to reflux for 2.5 h. After cooling, the solution was poured into 10 mL of saturated sodium bicarbonate and extracted with ethyl acetate (3 × 30 mL). The aqueous phase was acidified and extracted with ethyl acetate (3 × 40 mL). The organic phase was washed with water (2 × 20 mL) and dried (Na_2SO_4). Evaporation of the solvent gave 66 mg (68%) of **15a**: mp 148–149 °C; UV (MeOH) 207, 264 nm; IR (KBr) ~3600–2500 (br), 1735, 1650, 1635 cm^{-1}; ^1H NMR ($CDCl_3$ + Me_2SO-d_6) δ 1.95–2.65 (m, 4 H), 2.85 (t, J = 5.5 Hz, 2 H), 3.65 (s, 2 H), 6.50 (s, 1 H), ~9.0 (br, 1 H, interchangeable with D_2O); MS, m/e (relative intensity) 194 (M^+, 45), 166 (37), 149 (100), 138 (33).

Method B. A solution containing 112 mg (1 mmol) of 1,3-cyclohexanedione, 100 mg (1 mmol) of **1**, and 0.1 mL of 2% sodium hydroxide in 5 mL of ethanol was heated to reflux for 1 h. The ethanol was evaporated, the residue was treated with 5 mL of 4:1 THF–0.1 N HCl, and the resulting solution was heated to reflux for 2 h. After cooling, the solution was poured into 10 mL of saturated sodium bicarbonate and extracted with ethyl acetate (3 × 10 mL). The aqueous phase was acidified with dilute hydrochloric acid and extracted with ethyl acetate. The extracts were washed, dried, and concentrated, affording 147 mg of **15a**. Recrystallization of acetone–hexane gave pure material: 78 mg (40%); mp 148–150 °C. The spectroscopic data were identical with those given under method A.

4,5,6,7-Tetrahydro-6-methyl-4-oxobenzofuran-2-acetic Acid (15b). To 104 mg (0.5 mmol) of lactone **14b** was added 10 mL of 4:1 THF–0.1 N HCl, and the resulting solution was heated to reflux for 3 h. The reaction mixture was allowed to stand overnight at room temperature, and then 20 mL of saturated sodium bicarbonate was added. The solution was extracted with ethyl acetate (2 × 20 mL). The aqueous phase was acidified with dilute hydrochloric acid and extracted with ethyl acetate (2 × 20 mL). The organic phase was washed, dried, and evaporated to give an oil that solidifies on standing: mp 146–147 °C; IR ($CHCl_3$) ~3400–2500 (br), 1715, 1670 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.15 (d, J = 7 Hz, 3 H), ~2.15–3.10 (m, 5 H), 3.70 (s, 2 H), 6.50 (s, 1 H), 8.45 (br, 1 H, interchangeable with D_2O); MS, m/e (relative intensity) 208 (M^+, 100), 166 (97), 163 (94), 138 (44).

4,5,6,7-Tetrahydro-6,6-dimethyl-4-oxobenzofuran-2-acetic Acid (15c). A solution of 140 mg (1 mmol) of dimedone, 100 mg (1 mmol) of the hydroxy lactone **1**, and 0.1 mL of 2% sodium hydroxide in 5 mL of ethanol was heated for 1.5 h. The solvent was removed in vacuo, and the residue was treated with 5 mL of 4:1 THF–0.1 N HCl. The solution was heated to reflux for 2.5 h. After cooling, the solution was poured into 10 mL of saturated sodium bicarbonate and extracted with ethyl acetate (3 × 10 mL). The aqueous phase was acidified with 1 N hydrochloric acid and extracted with ethyl acetate (3 × 10 mL). The extract was washed with water, dried, and concentrated. The residue was purified by preparative chromatography on two chromatography plates with ethyl acetate–methanol (90:10) as the developing solvent. The acetone eluates gave 83 mg (37%) of **15c** as yellow crystals: mp 110–112 °C; IR ($CHCl_3$) 3500, ~3300–2500 (br), 1715, 1670 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.10 (s, 6 H), 2.35 (s, 2 H), 2.70 (s, 2 H), 3.67 (s, 2 H), 6.50 (s, 1 H), 7.10–7.90 (br, 1 H, interchangeable with D_2O); MS, m/e (relative intensity) 222 (M^+, 30), 166 (100), 138 (30), 121 (23).

Acknowledgment. We thank A. R. Toscano, R. Villena, R. Saucedo, J. Cárdenas, H. Bojórquez, and L. Velasco for their technical assistance.

