Synthesis and Rearrangement of 2-(Arylsulfinyl)- and 2-(Alkylsulfinyl)pyrroles[1]

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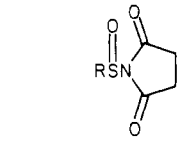
Pyrrole and *N*-methylpyrrole reacted with aryl- and alkylsulfinyl chlorides, at 0 °C, to give the corresponding 2-sulfinylpyrroles as the major products only when contact of the products with the liberated hydrogen chloride was minimized or eliminated. If this precaution was not taken, the 3-sulfinylpyrroles were the principle products. In contrast, *N*-(phenylsulfinyl)succinimide (**2a**) reacted, at room temperature, with a variety of pyrroles to produce the 2-phenylsulfinyl compounds in good yields. The 2-(arylsulfinyl)- and 2-(alkylsulfinyl)pyrroles undergo a remarkably facile acid-promoted rearrangement to the isomeric 3-sulfinylpyrroles. This transposition is, at least in part, an intermolecular process as demonstrated by crossover experiments.

In connection with other research in progress in these laboratories, a method was required for the synthesis of 2-(arylsulfinyl)pyrroles. Such compounds ought to be preparable by means of a two-step process involving sulfenylation of the pyrrole with an arylsulfenyl halide[3,4] followed by selective oxidation of the sulfide thus produced to the sulfoxide.[5,6] The polysubstitution of undeactivated pyrroles with sulfenyl halides can, however, be difficult to prevent,[3,7] and therefore, the direct introduction of the deactivating sulfinyl group would be synthetically attractive. Inasmuch as the transfer capacity of an arylsulfinyl moiety is equivalent to or exceeds that of an aryl carbonyl group in mixed sulfinic acid–carboxylic acid anhydrides,[8] it was considered probable that arylsulfinyl chlorides or *N*-(arylsulfinyl)imides would function as effective reagents for the synthesis of monoarylsulfinylpyrroles. In this connection it is noteworthy that sulfinyl halides have rarely[9] been utilized in Friedel–Crafts-type reactions with aromatic substrates, and reactions with heteroaromatic compounds have not heretofore been reported.

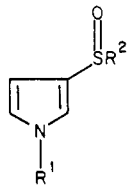
The reaction of phenylsulfinyl chloride (**1a**) or *p*-toluenesulfinyl chloride (**1b**) with pyrrole, in dichloromethane solution at 0 °C, was complete within 30 min. Removal of the solvent in vacuo and separation of the products by TLC on silica gel gave a major and a minor, less polar, monoarylsulfinylpyrrole (15:1 and 4:1 ratios for **1a** and **1b**, respectively) for each reaction. The NMR spectra (Table I) of the products possessed three multiplets situated at δ 6.1–7.0 with coupling constants of 1.7–1.8, 2.0–2.2, and 3.1–3.2 Hz for the major compounds and 1.5, 2.8, and 3.8 Hz for the minor components. This data clearly established[10] that the more and less abundant products were the 3-(arylsulfinyl)pyrroles (**4a,b**) and the 2-(arylsulfinyl)pyrroles (**3a,b**), respectively. The formation of a 3-(arylsulfinyl)pyrrole as the major kinetic product is most unlikely,[11] and therefore, rearrangement of the 2-arylsulfinyl compound, presumably catalyzed by the liberated hydrogen chloride, must have taken place during the course of the reaction and/or the workup procedure. If the reaction mixture was washed with sodium bicarbonate solution prior to removal of the solvent, then the proportion of the 3-isomer was greatly attentuated for phenylsulfinyl chloride (**3a**:**4a** = 4.3) but only moderately altered for *p*-toluenesulfinyl chloride (**3b**:**4b** = 0.7). 2-(*p*-Toluenesulfinyl)pyrrole (**3b**) was, however, the principle product (**3b**:**4b** = 5.0) if the sulfinylation reaction was effected in the presence of 2 equiv of triethylamine.

