Even in unstrained systems, LCAO-MO-SCF calculations and valence bond–structure resonance theory give much better correlations of the rate data (r = 0.987 and 0.977, respectively) than do the Dewar reactivity numbers and HMO localization energies (r = −0.900 and −0.873) as reported previously.[5]

Acknowledgment. Cyril Párkányi and William C. Herndon acknowledge the financial support of the Robert A. Welch Foundation.

Registry No. Hexahelicene, 187-83-7; pentahelicene, 188-52-3; tetrahelicene, 195-19-7; phenanthrene, 85-01-8; hydrogen, 1333-74-0.

Substitution at Tricoordinate Sulfur(IV). Rearrangement of Sulfinanilides to Anilino Sulfoxides[1]

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Seven *N*-methyl-*N*-aryl-*p*-toluenesulfinamides (**1**, 3-$Me_2NC_6H_4$; **2**, 3-$MeOC_6H_4$; **3**, 4-$MeOC_6H_4$; **4**, 3-MeC_6H_4; **5**, Ph; **6**, 3-ClC_6H_4; **7**, 3-FC_6H_4), *N*-(3-methoxyphenyl)-*p*-toluenesulfinamide (**8**), and two *N*-methyl-*N*-arylmethanesulfinamides (**9**, 3-$Me_2NC_6H_4$; **10**, 3-$MeOC_6H_4$) were prepared from the corresponding sulfinyl chloride and the substituted aniline. Sulfinanilides **2** and **7** were treated with alkyllithiums in vain attempts to induce rearrangement to the diaryl sulfoxides via endocyclic nucleophilic attack by carbon 2 of the aniline ring on sulfur. Instead, the alkyllithium cleaved the S–N bond to yield the aniline and alkyl *p*-tolyl sulfoxide. Upon treatment with gaseous HCl in chloroform, the sulfinanilides rearranged as follows: **1** gave 4-(dimethylamino)-2-(methylamino)-4′-methyldiphenyl sulfoxide (92% yield), **2** gave 2-methoxy-4-(methylamino)-4′-methyldiphenyl sulfoxide (26% yield) and 4-methoxy-2-(methylamino)-4′-methyldiphenyl sulfoxide (70% yield), **4** gave 2-methyl-4-(methylamino)-4′-methyldiphenyl sulfoxide (71% yield), **9** gave methyl 4-(dimethylamino)-2-(methylamino)phenyl sulfoxide (20% yield), and **10** gave methyl 2-methoxy-4-(methylamino)phenyl sulfoxide (5% yield). Sulfinanilides **3** and **5**–**8** did not rearrange. A tentative mechanism for the rearrangement is proposed.

Nucleophilic substitution at tricoordinate sulfur(IV), exemplified in this paper by sulfinyl sulfur, is a well-known much-studied reaction process of both synthetic importance and mechanistic interest (eq 1, n and m = 0, ±1,...).[2,3]

$$Nu:^{n} + R-\overset{O}{\overset{\|}{S}}-L^{m} \longrightarrow R-\overset{O}{\overset{\|}{S}}-Nu^{1-n} + L:^{m-1} \qquad (1)$$

Inversion of configuration at the sulfur atom has been observed in most cases subjected to stereochemical analysis, but retention and racemization have also been noted. The inversion reaction may follow an S_N2-like pathway via a trigonal-bipyramidal intermediate with the nucleophilic (Nu), sulfur atom, and leaving group (L) approximately colinear, but other stereochemical situations are conceivable and have been proposed; e.g., both nucleophile and leaving group could be arranged equatorially. Retention reactions are thought to proceed via equatorial-apical disposition of Nu and L with perhaps limited pseudorotation (ligand permutation) of an intermediate. Racemization could proceed in a number of ways.

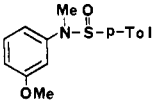
In order to investigate the stereochemistry of substitution as a function of the Nu–S–L angle, we synthesized the *N*-methyltoluene- and *N*-methylmethanesulfinanilides (**1**–**10**), which are listed in Table I.