Registry No. 1, 14032-66-7; 2, 5220-49-5; 3, 82544-29-4; 4, 82537-40-4; 5, 35308-68-0; 6, 41609-04-5; 7a, 82537-41-5; 8, 1118-66-7; 9a, 82537-42-6; 10a, 141-97-9; 10b, 123-54-6; 11a, 82537-43-7; 11b, 82537-44-8; 12, 82537-45-9; 13a, 504-02-9; 13b, 4341-24-6; 14a, 82537-46-0; 14b, 82537-47-1; 15a, 82537-48-2; 15b, 82537-49-3; 15c, 82537-50-6; furfural, 98-01-1; dimedone, 126-81-8.

Synthesis and Rearrangement of Pyrrolyl Sulfides and Sulfones[1]

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Received March 15, 1982

A general synthesis of 3-pyrrolyl sulfides was developed on the basis of the triphenylphosphine–iodine–sodium iodide reduction of the sulfoxides, which in turn were obtained by the acid-mediated rearrangement of the corresponding 2-sulfinylpyrroles. Methods were also devised for the reduction of 2-(alkylsulfinyl)pyrroles to the sulfides. 2-Pyrrolyl and 3-pyrrolyl sulfides were shown to undergo acid-induced equilibration under mild conditions. With trifluoroacetic acid in dichloromethane solution, at room temperature, the equilibrium always was in favor of the 2-isomer and the interconversion appeared to be intramolecular. 2-(Methylsulfonyl)pyrrole and 2-(phenylsulfonyl)pyrrole were transformed into the 3-substituted isomers when heated under strongly acidic conditions.

We recently described single-step syntheses of 2-(arylsulfinyl)- and 2-(alkylsulfinyl)pyrroles and the acid-mediated transposition of these compounds into the 3-substituted isomers.[2] Inasmuch as the sulfoxide moiety is very easily reduced, it was obvious that the corresponding sulfides would be readily available, and, therefore, a study of their properties could be undertaken.

From the many methods that are available for the reduction of sulfoxides, three were chosen for study that are notable for their mildness. These were reduction by means of the systems triphenylphosphine–iodine–iodide (method A),[3] triphenylphosphine–carbon tetrachloride (method B),[4] and sodium borohydride–cobalt chloride (method C).[5] Of these method A was examined the most extensively. The reduction of the 3-pyrrolyl sulfoxides by this technique was

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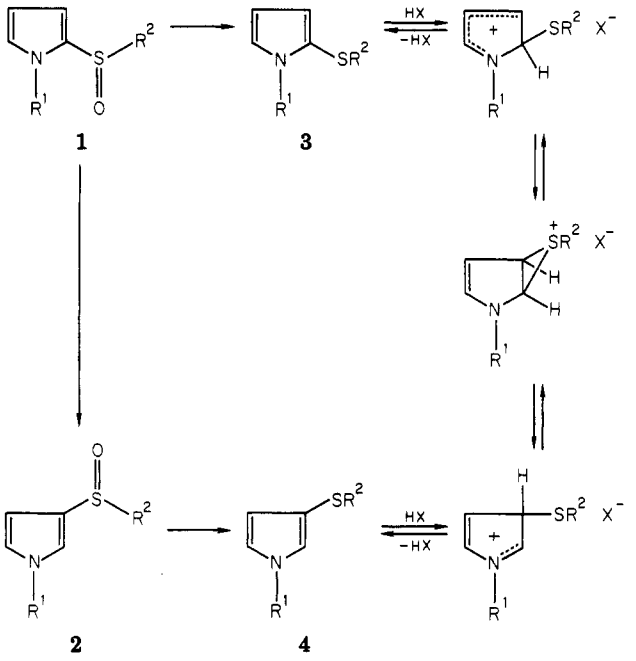
0022-3263/82/1947-3668$01.25/0

Table I. Reduction of Pyrrolyl Sulfoxides to Pyrrolyl Sulfides

sulfoxide	R^1	R^2	sulfide	method, % yield (rctn time) A	B	C
1a	H	C_6H_5	3a	33 (3 h)	83 (5 h)	62 (0.5 h)
1b	CH_3	C_6H_5	3b	13 (1 min)	58 (25 h)	85 (25 h)
1c	H	$C_6H_5CH_2$	3c			81 (5 h)
2a	H	C_6H_5	4a	95 (1 min)		
2b	CH_3	C_6H_5	4b	82 (1 min)		85 (3 h)
2c	H	$C_6H_5CH_2$	4c	72 (1 min)		
2d	H	CH_3	4d	97 (1 min)		