1a, R = C_6H_5
b, R = 4-$CH_3C_6H_4$
c, R = *n*-C_4H_9

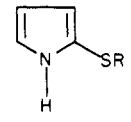


2a, R = C_6H_5
b, R = $C_6H_5CH_2$

3a, R^1, R^3 = H; R^2 = C_6H_5
b, R^1, R^3 = H; R^2 = 4-$CH_3C_6H_4$
c, R^1 = CH_3; R^2 = C_6H_5; R^3 = H
d, R^1 = CH_3; R^2 = 4-$CH_3C_6H_4$; R^3 = H
e, R^1 = R^3 = H; R^2 = *n*-C_4H_9
f, R^1 = $(CH_2)_2OAc$; R^2 = C_6H_5; R^3 = H
g, R^1 = H; R^2 = C_6H_5; R^3 = SCH_3
h, R^1, R^3 = H; R^2 = $CH_2C_6H_5$
i, R^1 = CH_3; R^2 = $CH_2C_6H_5$; R^3 = H



4a, R^1 = H; R^2 = C_6H_5
b, R^1 = H; R^2 = 4-$CH_3C_6H_4$
c, R^1 = CH_3; R^2 = C_6H_5
d, R^1 = CH_3; R^2 = 4-$CH_3C_6H_4$
e, R^1 = $(CH_2)_2OAc$; R^1 = C_6H_5
f, R^1 = H; R^2 = $CH_2C_6H_5$
g, R^1 = CH_3; R^2 = $CH_2C_6H_5$



5a, R = CH_3
b, R = *n*-C_4H_9
c, R = $CH_2C_6H_5$

The general pattern of the reaction of *N*-methylpyrrole with the sulfinyl chlorides **1a** or **1b** was similar to that observed for pyrrole, except that the proportion of the 2-isomers isolated was greatly reduced unless the reactions were effected in the presence of triethylamine.

The reaction of *n*-butanesulfinyl chloride (**1c**) was examined only in a cursory manner. After basic workup of the reaction mixture, 2-(butanesulfinyl)pyrrole (**3e**),

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Table I. NMR Data for Pyrrolyl Sulfoxides

compd	chemical shifts, δ				coupling constants, Hz[a]				
	H-2	H-3	H-4	H-5	$J_{2,4}$	$J_{2,5}$	$J_{3,4}$	$J_{3,5}$	$J_{4,5}$
3a		6.52 (q)	6.14 (q)	6.86 (q)			3.8	1.5	2.8
3b		6.47 (q)	6.12 (q)	6.86 (q)			3.8	1.5	2.8
3c		6.54 (q)	6.11 (q)	6.73 (t)			4.0	1.8	2.8
3d		6.50 (q)	6.09 (q)	6.70 (t)			4.0	1.9	2.8
3e		6.57 (q)	6.13 (q)	6.95 (q)			3.8	1.5	2.8
3f		6.53 (q)	6.15 (q)	6.84 (q)			4.1	1.8	2.9
3g		6.45 (d)	6.16 (d)				3.8		
3h		6.37 (q)	6.11 (q)	6.95 (q)			3.8	1.5	2.8
3i		6.59 (q)	6.15 (q)	6.64 (t)			4.3	1.5	2.9
4a	7.00 (t)		6.11 (q)	6.63 (q)	1.7	2.0			3.1
4b	6.95 (t)		6.07 (q)	6.57 (t)	1.8	2.1			3.2
4c	6.94 (t)		6.12 (q)	6.55 (t)	1.9	2.3			3.1
4d	6.91 (t)		6.11 (q)	6.54 (t)	1.8	2.2			3.0
4e	7.03 (t)		6.16 (q)	6.64 (q)	1.9	2.2			3.2
4f	6.76 (t)		6.40 (q)	6.67 (q)	1.7	2.1			3.1
4g	6.82 (t)		6.34 (q)	6.75 (t)	1.8	2.4			3.0

[a] Coupling constants of all N-unsubstituted compounds measured after D_2O exchange.