We hoped that removal of a proton ortho to the amide nitrogen by a base would lead to endocyclic nucleophilic attack on sulfur by carbon to give a sulfoxide. For example, sulfinamide **2** would give sulfoxide **11** if endocyclic substitution occurred.

Table I. Sulfinanilides, $RS(O)NR_1C_6H_4X$

sulfinanilide	R	R_1	X	mp, °C	yield, %
1	*p*-tolyl	Me	3-Me_2N	*a*	
2	*p*-tolyl	Me	3-MeO	46.5–47.5[b]	96
3	*p*-tolyl	Me	4-MeO	83.5–84.5[b]	73
4	*p*-tolyl	Me	3-Me	68.5–69.5[b]	70
5	*p*-tolyl	Me	H	79.5–81.0[c]	58
6	*p*-tolyl	Me	3-Cl	63.5–65.0[b]	71
7	*p*-tolyl	Me	3-F	77.5–78.5[b]	63
8	*p*-tolyl	H	3-MeO	87–88[b]	84
9	Me	Me	3-Me_2N	*a*	
10	Me	Me	3-MeO	*d*	100

[a] Not isolated. [b] Satisfactory analyses (±0.3% of theory for C, H, and N) were obtained. [c] Lit.[7] mp 76–78 °C. [d] Unstable oil.



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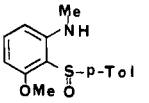

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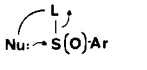
In endocyclic substitution the nucleophile and leaving group are bonded to one another so that the atom being substituted at, in our case, sulfur is transferred intramolecularly from L to Nu (**12**) in contrast to exocyclic reactions (**13**) where ring formation occurs and L is lost.[4–6]



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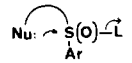

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(1) Supported in part by a grant from the National Science Foundation, Grant CHE790693, and a travel grant to O.M. from the Danish Natural Science Research Council.
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Table II. Sulfoxides, $RS(O)C_6H_3XY$, from the Acid-Catalyzed Rearrangement of Sulfinanilides

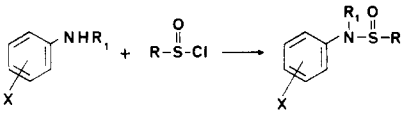
sulfoxide	sulfinanilide	rctn time[a]	R	X	Y	mp, °C	yield, %
14[b]	2	8 h	*p*-tolyl	2-MeO	4-MeNH	119.5-121	70
15[b]	2	8 h	*p*-tolyl	2-MeNH	4-MeO	162.5-163.5	26
16[b]	1	5 min	*p*-tolyl	2-MeNH	4-Me_2N	131-132	92
17[b]	4	8 days	*p*-tolyl	2-Me	4-MeNH	107-108	71
18[c]	9	5 min	Me	2-MeNH	4-Me_2N	oil	20
19[c]	10	8 h	Me	2-MeO	4-MeNH	oil	5

[a] In $CHCl_3$/HCl at room temperature. [b] Satisfactory analyses (0.3% for C, H, and N) were obtained. [c] Not purified. Yields are calculated from the ^1H NMR spectra. Structural assignments based on NMR and IR spectral data. See Experimental Section.

We were unable to cause a base-induced rearrangement, but instead we discovered an acid-catalyzed rearrangement that led to anilino sulfoxides. Since the rearrangement is synthetically useful and mechanistically interesting (it could conceivably have been an example of acid-catalyzed endocyclic substitution), we studied it further. In this paper we show a method to synthesize certain amino sulfoxides via rearrangements of sulfinamides.

Results and Discussions

Table I summarizes the yields and melting points of sulfinamides **1–10**, synthesized from the corresponding sulfinyl chlorides and anilines (eq 2). The yields were



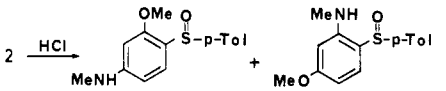
(2)

fairly good,[7,8] but the sulfinamides were hydrolytically[9,10] and photochemically[11] unstable and were used without delay in the following reactions.