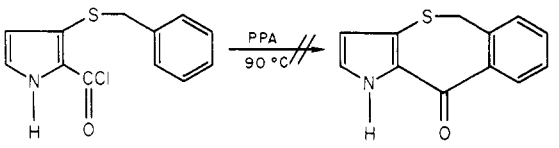
Scheme I



complete upon admixture of the reagents, and excellent yields of the alkyl- and aryl-3-pyrrolyl sulfides were obtained (Table I). Under these conditions, the reduction of the 2-(phenylsulfinyl)pyrroles **1a** and **1b** (Scheme I) did not proceed to completion and the sulfides were isolated only in low yields. Extension of the reaction period to 3 h for **1a** did not greatly improve the yield of 2-(phenylthio)pyrrole (**3a**). The reduction of the sulfoxides **1a** and **1b** could, however, be effected without difficulty by either method B or C.

The above results are of particular significance when viewed in the light of the facile rearrangement of 2-sulfinylpyrroles to the corresponding 3-isomers.[2] Because virtually any 2-pyrrolyl sulfoxide can now be made, either directly or by oxidation of the sulfide,[2] the very rare 3-pyrrolyl sulfides,[6-8] no general synthesis of which heretofore existed, thus become readily accessible. Furthermore, 2-(arylthio)pyrroles are also made generally available as a consequence of the ease of synthesis of 2-(arylsulfinyl)pyrroles.[2] Previous to this work, the synthesis of 2-(arylthio)pyrroles, free of polysubstituted contaminants, by the electrophilic substitution of pyrroles, was practical only when the aryl residue contained one or more electron-attracting substituents.[8,9]

One of the purposes of this study was to utilize the 3-pyrrolyl sulfides for the synthesis of tricyclic systems such as **6**. When the acid chloride **5**, obtained from 3-(benzylthio)pyrrole (**4c**) and phosgene,[10] was heated in polyphosphoric acid at 90 °C, the formation of the tricyclic ketone **6** was not observed. Instead, an approximately 2:1



mixture of 2-(benzylthio)pyrrole (**3c**) and 3-(benzylthio)pyrrole (**4c**), as well as variable amounts of dibenzyl disulfide, was isolated. The generation of 2-(benzylthio)pyrrole can be rationalized in terms of an acid-induced rearrangement of 3-(benzylthio)pyrrole subsequent to the dechlorocarbonylation of the acid chloride **5**. Literature reports on the acid-promoted rearrangement of pyrrolyl sulfides are exceedingly uncommon[11] and, therefore, a more detailed examination of this phenomenon was undertaken.

The conversion of **4c** into **3c** could also be effected by acidic reagents other than polyphosphoric acid such as *p*-toluenesulfonic acid, trifluoroacetic acid, and even boron trifluoride etherate. Trifluoroacetic acid, either neat or as a solution in dichloromethane, was the most useful because the isomerization in these media was cleaner. A study of the trifluoroacetic acid mediated transposition, at 20 °C in dichloromethane solution, by gas–liquid partition chromatography, showed that an equilibrium mixture of **3c** and **4c** (2.2:1) was reached in about 3 h. As expected the same equilibrium composition was achieved starting with pure 2-(benzylthio)pyrrole. Under similar conditions, 3-(phenylthio)pyrrole (**4a**) and 2-(phenylthio)pyrrole (**3a**) gave an equilibrium mixture that favored the 2-isomer over the 3-isomer by about 4.1:1, corresponding to a standard free-energy difference of ca. 0.8 kcal/mol. In addition, *N*-methyl-3-(phenylthio)pyrrole (**4b**) was equilibrated to a mixture in which *N*-methyl-2-(phenylthio)pyrrole (**3b**) predominated by a 1.7:1 ratio. When this equilibration was carried out in the presence of 60 equiv of pyrrole, no crossed products were formed. It would, therefore, appear that under these conditions the process is intramolecular in nature (Scheme I), in contrast to the acid-promoted rearrangement of 2-(phenylsulfinyl)pyrrole.[2,12] The formation of dibenzyl disulfide

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(12) It was previously reported[2] that the *p*-toluenesulfonic acid induced rearrangement of 2-(phenylsulfinyl)pyrrole (**1a**), in benzene solution, in the presence of 50 equiv of *N*-methylpyrrole gave 3-(phenylsulfinyl)pyrrole (**2a**) as well as the crossed transposed product *N*-methyl-3-(phenylsulfinyl)pyrrole (**2b**) in yields of 26% and 46%. When the rearrangement was conducted in the presence of 500 equiv of *N*-methylpyrrole, no **2a** was formed. Only the crossed transposed product (**2b**) and *N*-methyl-2-(phenylsulfinyl)pyrrole (**1b**) were formed in 57% and 26% yields, respectively, indicating that under suitable conditions the rearrangement of **1a** is entirely intermolecular.

