfur, to release a cyclic ether oxonium ion which undergoes further reaction. Formation of the 1-tetrahydropyranyl(furanyl) compound is envisaged as involving intermolecular formation of 1-tetrahydropyranyl(furanyl)-3-tetrahydropyranyl(furanyl)thioindole which, *via* a silver ion adduct, loses the cyclic ether moiety from sulfur. It is suggested that the C-2-substituted compound may arise by a process in which the cyclic ether moiety is first bonded to C-3 of the indole nucleus followed by migration to C-2.

Reaction of 3-[2′-Tetrahydropyranyl(furanyl)thio]indole with Silver Ion. In connection with studies directed toward achieving new C-nucleoside (*e.g.*, formycin, pseudouridine, pyrazomycin)[1] syntheses, an investigation of the reactions of silver ion with 3-(2′-tetrahydropyranylthio)indole (**1a**) and 3-(2′-tetrahydrofuranylthio)indole (**1b**) was undertaken. Holland and Cohen[2] discovered that the sulfur–hemiacetal linkage is cleaved readily by silver ion in aqueous solution to yield quantitatively a silver mercaptide and a hydroxy aldehyde.



The present study was undertaken in anticipation that, in the absence of a protic solvent, a 1,2 shift from sulfur to carbon[3] might occur.



a, $n = 1$
b, $n = 0$

In accordance with the results of Holland and Cohen,[2] treatment of 3-(2′-tetrahydropyranylthio)indole (**1a**) with aqueous silver nitrate at room temperature resulted in the immediate precipitation of a quantitative yield of the silver salt of 3-thioindole[4] and 5-hydroxyvaleraldehyde, isolated as the corresponding 2,4-dinitrophenylhydrazone.[5] When equimolar amounts of **1a** and silver perchlorate (chosen because of its availability in anhydrous form, its solubility in organic solvents, and the low nucleophilicity of the perchlorate ion) were combined in benzene at room temperature a precipitate was formed which darkened (decomposed) quickly. Evidence consistent with the formulation of this precipitate as the coordination compound **2a** was obtained from two additional experiments. When **1a** and silver perchlorate were mixed in pyridine at room temperature no reaction occurred, indicating that the affinity of pyridine for silver ion prevents its coordination with the sulfur of **1a**. When the reactants were combined in toluene at −78° a colorless precipitate accounting for two-thirds of added reactants formed immediately. Addition of pyridine to the reaction mixture at this point caused the precipitate to dissolve with quantitative regeneration of the starting material, **1a**, indicating that the precipitate was not a product involving cleavage or rearrangement of the organic reactant. However, if the reaction mixture in toluene was allowed to warm in the absence of added pyridine, the original precipitate decomposed and pyridine was no longer capable of removing the silver, indicating that the silver ion was present as a mercaptide.

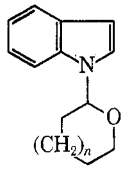
In addition to providing evidence consistent with the formation of coordination compound **2**, these experiments illustrate the extent to which the activity of silver ion is influenced by its interaction with solvent. After evaluation of a number of solvents, tetrahydrofuran was selected for use in the remainder of this study.

At −78° in tetrahydrofuran, no evidence for the reaction of **1a** with silver perchlorate was obtained. At higher temperatures (−15 to 25°) **1a** underwent reaction presumably *via* the intermediacy of complex **2a**, which, unlike its behavior in benzene and toluene, appears to be soluble in tetrahydrofuran. In contrast, 3-(2′-tetrahydrofuranylthio)indole (**1b**) reacted in the presence of silver ion even at −78°. Except for these differences in affinity for coordination and reaction rate (which parallel the behavior of 2-*O*-alkyl acetals of tetrahydropyran and tetrahydrofuran toward acid-catalyzed hydrolysis),[6,7] the reactions of **1a** and **1b** with silver perchlorate in tetrahydrofuran were similar.