First we describe the attempts at rearranging the sulfinamides in the presence of strong bases. Closson[12] and Hellwinkel[13] and their co-workers treated *N*-alkyl- and aryl-*N*-phenyl-*p*-toluenesulfonamide with excess *n*-BuLi in THF at 0 °C and got the 2-aminodiaryl sulfones in 52–78% yield. Repeating these reaction conditions for the analogous sulfinyl compound **5** gave quantitative yields of the undesired *n*-butyl phenyl sulfoxide and *N*-methylaniline, resulting from nucleophilic attack of *n*-BuLi at sulfur. The same results were obtained by using the more reactive monomeric *n*-BuLi/TMEDA and more hindered bases such as *t*-BuLi and lithium dicyclohexylamide and/or lowering the temperature to −78 °C.

To increase the likelihood of ortho lithiation in the aniline ring,[14] either by an acidifying inductive effect or by internal chelation, **2** and **7** were synthesized and similarly reacted with *n*-BuLi.[14] Again, nucleophilic attack at the sulfur took place and the aniline moiety was displaced. Similar examples of nucleophilic displacement caused by treating *N,N*-dialkyl- and *N*-alkyl-*N*-aryl sulfinamides with MeLi are known.[15-17]

When **2** was dissolved in $CDCl_3$ in an ^1H NMR experiment, a gradual disappearance of the NCH_3 signal at 2.80 ppm was noted, with a simultaneous appearance to two other peaks at 2.81 and 2.65 ppm in a ratio of ca. 3:1, respectively. Two rearranged amino sulfoxides were isolated: **14**, where the sulfinyl group is para to the amino group, in 70% yield, and **15**, the corresponding ortho compound, in 26% yield (eq 3).



14 15 (3)

When **2** was dissolved in carbon tetrachloride, no rearrangement to **14** and **15** took place until a catalytic amount of dry HCl gas was added. Trifluoroacetic acid in methylene chloride also promoted the rearrangement although not as cleanly.

To see what effect the substituents in the aniline ring had on the rearrangement and to see if arene- and alkanesulfinamides behaved similarly, the sulfinamides **1** and **3–10** were dissolved in dry $CHCl_3$, and catalytic amounts of HCl gas were added to the respective solutions. Compounds **1** and **4** rearranged to give sulfoxides **16** and **17**, respectively, in good yield; **9** and **10** rearranged to give **18** and **19**, respectively, in low yield (Table II). The remaining five sulfinamides **3** and **5–8** did not give any sulfoxides but yielded only recovered starting material plus small amounts of hydrolysis product; i.e., the corresponding aniline and *p*-toluenesulfinic acid. Apparently one additional activating group that directs ortho–para in electrophilic aromatic substitution, i.e., Me_2N, MeO, or Me, must be present in the aniline ring and must be meta to the MeNS(O)Tol group if rearrangement is to occur. A 4-MeO group does not sufficiently activate the sulfinamide to enable rearrangement to take place. Similarly the sulfinamides with H, Cl, or F as substituents meta to the MeNS(O)Tol did not rearrange. It is noteworthy that for both **1** and **9**, the sulfinyl group rearranged to a position para to the NMe_2 group but not para to the NHMe group.

A sharp increase in reaction times was noted on going from **1** to **2** and from **2** to **4**; this parallels a decrease in activation of the aniline ring toward electrophilic substitution. Sulfinamide **8**, in which the amide nitrogen is not methylated, did not rearrange.