Table II. NMR Data for Monosubstituted Pyrroles[a]

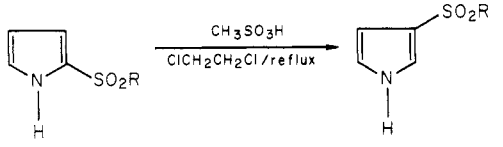
	chemical shifts, δ				coupling constants, Hz				
compd	H-2	H-3	H-4	H-5	$J_{2,4}$	$J_{2,5}$	$J_{3,4}$	$J_{3,5}$	$J_{4,5}$
2d	7.14 (t)		6.49 (dd)	6.83 (dd)	1.4	1.9			2.9
3a		6.53 (dd)	6.26 (dd)	6.86 (dd)			3.7	1.6	3.1
3b		6.54 (dd)	6.19 (dd)	6.86 (dd)			3.9	1.8	3.0
3c		6.29 (dd)	6.15 (dd)	6.68 (dd)			3.6	1.7	3.0
4a	6.94 (t)		6.31 (dd)	6.83 (dd)	1.5	2.2			3.0
4b	6.75 (t)		6.20 (dd)	6.61 (t)	1.9	2.2			2.8
4c	6.58 (dd)		6.12 (dd)	6.66 (dd)	1.6	2.2			3.0
4d	6.73 (t)		6.25 (dd)	6.76 (t)	1.6	2.0			2.8
13b		6.89 (dd)	6.30 (dd)	6.98 (dd)			3.8	1.3	~2.5
14a	7.37 (t)		6.56 (dd)	6.85 (dd)	1.5	1.7			3.1
14b	7.34 (t)		6.51 (dd)	6.79 (t)	1.4	~1.5			2.6

[a] Spectra recorded in $CDCl_3$ after D_2O exchange.

in the polyphosphoric acid mediated transposition of **4c** may, however, indicate that the rearrangement need not always be intramolecular.

Two additional examples of the acid-induced transposition of pyrrolyl sulfides were investigated. For example, a solution of 2,5-bis(phenylthio)pyrrole (**7**) in trifluoroacetic acid was completely transformed into the 2,4-disubstituted isomer **8** after 6 h at room temperature (Scheme II). Furthermore, the tricyclic keto sulfide **9**, on heating in polyphosphoric acid at 190 °C for at least 5 h, gave an apparent 1:6 equilibrium mixture of **9** and the isomeric keto sulfide **10**. This latter rearrangement is analogous to the reported[13] acid-promoted conversion of N-substituted 2-acylpyrroles into the corresponding 3-acylated isomers. It stands in contrast, however, to the preferential formation of the bicyclic ketones **12** from the carboxylic acid derivatives **11** (polyphosphoric acid/100–120 °C).[11,14] In these cases, the 2-acyl isomer was favored irrespective of the nature of the pyrrole nitrogen substituent.

Inasmuch as both 2-pyrrolyl sulfides and 2-pyrrolyl sulfoxides rearrange in acidic media, it was of interest to determine if the corresponding sulfones could be isomerized under similar conditions. Indeed, 2-(methylsulfonyl)pyrrole (**13a**) and 2-(phenylsulfonyl)pyrrole (**13b**) were converted into the 3-substituted isomers **14a** (88%) and **14b** (77%) upon heating with methanesulfonic acid in boiling 1,2-dichloroethane. These isomerizations could also be effected with a 1:1 mixture of trifluoroacetic and polyphosphoric acid at reflux temperature, but reproducibility was difficult to achieve under these conditions.