Silver ion mediated decomposition of **1a** or **1b** in tetrahydrofuran produced heterogeneous precipitates which, in favorable instances, accounted for essentially all of the added reactants (**1a** or **1b** and silver perchlorate). Removal of silver ion from a crude reaction product mixture (suspended in either the original tetrahydrofuran solution or in methanol) was accomplished by treatment with hydrogen sulfide, hydrogen chloride, or methyl iodide. The resulting product mixture was then subjected to chromatographic separation, either directly or following desulfurization with Raney nickel. In all instances, yields of characterized products were low, accompanied by highly colored, polar material[8] which was not characterized.

The precipitate obtained by reaction of **1b** with silver perchlorate in tetrahydrofuran at −15° was treated with hydrogen sulfide to remove silver followed by Raney nickel desulfurization. From the resulting product mixture, 1- and 2-(2′-tetrahydrofuranyl)indoles (**4b** and **5b**) were isolated. When **1a** was treated similarly and the reaction mixture was fractionated following removal of silver but without desulfurization, the disulfide (**6a**) of 1-(2′-tetrahydropyranyl)-3-thioindole and 1-(2′-tetrahydropyranyl)-3-(2′-tetrahydropyranylthio)indole (**8a**) were isolated.

In a reaction of **1a** with silver ion, when silver was removed after 30 min at 25° (during which time 25% of the reactants had formed a precipitate), **1a** was recovered unchanged from the solution. When the filtrate, formed in the same manner, was treated with excess methyl iodide (to methylate all silver coordination sites), 3-methylthioindole (**7**)[9] and 3-methylthio-1-(2′-tetrahydropyranyl)indole (**9a**) were produced.



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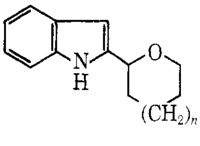

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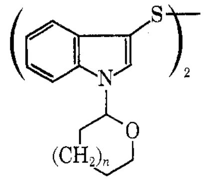

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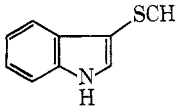

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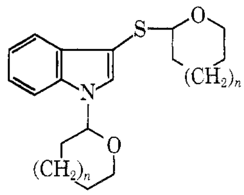

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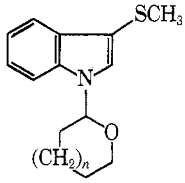

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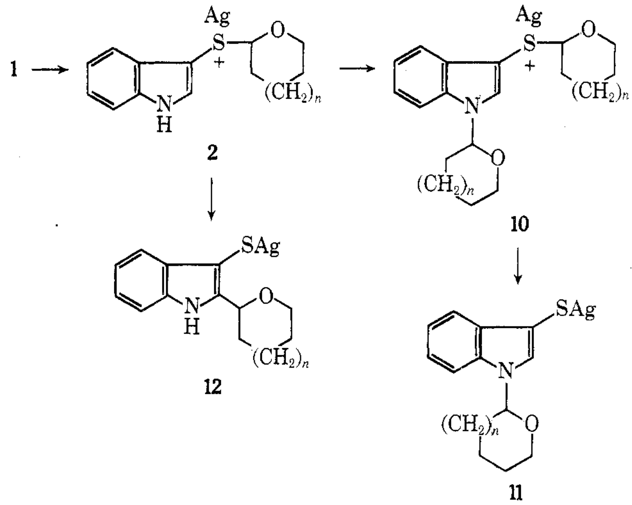
The results of this study allow the construction of Scheme I, which indicates the general features of the silver ion catalyzed reactions of **1**. The products isolated, irrespective of reaction conditions (*i.e.*, **4**, **6**, **8**, **9**), all possess a 2′-tetrahydropyranyl(furanyl) substituent on the indole nitrogen. The formation of such "rearrangement" products clearly must occur *via* an intermolecular pathway. The probable presence in solution of the secondary coordination compound **10**, as evidenced by the isolation of **8a** (and of **9a** from reactions in which methyl iodide was used), and the insolubility of 3-thioindole silver salt indicate that this "migration" of a cyclic ether moiety from sulfur to nitrogen is likely to occur exclusively *via* the path **2** → **10** → **11**. Interestingly, this sequence does not require formation of significant amounts of 3-thioindole silver salt, since, once some **10** is available, the reaction **2** + **10** → **11** + **10** → etc. is possible.