Structural assignment to a particular amino sulfoxide necessitated distinguishing among four possible isomers, e.g., **11**, **14**, **15**, and a fourth isomer in which the *p*-toluenesulfinyl group is attached to the 5-position of the aniline ring. ^1H NMR selective decoupling experiments

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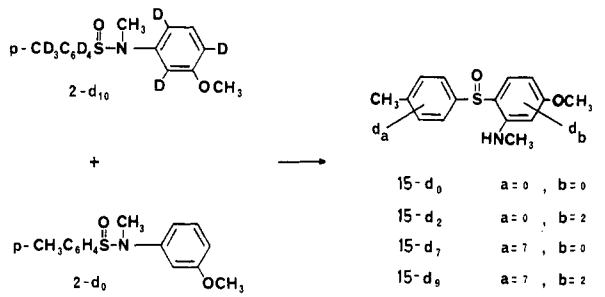
Scheme I



showed that the aromatic regions of the sulfoxide spectra were due to an AA'BB' pattern arising from the *p*-tolyl group and an ABM pattern from the aniline ring. The apparent coupling constants of the latter were consistent with a 1,2,4-substitution pattern and not with any other arrangement of the three groups; i.e., there was an ortho, a meta, and a para coupling. Since the methylamino group and the dimethylamino, methoxy, or methyl group were fixed meta to one another, two positional possibilities remained for the *p*-toluenesulfinyl group. It could be ortho or para to the methylamino group. The final distinction between structures for **14** and **15** was made by dilution IR experiments. Intramolecular hydrogen bonding in aromatic sulfoxides in known.[18] As expected one of the two isomers showed a broad band at 3350 cm^{-1} from intramolecular hydrogen bonding, which did not disappear upon dilution. This compound was assigned structure **15**. The other isomer, **14**, showed two NH-stretching bands in its spectrum, one broad band at 3332 cm^{-1}, which disappeared upon dilution (intermolecular hydrogen bonding), and one sharp band at 3462 cm^{-1} (free NH). The structure of the sulfoxides **16–19** were assigned in a similar way.

In addition, the N–H proton chemical shift was found at 5.5–6.3 ppm for sulfoxides **15**, **16**, and **18** and at 4.3–4.6 ppm for sulfoxides **14**, **17**, and **19**. These shifts are consistent with the first three compounds having intramolecular hydrogen bonds and the second three not.[18]

Although the rearrangements appeared to be examples of electrophilic aromatic substitution, a search for the involvement of free radicals was made. Free radicals have been implicated in some sulfinamide chemistry.[19] An attempted rearrangement of **2** was carried out in acid-free benzene in the cavity of an ESR spectrometer with α-phenyl-*N*-*tert*-butylnitrone (PBN) as a spin trap. No radical signals were detected.

The stereochemistry at sulfur during rearrangement was also probed. Sulfinamide **2** was prepared presumably in an optically active form by treating (–)-menthyl *p*-toluenesulfinate with lithium *N*-methyl-3-methoxyanilide and without isolation immediately rearranged to sulfoxides **14** and **15**.[2,16,20] The latter compounds exhibited no optical activity. Sulfoxides are known to be racemized by HCl in inert solvents so it is not clear if the absence of optical activity is due to their racemization by the HCl catalyst after the formation or due to some step in the rearrangement process.[21]

A crossover experiment was carried out to see if the rearrangement products amino sulfoxides **14** and **15** arising from **2** were formed intra- or intermolecularly. To avoid the ambiquities inherent in crossover experiments involving a pair of compounds that might rearrange with large differences in rate, a deuterium isotopomer of **2**, **2-*d***, was synthesized. A mixture of **2-*d*** and **2** in chloroform was treated with HCl, and the amino sulfoxides produced were examined for deuterium labeling by mass spectrometry. Scheme I shows the four possible isotopomers for amino sulfoxide **15** where *a* and *b* are the number of deuterium atoms in the *p*-tolyl and aniline moieties, respectively.