Table II. Pyrrolyl Sulfoxides

compd	yield, %	mp, °C	recryst solvent	% calcd			% found		
				C	H	N	C	H	H
3a	77[a]	92-93	ether	62.80	4.74	7.32	62.93	4.85	7.35
3b	35[b]	100-103	CH_2Cl_2-ether	64.36	5.40	6.82	64.71	5.26	6.79
3c	65[a]	57-58	ether-hexane	64.36	5.40	6.82	64.40	5.48	6.75
3d	90[b]	47.5-48.5	ether-hexane	65.72	5.98	6.39	65.34	5.96	6.35
3e	58[c]	48-49	hexane	56.10	7.65	8.18	56.21	7.55	8.19
3f	74[a]	oil		60.62	5.45	5.05	60.70	5.53	5.12
3g	73[a]	75-76	CH_2Cl_2-hexane	55.66	4.67	5.90	55.65	4.66	5.89
3h	72[d]	164-165	CH_2Cl_2-hexane	64.36	5.40	6.82	64.17	5.42	6.72
3i	91[e]	93	ether-hexane	65.72	5.98	6.39	65.80	6.09	6.24
4a	70[f]	139-140	benzene	62.80	4.74	7.32	62.66	4.75	7.33
4b	62[g]	151-151.5	benzene	64.36	5.40	6.82	64.16	5.33	6.90
4c	71[h]	82-83	EtOAc-hexane	64.36	5.40	6.82	64.60	5.36	6.77
4d	55[g]	85-86	benzene-hexane	65.72	5.98	6.39	65.56	5.97	6.49
4e	68[h]	69-70	ether	60.62	5.45	5.05	60.65	5.39	5.02
4f	41[f]	96-97	EtOAc	64.36	5.40	6.82	64.17	5.48	6.63
4g	74[f]	66-67	CH_2Cl_2-ether	65.72	5.98	6.39	65.59	6.02	6.45

[a] From *N*-(phenylsulfinyl)succinimide. [b] From *p*-toluenesulfinyl chloride in presence of triethylamine (2 equiv). [c] By *m*-chloroperbenzoic acid oxidation of **5b**. [d] By periodate oxidation of **5c**. [e] By alkylation of **3h**. [f] By *p*-toluenesulfonic acid rearrangement of the corresponding 2-isomer. [g] From *p*-toluenesulfinyl chloride with evaporative workup. [h] Formed on attempted crystallization of the corresponding 2-isomer.

identical with the *m*-chloroperbenzoic acid oxidation product of 2-butylthiopyrrole (**5b**), was the sole compound isolated.

Whereas the formation of 3-substituted pyrroles could not be prevented when sulfinylation was effected with arylsulfinyl chlorides, *N*-(phenylsulfinyl)succinimide (**2a**) reacted with a variety of pyrroles, in dichloromethane at room temperature, to give the corresponding pyrroles **3a**, **3c**, **3f**, and **3g** in good yields (Table II). These reactions were very clean and, although the 3-isomers could be detected in the crude reaction mixtures by TLC, particularly after very long reaction periods, the amounts thereof were usually minor (≤10%).

In contrast to the imide **2a**, *N*-(benzylsulfinyl)succinimide (**2b**) did not react with pyrrole or *N*-methylpyrrole at room temperature. Sulfinylation did, however, take place in benzene at reflux temperature (72 °C in Mexico City!), and the 2-substituted products **3h** and **3i** could be isolated in low yields after short reaction periods. Longer reaction times resulted in the formation of complex mixtures from which small amounts of the 3-(benzylsulfinyl)pyrroles (**3f**) and (**3g**) could be isolated. Authentic 2-(benzylsulfinyl)pyrrole was more conveniently prepared by the periodate oxidation of 2-(benzylthio)pyrrole (**5c**) which in turn was synthesized by the alkylation of in situ generated sodium pyrrole-2-thiolate[6] with benzyl bromide. *N*-Methyl-2-(benzylsulfinyl)pyrrole (**3i**) was prepared in high yield by alkylation of the sodium salt of 2-(benzylsulfinyl)pyrrole with methyl iodide.