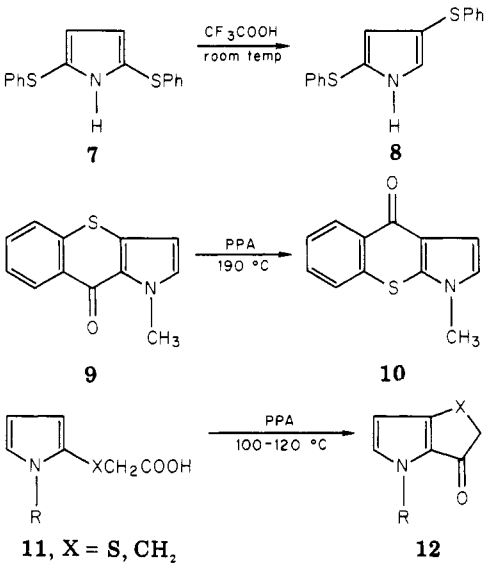


13a, R = CH_3
b, R = C_6H_5

14a, R = CH_3
b, R = C_6H_5

It has become evident that 2- or 3-substituted pyrroles have a pronounced tendency to undergo acid-mediated rearrangement, in some cases under exceedingly mild conditions. The migration of acyl,[11,13,14] sulfinyl,[2] chloro,[15] bromo,[15] sulfenyl (this work), and sulfonyl (this work) groups has now been demonstrated, and this list will undoubtedly be expanded in the future. This phenomenon has several important consequences.

Scheme II



1. The electrophilic substitution of pyrroles and the acid-mediated rearrangement of the products obtained thereby can take place at comparable rates.[2,15] Thus, as pointed out previously,[2] mechanistic conclusions based on the product distribution in such reactions should be made with caution, unless kinetic data on each of the products is available. This is a precaution that in many examples reported in the literature (e.g., ref 16) has not been taken. It would, therefore, seem worthwhile to reexamine the electrophilic substitution of pyrrole(s) in general with this point in mind.

2. The acid-promoted conversion of 2-substituted into 3-substituted pyrroles has preparative significance. Such compounds, heretofore prepared by several-step sequences,[17] can now often be obtained in one step from the readily available 2-substituted pyrrole. This technique is complementary to the recently reported[18] direct 3-substitution of 1-(benzenesulfonyl)pyrrole with certain electrophiles.

3. It is probable that the acid-mediated rearrangements discussed above will also be encountered with other monoheteroatomic aromatic systems such as thiophene and furan. Indeed, a few transpositions of this type have al-

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Table III. Physical Constants of Monosubstituted Pyrroles

compd	mp (°C); bp (°C/mm)	recryst solvent	% calcd C	% calcd H	% calcd N	% found C	% found H	% found N
2d	125-126	MeOH-Et_2O	46.49	5.46	10.84	46.65	5.50	10.76
3a	oil		68.53	5.17	7.99	68.30	5.09	7.91
3b	oil		69.80	5.86	7.40	70.15	6.10	6.91
3c	oil		69.80	5.86	7.40	69.51	6.01	7.26
4a	48.5-49.5	CH_2Cl_2-hexane	68.53	5.17	7.99	68.67	5.25	7.81
4b	51-53[a]		69.80	5.86	7.40	69.76	5.81	7.23
4c	170-180/0.35		69.80	5.86	7.40	69.94	6.01	7.38
4d	65-75/200		53.06	6.23	12.37	52.72	6.36	12.26
13b	105	CH_2Cl_2-hexane	57.95	4.37	6.75	58.11	4.25	6.75
14a	64-65	CH_2Cl_2-Et_2O	41.36	4.86	9.65	41.38	4.88	9.62
14b	148.5-149.5	CH_2Cl_2-Et_2O	57.95	4.37	6.75	58.02	4.51	6.82

[a] Melting point of material that crystallized spontaneously after chromatographic purification.

ready been reported in the thiophene series.[14,19]

Experimental Section

The melting points were determined in a Mel-Temp melting point apparatus and are corrected. The NMR spectra were measured with a Varian HA-100 or a Bruker WM 300 spectrometer and are expressed in parts per million (δ) from internal tetramethylsilane. The N-unsubstituted compounds were exchanged with deuterium oxide before the spectra were recorded. The NMR spectral data for the pyrrole protons of the monosubstituted pyrroles are found in Table II. The infrared spectra were recorded with a Perkin-Elmer Model 237 grating infrared spectrometer. The ultraviolet spectra were obtained with a Perkin-Elmer Model 402 ultraviolet–visible spectrometer.

The sulfoxides **1a–2c** were prepared as described previously.[2] 2-(Methylsulfinyl)pyrrole (**1d**), a known compound,[20] was prepared (80% yield) by the periodate oxidation of 2-(methylthio)pyrrole,[11] as described[2] for the synthesis of 2-(benzylsulfinyl)pyrrole. 2-(Methylsulfonyl)pyrrole (**13a**), also a known compound, was synthesized in the manner described herein (see below) for 2-(phenylsulfonyl)pyrrole (**13b**).