While the pathway to the 1-substituted compound **11** is clearly intermolecular, the origin of the 2-substituted product **12** is less certain. It is possible that a 2-substituted coordination compound analogous to **10** is an intermediate; however, as no evidence for such was found, the possibility that **12** arises *via* an intramolecular process must be considered. It is well known[10] that electrophilic substitution of 3-substituted indoles occurs readily at carbon 2, probably *via* a mechanism involving rearrangement of the adduct formed by initial attack at C-3.[11,12] In this light, although no direct evidence for the reaction process **1** → **3** was found, the possibility that **12** is formed *via* the pathway **1** → **2** → **3** → **12** is an attractive one.

Scheme I



The spectral properties of the variously substituted indoles comprising this study are highly characteristic and facilitated structural assignments. Among the isolated products from reactions of **1** with silver ion are compounds in which cyclic ether moieties are bonded variously to carbon, sulfur, or nitrogen in the 3-thioindole nucleus. The nuclear magnetic resonance (nmr) chemical shift exhibited by the proton on C-2′ of the cyclic ether moiety was, in every case, clearly identifiable and led readily to the correct assignment of the indole bonding site. Thus, the C-2′ proton of **1b** (C-2′ bonded to S) appears at δ 5.34, the corresponding resonance for 1-(2′-tetrahydrofuranyl)indole (**4b**, C-2′ bonded to N) appears at δ 5.92, and the signal in the spectrum of **5b** (C-2′ bonded to C) appears at δ 5.12. The compounds in the 2′-tetrahydropyranyl series exhibited analogous resonances, although shifted toward higher field; *e.g.*, for **1a** (C-2′ bonded to S) the signal appears at δ 4.84 and for **4a** (C-2′ bonded to N) the signal is at δ 5.35.

Definitive assignment of structure **5b** [as opposed to the isomeric structure 3-(2′-tetrahydrofuranyl)indole] was made by consideration of the nmr chemical shifts observed for the 2 and 3 protons of various indole derivatives. Thus, in the nmr spectrum[13] of 3-methylindole, the hydrogen at C-2 gives rise to a signal at δ 6.78 whereas the C-3 hydrogen in 2,5-dimethylindole appears at δ 6.10.[13,14] In the spectrum of 1-(2′-tetrahydrofuranyl)indole (**4b**) the C-2 hydrogen is observed at δ 6.9 and the C-3 hydrogen appears at δ 6.30. The resonance at δ 6.27 in the spectrum of **5b** clearly is that of the C-3 hydrogen and establishes the attachment of the tetrahydrofuranyl moiety as occurring at C-2.

These assignments are corroborated by examination of the mass spectra of the variously substituted compounds. The fragmentation of 1-(2′-tetrahydrofuranyl)indole (**4b**; see Figure 1A) is dominated by cleavage of the tetrahydrofuranyl moiety from the indole nucleus (*i.e.*, *m/e* 71 and 117). The fragmentations of the various *S*-tetrahydrofuranyl and *S*-tetrahydropyranyl compounds are similar in this respect (see Experimental Section). In contrast, the electron bombardment induced fragmentation of 2-(2′-tetrahydrofuranyl)indole (**5b**, see Figure 1B), in which the cyclic ether is linked to the indole nucleus *via* a carbon–carbon bond, is considerably more complex. Whereas the

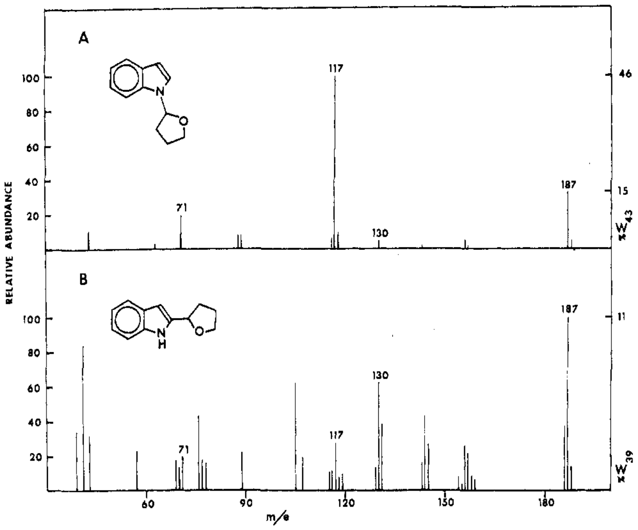


Figure 1. Mass spectra of 1-(2′-tetrahydrofuranyl)indole (**4b**), A, and 2-(2′-tetrahydrofuranyl)indole (**5b**), B.