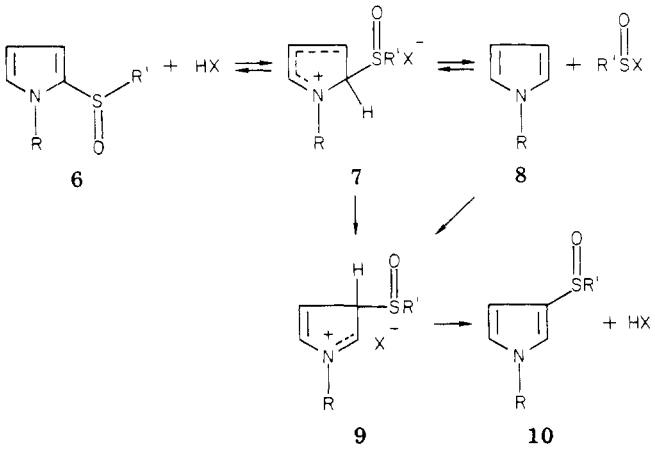
Evidence in support of the acid-promoted transposition of 2-(arylsulfinyl)pyrroles to 3-(arylsulfinyl)pyrroles was presented at the beginning of this paper. The rearrangement was, in fact, readily effected, commencing with the pure 2-substituted compounds. Thus, 2-(phenylsulfinyl)pyrrole was entirely converted into the 3-isomer (45% yield) in 1 h at room temperature in dichloromethane containing 1 equiv of hydrochloric acid. The yield of 3-(phenylsulfinyl)pyrrole was considerably improved (70%) when the rearrangement was carried out in benzene containing *p*-toluenesulfonic acid hydrate (1 equiv). The 3-sulfinylpyrroles **4f** and **4g** were also prepared by means of this technique.

Although rate constants were not determined, the rearrangement of the 2-(arylsulfinyl)pyrroles was distinctly more rapid (≤6 h) than that of the 2-benzylsulfinyl compounds **4h** and **4i** (≥15 h). Furthermore the N-substituted compounds underwent the transposition with greater facility (Indeed, in some cases extraordinary facility!) than did the N-substituted analogues. For example, 1-(2-acetoxyethyl)-2-(phenylsulfinyl)pyrrole (**3f**, an oil) gave the

3-isomer **4c** (a solid) on attempted crystallization from chlorinated hydrocarbon solvents, and *N*-methyl-2-(phenylsulfinyl)pyrrole (**3c**) rearranged at room temperature if it was stored in an acid-washed glass container.

Additional information concerning the mechanism of the isomerization was derived from crossover experiments. Rearrangement of 2-(phenylsulfinyl)pyrrole (**3a**, 1 equiv) in the presence of *N*-methylpyrrole (1 equiv), under standard conditions (benzene, 1 equiv of *p*-toluenesulfonic acid hydrate, room temperature, 6 h), gave 3-(phenylsulfinyl)pyrrole (**4a**, 73%) and *N*-methyl-3-(phenylsulfinyl)pyrrole (**4c**, 18%). When the reaction was carried out in the presence of 50 equiv of *N*-methylpyrrole the crossover product **4c** was isolated in 46% yield together with a lesser amount (26%) of 3-(phenylsulfinyl)pyrrole. During the course of these reactions, a small amount of *N*-methyl-2-(phenylsulfinyl)pyrrole (**3c**) could be detected by TLC. Finally, rearrangement of *N*-methyl-2-(phenylsulfinyl)pyrrole (1 equiv) in the presence of 1 molar equiv of pyrrole gave both the normal and crossed transposed products **4c** and **4a** in 64% and 26% yields, respectively.

The above data is consistent with a transposition mechanism where the process is initiated by protonation of the 2-sulfinylpyrrole **6** at C-2. The σ complex **7** thus produced, could dissociate to the pyrrole **8** or undergo a sigmatropic rearrangement to the isomeric σ complex **9**. Proton loss from **9**, which could also be formed by direct electrophilic substitution of the pyrrole **8** at C-3, would complete the isomerization to the 3-sulfinylpyrrole **10**.



The rearrangement reaction described in this paper is undoubtedly mechanistically similar to the acid-induced transposition of 2-acylpyrroles to 3-acylpyrroles which was recently reported by Carson.[12] The latter reactions are, however, at least two orders of magnitude slower than the sulfinyl group migrations described herein. *Finally, the data given herein, as well as that of Carson, demonstrate that the formation and rearrangement of 2-substituted pyrroles can take place at comparable rates. Therefore, mechanistic conclusions based on product distributions obtained in the electrophilic substitution of pyrroles should be made with circumspection in the absence of kinetic information on the ratios of the products.*

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 spectrometer, in deuteriochloroform solution, and are expressed as parts per million (δ) from internal tetramethylsilane.