Field-desorption low-resolution mass spectra were measured for the molecular ion region of **15** formed from the rearrangement of a 1:1 mixture of **2-*d*$_{10}$** and **2-*d*$_0$**, from **2-*d*$_3$**, from **2-*d*$_7$**, and from **2-*d*$_{10}$**. The abundances contributed by the natural isotopes using those determined from **15-*d*$_0$** were subtracted from the experimental values of the deuterium-labeled compounds to calculate the percent of incomplete labeling. For the sample from the crossover experiment, both natural isotopic and incomplete labeling contributions were subtracted. The resulting corrected molecular ion relative abundance ratio **15-*d*$_0$**/**15-*d*$_2$** was 100:36; the **15-*d*$_7$**/**15-*d*$_9$** ratio was 55:21. The d_2 and d_7 sulfoxides arise from intermolecular processes only. The d_0 and d_9 sulfoxides could arise from both inter- and intramolecular processes. Thus, the ratio of inter to (inter + intra)molecular ion abundances arising from the d_0 toluenesulfinyl moiety reacting with the d_0 and d_2 aniline moieties was 100:(100 + 36) or 0.74. Similarly, the d_7 moiety gave 55:(55 + 21) or 0.72. The ratios are equal within experimental error. It follows that the ratio 1:(1 + intra/inter) should also be equal for each pair. That is, 1:(1 + intra/36) for the d_0–d_2 pair should equal 1:(1 + intra/55) for the d_7–d_9 pair. This can only be so if the amount of the intramolecular process is zero. That is, no intramolecular component could be detected.

A similar investigation of **14** gave $d_0/(d_0 + d_2) = 100:153 = 0.65$ and $d_7:(d_7+d_9) = 46:65 = 0.71$. Again it appears that there is no detectable intramolecular component to the reaction.

The rearrangement appears to be an example of electrophilic aromatic substitution with the HCl aiding in creation of the electrophile. Tillet and Asefi studied the acid-catalyzed hydrolysis of some *N*-arylarenesulfinamides and concluded that the reaction proceeded via an A-2 mechanism and, if hydrochloric or hydrobromic acid was the acid used, by an acid-catalyzed nucleophilic attack by halide ion.[10] The A-2 pathway proceeded by a preequilibrium protonation on nitrogen followed by slow nucleophilic attack by water on sulfur to give the products, a sulfinic acid and an aniline. If halide ion was present, it attacked the protonated sulfinamide at sulfur to give the sulfinyl chloride, which was subsequently hydrolyzed.

In our cases a similar preequilibrium protonation on nitrogen followed by nucleophilic attack by chloride ion on sulfur would give the *N*-methylaniline plus *p*-toluenesulfinyl chloride. The sulfinyl chloride would act as an electrophile sulfinylating the more reactive anilines but reverting to starting material with the less activated ones. Sulfinyl chlorides are known to react with aromatic substrates in the presence of aluminum chloride to form sulfoxides.[22–25] In the case of the trifluoroacetic acid induced rearrangement where halide ion is absent, it is conceivable that the aniline is the nucleophile.

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It is curious that the N-unmethylated sulfinanilide 8 did not rearrange, but the same situation is true for the acid-catalyzed rearrangement of *N*-arylarenesulfonamides.[26] These compounds rearrange to amino sulfones if the aniline ring is activated and the nitrogen is methylated but not if the nitrogen is unmethylated. Also, we have observed that *N*-mesitylarenesulfinamides[9] are shelf-stable at room temperature for years, whereas the *N*-aryl-*N*-methyl-*p*-toluenesulfinamides prepared in this present study are unstable to storage.

Experimental Section

Melting points determined in capillary tubes are uncorrected. Microanalyses were performed by J. Gould and D. Cardin using a Perkin-Elmer 240b elemental analyzer. NMR spectra were recorded on a JEOL FX90Q and a Varian EM 360 spectrometer with Me_4Si (δ = 0 ppm) as an internal standard. Coupling constants are apparent and were not verified by spectral simulation. IR spectra were recorded on a Perkin-Elmer 283b spectrophotometer. Dilution IR experiments were carried out in spectral grade $CHCl_3$. Mass spectra were obtained on a Hitachi Perkin-Elmer RMU-6E spectrometer. Tetrahydrofuran (THF) and diethyl ether were distilled from sodium benzophenone ketyl prior to use. *n*-Butyllithium was a 2.0 M solution to hexane (Alfa). Silica gel used for flash chromatography was from Baker, average particle size 40 μm.