indole·$^+$ rearrangement ion (*m/e* 117), formed by loss of dihydrofuran, is the most abundant ion (Σ_{43} = 46%) in the spectrum of **4b** (Figure 1A), this is a low-abundance ion (Σ_{39} = 3%) in the spectrum of **5b** (Figure 1B). Although the molecular ions represent comparable percentages of total ionization (*i.e.*, 15% for **4b** and 11% for **5b**), this ion is the base peak in the spectrum of **5b** (Figure 1B). These differences are strikingly similar to those observed in the spectra of N and C nucleosides.[15]

To facilitate structural assignments, authentic 1-(2′-tetrahydropyranyl)indole (**4a**) was synthesized by treatment of indolyllithium[16] with 2-chlorotetrahydropyran.[17] An attempt was made to prepare 3-(2′-tetrahydropyranyl)indole from the indole Grignard reagent[16,18] and 2-chlorotetrahydropyran[17] in ether; however, the only product formed in greater than trace amounts was again the N-substituted compound **4a**. This result is surprising in view of the absence of reports of such exclusive N-alkylation of an indole Grignard reagent in ether.[16,18,19]

Experimental Section

Infrared spectra were determined on a Perkin-Elmer 337 grating spectrophotometer. Nmr spectra were determined with a Varian HA-100 spectrometer using CCl_4 solutions; chemical shifts are expressed as parts per million (δ) downfield from an internal standard of tetramethylsilane. Mass spectra were obtained with a CEC Du Pont Model 21-110B spectrometer operated at 70 eV. Thin layer chromatography (tlc) was done on silica gel G. Melting points were determined on a microscope hot stage and are uncorrected. Elemental analyses were by Heterocyclic Chemical Corp., Harrisonville, Mo.

3-(2′-Tetrahydropyranylthio)indole (1a). To 250 ml of dimethylformamide, freshly distilled from calcium hydride and maintained under nitrogen, was added 0.5 g of an oil dispersion of sodium hydride, followed by 1.5 g (0.01 mol) of 3-thioindole.[4] After 2 hr, 1.2 g (0.01 mol) of 2-chlorotetrahydropyran[17] was added to the stirred solution. After several additional hours the reaction mixture was poured into ether and was extracted with brine and water. The ether solution was dried, decolorized with charcoal, and evaporated. The resulting crude product was crystallized from a mixture of hexane and ether to yield 0.56 g (24%) of 3-(2′-tetrahydropyranylthio)indole (**1a**) as cream-colored crystals: mp 84–85°; nmr δ 1.4–2.0 (m, 3′,5′-H), 3.45 (m, 6′-H), 4.16 (m, 6′-H), 4.84 (dd, J_1 = 6, J_2 = 3 Hz, 2′-H), 6.84 (d, J = 3 Hz, 2-H), 7.05–7.14 (m, 5–7-H), 7.64 (m, 4-H), 8.39 (br, NH).

Anal. Calcd for $C_{13}H_{15}NOS$: C, 66.9; H, 6.49; N, 6.0. Found: C, 67.0; H, 6.34; N, 5.82.

3-(2′-Tetrahydrofuranylthio)indole (1b). Employing 2-chlorotetrahydrofuran,[20] **1b** was synthesized in the same manner as **1a** in a yield of 28%. Recrystallization from 95% ethanol afforded colorless crystals: mp 98–100°; nmr δ 1.8–2.4 (m, 3′,4′-H), 3.8–4.15 (m, 5′-H), 5.3–5.42 (m, 2′-H), 7.02 (d, J = 2 Hz, 2-H), 7.1–7.2 (m, 5–7-H), 7.7–7.86 (m, 4-H), 8.48 (br, NH).