The following compounds are known and the synthesis thereof has been described in the literature: phenylsulfinyl chloride,[13] *p*-toluenesulfinyl chloride,[14] *n*-butanesulfinyl chloride,[13] 1-(2-acetoxyethyl)pyrrole,[15] and 2-(methylthio)pyrrole.[6,7]

***N*-(Phenylsulfinyl)succinimide (2a).** *N*-(Phenylsulfenyl)succinimide, the precursor of **2a**, was synthesized by the method of Buchel and Conte[16] from *N*-bromosuccinimide and diphenyl disulfide, except that the reaction was initiated and sustained by irradiation with a sun lamp (four 5-min irradiations during a 3-h reaction period). This compound was then oxidized to the sulfinylimide **2a** with *m*-chloroperbenzoic acid (in dichloromethane instead of chloroform solution) according to a published procedure.[17] The crude product (72–84% yield), after evaporation of the solvent and trituration with ether, had mp 79–81 °C. The sulfoxide obtained in this way was sufficiently pure to be used as such. It was unstable at room temperature, but could be stored at 0 °C for short periods of time without appreciable decomposition.

***N*-(Benzylsulfinyl)succinimide (2b).** *N*-(Benzylsulfinyl)-succinimide was prepared according to a method provided by Kluge (see acknowledgment). To a stirred and boiling solution of *N*-chlorosuccinimide (2.70 g) in dry benzene (75 mL), maintained in a nitrogen atmosphere, was added a solution of benzyl mercaptan (2.48 g), in the same solvent (25 mL), over a 1-h period. After a further 1 h at reflux, the solution was cooled to room temperature and triethylamine (2.10 g) was added in a dropwise manner. Heating at reflux temperature was reinitiated and maintained for 50 min. The mixture was then stirred at room temperature for 1.5 h, the solvent was removed in vacuo, and the residue was suspended in hexane. The solid was collected by filtration, washed well with hexane and water, taken up in dichloromethane, and then dried. Removal of the solvent in vacuo gave a solid (1.30 g) which after crystallization from dichloromethane–hexane had mp 157–159 °C (lit.[16] mp 165–166 °C). This material was then oxidized to the sulfinyl compound in the manner described above (90% yield). The crude, unstable sulfoxide (mp 116–117 °C) was used without further purification.

Sulfinylation of Pyrroles with Sulfinyl Chlorides. Method A. To a solution of the freshly prepared sulfinyl chloride (1 equiv) in anhydrous dichloromethane (2.5 mL/mmol of sulfinyl chloride), maintained in a nitrogen atmosphere and cooled in an ice bath, was added a solution of the pyrrole (1 equiv) in dichloromethane (2.5 mL/mmol of pyrrole). The reaction was usually complete within 30 min. The solvent was removed in vacuo at 30 °C, dichloromethane was added to the residue, and the solution was evaporated again. A few drops of triethylamine was added to the crude product which was then purified in a manner dependent on the sulfinyl compounds being synthesized (see below).

Method B. The procedure was identical with that of method A except that when the reaction had ended the solution was washed with 10% sodium bicarbonate or 10% sodium carbonate solution. The organic phase was dried over a mixture of sodium sulfate and sodium bicarbonate and then evaporated in vacuo. A few drops of triethylamine was added to the residue which was then purified as described below.

Method C. To a solution of the sulfinyl chloride (1 equiv) in dry dichloromethane (2.5 mL/mmol of sulfinyl chloride), cooled to 0 °C in a nitrogen atmosphere, was added a solution of the pyrrole (1 equiv) in dichloromethane (2.5 mL/mmol of pyrrole) containing triethylamine (2 equiv). After 20 min, the solution was washed with water, dried over sodium sulfate, and evaporated in vacuo. Triethylamine was added to the residue before separation of the mixture was effected.