3-(Methylsulfinyl)pyrrole (2d). A solution of 2-(methylsulfinyl)pyrrole (**1d**; 1.29 g, 10 mmol) in benzene (200 mL) containing *p*-toluenesulfonic acid monohydrate (1.90 g, 10 mmol) was stirred at room temperature for 16 h. The solvent was removed in vacuo and the residue was dissolved in dichloromethane. Excess solid sodium bicarbonate was added and, after vigorous agitation, the mixture was filtered. The filtrate and a dichloromethane wash of the solid were combined and evaporated in vacuo. The residue (1.24 g, mp 121.5–124.5 °C) was washed with ether and then subjected to column chromatography on neutral alumina (Fluka, Activity II, 25 g), using dichloromethane to elute the product (0.877 g, 68%), which was crystallized from methanol–ether for analysis; UV (MeOH) 215 nm, 230 (ϵ 5130, 4270). The NMR spectral data for the pyrrole protons of this and the other new monosubstituted pyrroles are found in Table II.

The melting points, microanalytical figures, etc., for this and the other monosubstituted pyrroles are found in Table III.

Reduction of the Sulfoxides. Method A. Triphenylphosphine–Iodine–Sodium Iodide. Triphenylphosphine (1.125 mmol) was added in small portions to a stirred solution of iodine (1.00 mmol) in acetonitrile (10 mL) at room temperature. Immediately thereafter the sulfoxide (1.00 mmol) and anhydrous sodium iodide (2.00 mmol) were added simultaneously. For the 3-sulfinylpyrroles the reduction was complete almost immediately. The mixture was then poured into 10% sodium thiosulfate solution (25 mL) and the product was extracted into ether. The extract was washed successively with 5% sodium bicarbonate solution and water, and then it was dried over sodium sulfate. The solvent was removed in vacuo and the residue was purified in a manner that depended on the compound being synthesized (see below).

3-(Phenylthio)pyrrole (4a). The crude product was chromatographed on neutral alumina (Fluka, Activity II, 60 g/5 mmol reaction). The column was eluted first with hexane and then with hexane–dichloromethane (4:1) to give the TLC pure product (95%); UV (MeOH) 213 nm, 255 (ϵ 13500, 12000).

***N*-Methyl-3-(phenylthio)pyrrole (4b).** The crude product was purified by chromatography on Activity II neutral alumina (20 g/5 mmol reaction), eluting first with hexane and with hexane–ethyl acetate (95:5) to give an oil. This oil was subjected to TLC on silica gel, using hexane–ethyl acetate (9:1) as the developing solvent, to give the crystalline product (82%); UV (MeOH) 211 nm, 255 (ϵ 18600, 14100).

3-(Benzylthio)pyrrole (4c). The crude product was chromatographed on Florisil (45 g/8.85 mmol reaction), eluting with hexane and then with hexane–dichloromethane to remove the product. The oily material thus obtained was further purified by TLC on silica gel, using hexane–ethyl acetate (4:1) as the developing solvent. This material was an oil (72%) homogeneous by TLC. For analysis, a specimen was purified by distillation in vacuo; UV (MeOH) 217 nm (ϵ 14100).

3-(Methylthio)pyrrole (4d). Purification of the crude product by TLC on silica gel, using hexane–ethyl acetate (85:15), gave the sulfide as an oil (97%), which was distilled in vacuo for analysis; UV (MeOH) 216 nm, 245 (ϵ 4570, 1510).

Method B. Triphenylphosphine–Carbon Tetrachloride. 2-(Phenylthio)pyrrole (3a). A solution 2-(phenylsulfinyl)pyrrole (0.096 g, 0.5 mmol) and triphenylphosphine (0.301 g, 1.15 mmol) in carbon tetrachloride (25 mL) was heated at reflux temperature for 5 h. The solvent was removed in vacuo and the residue was subjected to TLC on silica gel, using hexane–ethyl acetate (9:1) as the developing solvent, to give the TLC pure oil (0.080 g, 88%); UV (MeOH) 210 nm, 245 (ϵ 15500; 14800).

Method C. Sodium Borohydride–Cobalt Chloride. Cobalt chloride hexahydrate (1.0 mmol) was added to a cooled (4 °C), stirred solution of the sulfinyl compound (1.0 mmol) in 95% ethanol (50 mL). Immediately thereafter, sodium borohydride (10 mmol) was added and the reaction temperature was left to reach ambient. After reaction for the appropriate length of time (Table I) at room temperature, the mixture was heated on a steam bath for 0.5 h and then the alcohol was removed in vacuo. Water was added to the residue, the product was extracted into ether, and the extract was dried over sodium sulfate and evaporated in vacuo. The individual sulfides were purified as described below.