Anal. Calcd for $C_{12}H_{13}NOS$: C, 65.8; H, 5.94; N, 6.39. Found: C, 65.8; H, 6.16; N, 6.18.

1-(2′-Tetrahydropyranyl)indole (4a). Method A. To a stirred solution of 2 g (0.017 mol) of indole in 50 ml of tetrahydrofuran was added 7.7 ml (0.017 mol) of a hexane solution of *n*-butyllithium. After 5 min, 2.04 g (0.017 mol) of 2-chlorotetrahydropyran[17] was added. After 30 min the solvent was evaporated and was replaced with 50 ml of methylene chloride. The methylene chloride solution was washed with water (2 × 50 ml), dried, and removed. The residue was chromatographed on a column of silicic acid (3 × 30 cm). 1-(2′-Tetrahydropyranyl)indole (**4a**), 1.44 g (42%), was eluted with 25% petroleum ether (bp 30–60°) in benzene as a colorless oil: bp 118° (0.2 mm); nmr δ 1.4–2.1 (m, 3′,5′-H), 4.58 (m, 6′-H), 4.96 (m, 6′-H), 5.35 (dd, J_1 = 8, J_2 = 4 Hz, 2′-H), 6.36 (d, J = 3.5 Hz, 3-H), 6.9–7.5 (m, 2,4–7-H); mass spectrum *m/e* (rel intensity), 201 (44), 144 (7), 130 (13), 117 (110), 85 (16).

Anal. Calcd for $C_{13}H_{15}NO$: C, 77.6; H, 7.46; N, 6.96. Found: C, 77.3; H, 7.44; N, 6.87.

Method B. To a solution of methylmagnesium iodide [prepared from 0.23 g (0.01 mol) of magnesium and 1.4 g (0.01 mol) of methyl iodide] in anhydrous ether was added 0.7 g (0.006 mol) of indole, and, after stirring for 3 hr, 0.72 g (0.006 mol) of 2-chlorotetrahydropyran[17] was added. After an additional 1 hr. water was added, and the ether phase was separated, washed several times with brine and water, and then dried. Removal of the solvent yielded crude 1-(2′-tetrahydropyranyl)indole (**4a**), which was separated from unreacted indole by preparative tlc. This material, 0.21 g (17%), was identical in all respects with the product prepared by method A.

Reaction of 3-(2′-Tetrahydropyranylthio)indole (1a) with Aqueous Silver Nitrate. Solutions of 23.3 mg (0.1 mmol) of 3-(2′-tetrahydropyranylthio)indole (**1a**) in 5 ml of 50% aqueous methanol and of 17 mg (0.1 mmol) of silver nitrate in 5 ml of water were cooled to 0° and combined. Immediately the silver salt of 3-thioindole precipitated, and was filtered and dried to yield 23 mg (90%) as an amorphous powder. Removal of the silver was accomplished by suspending the precipitate in methanolic hydrogen chloride. Tlc of the filtrate after removal of the silver chloride indicated the presence of 3-thioindole[4] and the corresponding disulfide. Treatment of the original filtrate with 2,4-dinitrophenylhydrazine reagent[21] yielded 15.8 mg (56%) of red crystals of the 2,4-dinitrophenylhydrazone of 5-hydroxyvaleraldehyde, mp 110–112° (lit.[5] mp 109°, 113–114°).