Separation and Purification of Sulfinyl Compounds. For all of the cases examined to date, the 3-sulfinylpyrroles were more polar than the isomeric 2-sulfinylpyrroles. Compounds **3a** or **3b** could be separated from compounds **4a** or **4b** by TLC on silica gel, using dichloromethane–methanol (97.5:2.5) as the developing

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solvent system. Compounds **3b** and **4b** could also be separated by column chromatography on Florisil. The 2-isomer **3b** was eluted with ether and 3-(*p*-toluenesulfinyl)pyrrole (**4b**) was eluted with ethyl acetate. Compounds **4b** and **4d** could be obtained pure from mixtures rich in these substances by direct crystallization. 2-(Butanesulfinyl)pyrrole (**3e**) was isolated from the reaction mixture by column chromatography on silica gel, using chloroform–methanol (99:1) as the eluting solvent.

The combined yields of the (arylsulfinyl)pyrroles obtained in this way were 50–90%. 2-(Butanesulfinyl)pyrrole was isolated in 21% yield.

Sulfinylation of Pyrroles with *N*-(Phenylsulfinyl)-succinimide. Equimolar amounts of the pyrrole and *N*-(phenylsulfinyl)succinimide in dichloromethane solution (5–10 mL/mmol) were stirred at room temperature in a nitrogen atmosphere until the 3-phenylsulfinyl isomer was detectable (ca. 40 h) by TLC. Reactions which were extended much beyond this time yielded the 2-(phenylsulfinyl)pyrrole contaminated with 15–20% of the 3-isomer. The solvent was removed in vacuo and the residue was purified by TLC, using ethyl acetate–hexane (1:1) as the developing solvent for compounds **3a**, **3f**, and **3g** and ethyl acetate–hexane (3:2) for **3c**.

Sulfinylation of Pyrroles with *N*-(Benzylsulfinyl)-succinimide. A solution of the pyrrole (1 equiv) in anhydrous benzene (10 mL/mmol of pyrrole) containing *N*-(benzylsulfinyl)succinimide (1.1 equiv) was heated at reflux temperature in a nitrogen atmosphere for 4–4.5 h at which time the amount of the rearranged products was still minimal. The solution was washed well with water, dried over sodium sulfate, and evaporated in vacuo. The residue was percolated through a short column of Florisil, using dichloromethane for compound **3h** and ethyl acetate–hexane (1:1) for **3i**. The mixture obtained in this was subjected to TLC on silica gel, using dichloromethane–methanol (9:1) as the developing solvent. Both of the sulfinyl compounds were obtained in about 12% yield.

***p*-Toluenesulfonic Acid Promoted Rearrangement of 2-Sulfinylpyrroles.** Equimolar amounts of the 2-sulfinylpyrrole and *p*-toluenesulfonic acid hydrate were dissolved in anhydrous benzene (2.5 mL/mmol of pyrrole) and stirred at room temperature until TLC showed that the starting material had disappeared (ca. 6 h for the (arylsulfinyl)pyrroles, 16–30 h for the (benzylsulfinyl)pyrroles). The solution was poured into water, and the organic phase was separated and combined with an ethyl acetate extract of the aqueous phase. The combined organic phases were washed with water, dried over sodium sulfate, and evaporated in vacuo. *N*-Methyl-3-(benzylsulfinyl)pyrrole (**4g**) was purified by TLC on silica gel, using ether–triethylamine (95:5) as the eluting solvent. The other 3-substituted compounds could be crystallized directly.

Synthesis of 2-(Aklylsulfinyl)pyrroles by Oxidation of 2-(Alkylthio)pyrroles. Equimolar amounts of 2-(thiocyano)-pyrrole[6] and the alkyl bromide were dissolved in methanol (2 mL/mmol) and cooled to 0 °C. A solution of potassium hydroxide (1 equiv) in 50% aqueous methanol (4 mL/mmol) was then added at a rate such that the reaction temperature did not exceed 15 °C. The reaction was then stirred in an ice bath until the thiocyano compound was consumed (≤3 h). The reaction was poured into water, the product was extracted into ether, and the extract was dried over sodium sulfate and evaporated in vacuo. 2-(Butylthio)pyrrole (**5b**) was isolated from the crude product by column chromatography on silica gel, using dichloromethane–ethyl acetate (9:1) as the eluant. The product thus obtained (42% yield) was used without characterization in the next step. 2-(Benzylthio)-pyrrole (**5c**) was obtained from the crude product by column chromatography on Florisil, using hexane as the eluant. The benzylthio compound [90% yield; NMR ($CDCl_3$) δ 3.76 (s, 3 H), 6.03–6.63 (m, 2 H), 6.66 (m, 1 H), 6.98–7.30 (m, 5 H), 7.70 (m, 1 H)] was used as such in the next reaction.