***N*-Methyl-2-(phenylthio)pyrrole (3b).** The crude product was chromatographed on Activity II neutral alumina, using hexane to elute the oily product (74%); UV (MeOH) 213 nm, 246 (ϵ 12900, 16600).

2-(Benzylthio)pyrrole (3c). The residue obtained from the reaction (81%) was pure by TLC. For analysis a portion was passed over a short column of Activity II neutral alumina, using hexane–ethyl acetate (9:1) as the eluting solvent. An oil was obtained; UV (MeOH) 218 nm, 249 (ϵ 10700, 6600).

Trifluoroacetic Acid Promoted Rearrangement of the Pyrrolyl Sulfides. A solution of the pyrrolyl sulfide (1.0 mmol) in anhydrous dichloromethane (100 mL) containing trifluoroacetic acid (2 mL) was stirred at 20 °C. Aliquots (3 mL) of this solution were periodically removed and washed with 5% sodium bicarbonate solution (20 mL). The organic phase was separated and combined with a dichloromethane extract (20 mL) of the aqueous phase, and the combined dichloromethane solutions were

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(20) Olson, R. K.; Snyder, H. R. *J. Org. Chem.* **1963**, *28*, 3050.

washed with water and dried over sulfate. The solvent was removed in vacuo, and the residue was dissolved in dichloromethane (ca. 0.5 mL) and subjected to quantitative analysis by gas–liquid chromatography on a 6-ft 3% silicone rubber SE 30 column, at a column temperature of 220 °C, using a Hewlett-Packard Model 5750 research chromatograph.

2,5-Bis(phenylthio)pyrrole (7). Sulfuryl chloride (10.0 g, 74 mmol) in dry dichloromethane (10 mL) was added dropwise to a stirred solution of diphenyl disulfide (16.0 g, 118.5 mmol) in anhydrous dichloromethane (70 mL) at −20 °C. When the addition was completed, the mixture was warmed to room temperature, and after 1 h this solution was added in a dropwise manner to a stirred solution of pyrrole (5.0 g, 74.5 mmol) and triethylamine (15 g, 148.5 mmol) in dimethylformamide (50 mL) at 0 °C. The mixture was stirred at room temperature for 2 h beyond the addition and then it was poured into a water–dichloromethane mixture. The organic phase was separated, washed successively with water and 10% sodium bicarbonate solution, dried over sodium sulfate, and evaporated in vacuo. The residue was dissolved in ether (200 mL), washed several times with water, dried, and evaporated in vacuo. The residue (21.7 g) was subjected to column chromatography on silica gel (500 g). Elution with hexane removed diphenyl disulfide. Elution with benzene–hexane (5:95) gave pure **7**, and further elution with benzene–hexane (1:9) gave **7** contaminated with 2-(phenylthio)pyrrole. Crystallization of both batches of the product from hexane gave the desired material (4.97 g, 24%) with mp 83–84 °C; UV (MeOH) 215 nm, 249 nm (ε 16 600, 22 300); NMR ($CDCl_3$) δ 6.62 (s, 2 H, H-3,4), 7.17 (m, 10 H, C_6H_5).

Anal. Calcd for $C_{16}H_{13}NS_2$: C, 67.80; H, 4.62; N, 4.94. Found: C, 67.84; H, 4.62; N, 5.01.

2,4-Bis(phenylthio)pyrrole (8). A solution of compound **7** (0.50 g) in trifluoroacetic acid (10 mL) was left at room temperature for 6 h. The mixture was diluted with benzene and evaporated to dryness. Benzene was added to the residue, and after evaporation in vacuo again, the solid crude product was chromatographed on a short column of Florisil. The product was eluted with hexane (0.384 q, 77%) and after one crystallization from this solvent it had mp 74–5 °C; UV (MeOH) 214 nm, 251 (ε 19 500, 23 400); NMR ($CDCl_3$) δ 6.70 (d, 1 H, J = 1.5 Hz, H-3), 7.07 (d, 1 H, J = 1.5 H-, H-5), 7.25 (m, 10 H, C_6H_5).

Anal. Calcd for $C_{16}H_{13}NS_2$: C, 67.80; H, 4.62; N, 4.94. Found: C, 67.80; H, 4.64; N, 5.02.