Reaction of 3-(2′-Tetrahydrofuranylthio)indole (1b) with Silver Perchlorate in Tetrahydrofuran. To a stirred, cooled (−15°) solution of 2.19 g (0.01 mol) of 3-(2′-tetrahydrofuranylthio)indole (**1b**) in 75 ml of dry tetrahydrofuran was added a cooled (−15°) solution of 2.07 g (0.01 mol) of silver perchlorate in 10 ml of dry tetrahydrofuran, whereupon the solution immediately became yellow. After 30 min the precipitate which had formed was collected, resuspended in 50 ml of methanol, and treated with hydrogen sulfide, the excess hydrogen sulfide being discharged with a nitrogen jet. The precipitated silver sulfide was removed with the filtrate passing directly into a suspension of *ca.* 10 g of Raney nickel in 150 ml of 7 *N* ammonium hydroxide. This mixture was heated under reflux on a steam bath for 2 hr. The hot mixture was then filtered to remove the Raney nickel, which was washed with 95% ethanol. The combined filtrate was evaporated and the resulting residue was triturated with methylene chloride (3 × 25 ml). The methylene chloride soluble portion was subjected to preparative chromatography to yield two products: 1-(2′-tetrahydrofuranyl)indole (**4b**, 50 mg) and 2-(2′-tetrahydrofuranyl)indole (**5b**, 5 mg). 1-(2′-Tetrahydrofuranyl)indole (**4b**) had nmr δ 1.62–2.16 (m, 3′,4′-H), 3.6–4.0 (m, 5′-H), 5.92 (t, J = 4 Hz, 2′-H), 6.30 (d, J = 3.5 Hz, 3-H), 6.8–7.3 (m, 2,5–7-H), 7.4 (m, 4-H); mass spectrum *m/e* (rel intensity), 187 (33), 130 (5), 117 (100), 71 (20); ir no NH. 2-(2′-Tetrahydrofuranyl)indole (**5b**) had nmr δ 1.86–2.44 (m, 3′,4′-H), 3.84–4.02 (m, 5′-H), 5.12 (dd, J_1 = 8, $J_2 \cong$ 1 Hz, 2′-H), 6.2 (m, 3′-H), 6.9–7.3 (m, 5–7-H), 7.44 (m, 4-H), 8.36 (br, NH); mass spectrum *m/e* (rel intensity) 187 (100), 154 (80), 144 (43), 130 (63), 117 (28), 71 (20); ir 3420 and 3310 cm^{-1} (NH).

Reaction of 3-(2′-Tetrahydropyranylthio)indole (1a) with Silver Perchlorate in Tetrahydrofuran. To a solution of 233 mg (1 mmol) of 3-(2′-tetrahydropyranylthio)indole (**1a**) in anhydrous tetrahydrofuran was added a solution of 207 mg (1 mmol) of silver perchlorate in anhydrous tetrahydrofuran. Concentrations in various reactions ranged from 0.01 to 0.002 *M* with no discernible difference in results. When the two solutions were combined at −78° a colorless solution resulted. The analysis of the solution (tlc) showed the presence of uncomplexed starting material, **1a**. No change was observed after several hours at −78°. When warmed (−15 to 25°), the solution turned yellow and an orange precipitate was formed; no uncomplexed starting material was evident in the solution by tlc analysis. The collected, dried precipitate, which appeared during 30 min at 25°, weighed 100 mg and accounted for approximately 25% of the combined weight of the thioketal **1a** and the silver perchlorate. The precipitate (fraction A), resuspended in tetrahydrofuran, and the filtrate (fraction B) were treated separately with hydrogen sulfide in ether and the resulting silver sulfide was removed. Water was added to each of the filtrates, followed by extraction with ether. The solvents were removed from the ether-soluble portions and the residues were separated by tlc (chloroform–acetone 95:5). From the original filtrate (fraction B) unreacted starting material **1a** was obtained; no **1a** was present in the precipitate (fraction A).

The components isolated from the precipitate (fraction A) were 3-thioindole,[4] 3-thioindolyl disulfide,[4] and 1-(2′-tetrahydropyranyl)-3-thioindolyl disulfide (**6a**): mp 136–140°; nmr δ 1.5–2.1 (m, 3′-5′-H), 3.68 (m, 6′-H), 4.0 (m, 6′-H), 5.39 (m, 2′-H), 6.9–7.6 (m, 2,4–7-H); mass spectrum *m/e* (rel intensity) 464 (3), 432 (4), 348 (4), 264 (19), 149 (100), 148 (20), 117 (20), 85 (60).