2-(Butanesulfinyl)pyrrole (3e) was prepared from **5b** as follows. *m*-Chloroperbenzoic acid (1.30 g, 7.55 mmol) was added portionwise to a solution of 2-(butylthio)pyrrole (1.10 g, 7.1 mmol) in dichloromethane (30 mL). After a further 30 min, the solution was poured into water, and the organic phase was separated, washed with 2% aqueous potassium hydroxide solution, and dried. The solvent was removed in vacuo and the residue was subjected to column chromatography on silica gel (30 g). The product (0.70 g, 58%) was eluted with dichloromethane–ethyl acetate (1:1). After crystallization from hexane it had mp 48–49 °C and was identical with **3e** prepared from butanesulfinyl chloride.

2-(Benzylsulfinyl)pyrrole (3h) was synthesized by periodate oxidation of **5c**. Thus, to a stirred soolution of the benzylthio compound (1.89 g, 10 mmol) in 50% aqueous methanol (40 mL), at 0 °C, was added 0.25 M sodium periodate solution (42 mL, 50% aqueous methanol) in a dropwise manner. When the starting material was no longer observable by TLC, the solution was extracted with dichloromethane. The extract was washed with water, dried, and evaporated. Crystallization of the residue from dichloromethane–hexane gave the sulfinyl compound (1.47 g, 72%), mp 164–165 °C, identical with 2-(benzylsulfinyl)pyrrole synthesized from **2b** and pyrrole.

***N*-Methyl-2-(benzylsulfinyl)pyrrole (3i).** Sodium hydride in mineral oil (0.060 g, 50%) was added in one lot to a stirred solution of 2-(benzylsulfinyl)pyrrole (0.205 g, 1 mmol) in anhydrous dimethylformamide (5 mL) at 0 °C (nitrogen atmosphere). After 1.2 h, methyl iodide (0.2 mL) was added; the reaction was complete in a few seconds. The reaction was diluted with water and the product was extracted into ethyl acetate. The extract was washed with water, dried, and evaporated. Crystallization of the residue from ethyl acetate–hexane gave the product (0.198 g, 91%), mp 93 °C. It was identical with *N*-methyl-2-(benzylsulfinyl)pyrrole obtained by direct sulfinylation of *N*-methylpyrrole.

Crossover Experiments. A solution of equimolar amounts of the appropriate 2-(phenylsulfinyl)pyrrole (**3a** or **3c**) and *p*-toluenesulfonic acid monohydrate in benzene (30 mL/mmol of sulfinyl compound) containing the required quantity (1 or 50 equiv) of *N*-methylpyrrole or pyrrole was stirred at room temperature for 6 h. The solvent was removed in vacuo and the mixture thus obtained was subjected to TLC on silica gel, using ether–triethylamine (95:5) as the developing solvent.

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Registry No. **1a**, 4972-29-6; **1b**, 10439-23-3; **1c**, 13455-88-4; **2a**, 75421-77-1; **2b**, 75421-78-2; **3a**, 75421-79-3; **3b**, 75421-80-6; **3c**, 75421-81-7; **3d**, 75421-82-8; **3e**, 75421-83-9; **3f**, 75421-84-0; **3g**, 75421-85-1; **3h**, 75421-86-2; **3i**, 75421-87-3; **4a**, 75421-88-4; **4b**, 75421-89-5; **4c**, 75421-90-8; **4d**, 75421-91-9; **4e**, 75421-92-0; **4f**, 75421-93-1; **4g**, 75421-94-2; **5a**, 53391-61-0; **5b**, 75421-95-3; **5c**, 75421-96-4; diphenyl disulfide, 882-33-7; *N*-bromosuccinimide, 128-08-5; *N*-phenylsulfenylsuccinimide, 14204-24-1; benzyl mercaptan, 100-53-8; 2-(thiocyano)pyrrole, 66786-05-8; *N*-benzylsulfenylsuccinimide, 14204-23-0.