1-Methyl-4*H*-[1]benzothiopyrano[2,3-*b*]pyrrol-4-one (10). A mixture of compound **9** (0.228 g)[21] and polyphosphoric acid (5 g) was heated to 190 °C for 7.5 h (no progress in reaction after 5 h by TLC). The mixture was poured into water and the product was extracted into dichloromethane. The extract was washed with water, dried over magnesium sulfate, and evaporated in vacuo. The residue was subjected to TLC on silica gel (dichloromethane) to give starting material (0.028 g) and the desired product (0.164 g, 72%). On crystallization from ether–dichloromethane this material had mp 146.5–147 °C; UV (MeOH) 223 nm, 249, 351 (ε 18 200, 28 200, 6610); IR (KBr) 1623 (sh), 1618, 1590, 1559 cm^{-1}; NMR ($CDCl_3$) δ 3.72 (s, 3 H, CH_3), 6.90 (d, 1 H, J = 3.1 Hz, H-3), 7.04 (d, 1 H, J = 3.1 Hz, H-2), 7.49–7.65 (m, 3 H, H-5,6,7), 8.73 (m, 1 H, J_o = 7.8 Hz, J_m = 0.9 Hz, J_p = 0.6 Hz).

Anal. Calcd for $C_{12}H_{19}NOS$: C, 66.95; H, 4.21; N, 6.51. Found: C, 66.87; H, 4.24; N, 6.49.

2-(Phenylsulfonyl)pyrrole (13b). A solution of 2-(phenylthio)pyrrole (1.08 g, 6.17 mmol) in dry dichloromethane (200 mL) containing 86% *m*-chloroperbenzoic acid (2.75 g, 13.7 mmol) was stirred at 0 °C for 1 h. The solution was washed successively with 5% sodium bicarbonate solution and water and then dried over sodium sulfate. The solvent was removed in vacuo and the residue was purified by TLC on silica gel, using hexane–ethyl acetate (3:2) as the developing solvent. This procedure gave a solid (0.772 g, 37%); UV (MeOH) 213 nm, 260 (ε 10 200, 10 700).

Methanesulfonic Acid Mediated Rearrangement of 2-Pyrrolyl Sulfones. Synthesis of 3-(Methylsulfonyl)pyrrole (14a) and 3-(Phenylsulfonyl)pyrrole (14b). A solution of the 2-sulfonylpyrrole (1 mmol) in 1,2-dichloroethane (10 mL) containing methanesulfonic acid (0.5 mL) was heated at reflux temperature, with protection from moisture, until TLC analysis showed that the reaction was not advancing further (6 h for **13a**, 2 h for **13b**). The solution was slurried with solid sodium carbonate (5 g) suspended in dichloromethane and the organic layer was poured onto a short column of silica gel. The column was first eluted with dichloromethane and then the product was washed off the column with ether.

3-(Methylsulfonyl)pyrrole was obtained in 88% yield; UV (MeOH) 230 nm (ε 2820).

3-(Phenylsulfonyl)pyrrole was isolated in 77% yield; UV (MeOH) 232 nm, 275 (ε 8320, 1415).

Registry No. 1a, 75421-79-3; **1b**, 75421-81-7; **1c**, 75421-86-2; **1d**, 82511-53-3; **2a**, 75421-88-4; **2b**, 75421-90-8; **2c**, 75421-93-1; **2d**, 82511-47-5; **3a**, 79600-35-4; **3b**, 82511-48-6; **3c**, 75421-96-4; **4a**, 82511-49-7; **4b**, 82511-50-0; **4c**, 82511-51-1; **4d**, 82511-52-2; **7**, 82511-54-4; **8**, 82511-55-5; **9**, 82511-56-6; **10**, 82511-57-7; **13a**, 82511-61-3; **13b**, 82511-58-8; **14a**, 82511-59-9; **14b**, 82511-60-2; diphenyl disulfide, 882-33-7; pyrrole, 109-97-7; *N*-methylpyrrole, 96-54-8; *o*-chlorothiobenzoyl chloride, 3950-02-5.

(21) Compound **9** was prepared from *N*-methylpyrrole and *o*-chlorothiobenzoyl chloride[22] in pyridine at room temperature. It had mp 100–101 °C; UV (MeOH) 215 nm, 242, 267, 308, 362 (sh) (ε 19 500, 13 800, 10 500, 7590). Full details concerning the synthesis of this compound, and derivatives thereof, will be published elsewhere (Greenhouse, R.).

(22) Morley, J. S. British Patent 848 130, 1960; *Chem. Abstr.* **1961**, *55*, 9430c.