Reaction of Silver Complex 2a with Methyl Iodide. To a solution of silver complex **2a** (methyl iodide was unreactive toward **1a** in the absence of silver ion) prepared in tetrahydrofuran as described above was added an excess of methyl iodide. After several hours at room temperature (at lower temperatures, no reaction occurred) a yellow precipitate of silver iodide had formed. The mixture was filtered, water was added to the filtrate, and the solution was extracted with ether. By preparative chromatography the starting thioketal (**1a**), 3-methylthioindole[9] (**7**), 1-(2′-tetrahydropyranyl)-3-(2′-tetrahydropyranylthio)indole (**8a**), and 1-(2′-tetrahydropyranyl)-3-methylthioindole (**9a**) were isolated. 3-Methylthioindole[9] (**7**) had nmr δ 2.32 (s, SMe), 7.05–7.24 (m, 2,5–7-H), 7.68 (m, 4-H), 7.9 (br, NH). 1-(2′-Tetrahydropyranyl)-3-(2′-tetrahydropyranylthio)indole (**8a**) had nmr δ 1.5–2.1 (m, 3′-5′, 3″-5″-H), 3.4–3.8 (m, 6′,6″-H), 3.9–4.2 (m, 6′,6″-H), 4.80 (m, 2′-H), 5.38 (m, 2″-H), 6.9–7.7 (m, 2,4–7-H); mass spectrum *m/e* (rel intensity) 317 (11), 233 (43), 149 (100), 117 (6), 85 (63). 1-(2′-Tetrahydropyranyl)-3-methylthioindole (**9a**) had nmr δ 1.5–2.1 (m, 3′-5′-H), 2.29 (s, SMe), 3.60 (m, 6′-H), 4.0 (m, 6′-H), 5.32 (dd, $J_1 = 8$, $J_2 = 4$ Hz, 2′-H), 7.0–7.4 (m, 2,5–7-H), 7.62 (m, 4-H); mass spectrum *m/e* (rel intensity) 247 (51), 163 (100), 148 (32), 117 (6), 85 (50).

Reactions of Raney Nickel with 3-(2′-Tetrahydropyranylthio)indole (1a), 3-Methylthioindole[9] (7), and 1-(2′-Tetrahydropyranyl)-3-methylthioindole (9a). A few milligrams of **1a**, **7**, or **9a** in methanol was treated with a large excess (*ca.* tenfold by weight) of Raney nickel. After standing at room temperature for 0.5 hr, the suspension was filtered and the filtrate was evaporated. In the case of **1a** or **7**, the resulting product was identified as indole by tlc and comparison of spectra. In the case of **9a** the product was indistinguishable from 1-(2′-tetrahydropyranyl)indole (**4a**), prepared as described.

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Registry No.—**1a,** 50639-97-9; **1b,** 50639-98-0; **4a,** 50639-99-1; **4b,** 50640-00-1; **5b,** 50640-01-2; **6a,** 50640-02-3; **7,** 40015-10-9; **8a,** 50640-03-4; **9a,** 50640-04-5; Ag$^+$, 14701-21-4; silver nitrate, 7761-88-8; silver perchlorate, 7783-93-9; 3-thioindole, 480-94-4; 2-chlorotetrahydropyran, 3136-02-5; 2-chlorotetrahydrofuran, 13369-70-5.

References and Notes

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Stereoselective Formation of Some Thietane 1,1-Dioxides

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The reaction of substituted methanesulfonyl chlorides and ethanesulfonyl chlorides with triethylamine in the presence of 2-methyl-1-propenylamines is discussed. The observed stereoselectivity in the formation of products can be explained on the basis of a zwitterionic intermediate or a concerted [$_\pi 2_s + _\pi 2_s$] process.

The chemistry of sulfenes has received considerable attention in the past decade and several reviews have appeared.[1] The reaction of sulfenes with enamines is probably the most extensively investigated reaction of these chemical intermediates, but data concerning the stereochemistry of the products derived from the reaction of substituted sulfenes with enamines is meager and inconclusive.[2] The present study deals with the stereochemistry of the products obtained in the reaction of a number of substituted methanesulfonyl and ethanesulfonyl chlorides with triethylamine in the presence of N,N-disubstituted 2-methyl-1-propenylamines.