Known Starting Materials. The following substituted *N*-methylanilines were prepared by known procedures: *m*-MeO,[27,28] *p*-MeO,[28] *m*-Cl,[28] *m*-Me,[28] *m*-F,[28] *m*-Me,[28] and *m*-$N(CH_3)_2$.[29] Methanesulfinyl chloride[30] [bp 32–34 °C (15 mm)] and *p*-toluenesulfinyl chloride[31] [bp 75–77 °C (0.13 mm), mp 2–3.5 °C] were purified by distillation and stored under N_2 in ampules at 5 °C.

Sulfinamides. General Procedure. The reactions were carried out under nitrogen in flame-dried Schlenck flasks. Sulfinyl chloride (10 mmol) in 15 mL of ether was cooled to −78 °C in an acetone–dry ice bath. A solution of 10 mmol of aniline and 10 mmol of pyridine, both freshly distilled, in 5 mL of ether was added with a syringe during 1 min with vigorous stirring. A white crystalline precipitate formed immediately. This slurry was quickly heated to room temperature and filtered. If necessary, additional ether was added to dissolve the sulfinamide and thereby separate it from the insoluble pyridinium hydrochloride. The filtrate was then again cooled, causing the sulfinamide to precipitate. Quick, cold filtration and drying in a desiccator gave the sulfinamide. By repeated recrystallizations, analytically pure samples were obtained. Yields and melting points are listed in Table I.

***N*-(3-Methoxyphenyl)-*N*-methyl-4-toluenesulfinamide (2)**: NMR ($CDCl_3$) δ 2.42 (s, 3 H, Ar CH_3), 2.80 (s, 3 H, NCH_3), 3.83 (s, 3 H, OCH_3), 6.6–7.0 (m, 3 H, Ar H), 7.2–7.9 (m, 5 H, Ar H). Anal. Calcd for $C_{15}H_{17}NO_2S$: C, 65.43; H, 6.22; N, 5.09. Found: C, 65.13; H, 6.33; N, 5.10.

***N*-(4-Methoxyphenyl)-*N*-methyl-4-toluenesulfinamide (3)**: NMR ($CDCl_3$) δ 2.42 (s, 3 H, Ar CH_3), 2.85 (s, 3 H, NCH_3), 3.82 (s, 3 H, OCH_3), 6.8–7.8 (m, 8 H, Ar H). Anal. Calcd for $C_{15}H_{17}NO_2S$: C, 65.43; H, 6.22; N, 5.09. Found: C, 65.52; H, 6.36; N, 5.12.

***N*-Methyl-*N*-(3-tolyl)-4-toluenesulfinamide (4)**: NMR ($CDCl_3$) δ 2.32 (s, 3 H, Ar CH_3), 2.42 (s, 3 H, Ar CH_3), 2.80 (s, 3 H, NCH_3), 6.8–7.8 (m, 8 H, Ar H). Anal. Calcd for $C_{15}H_{17}NOS$: C, 69.46; H, 6.61; N, 5.40. Found: C, 69.31; H, 6.56; N, 5.33.

***N*-(3-Chlorophenyl)-*N*-methyl-4-toluenesulfinamide (6)**: NMR ($CDCl_3$) δ 2.42 (s, 3 H, Ar CH_3), 2.83 (s, 3 H, NCH_3), 7.1–7.7 (m, 8 H, Ar H). Anal. Calcd for $C_{14}H_{14}ClNOS$: C, 60.10; H, 5.04; N, 5.09. Found: C, 60.03; H, 4.75; N, 5.09.

***N*-(3-Fluorophenyl)-*N*-methyl-4-toluenesulfinamide (7)**: NMR ($CDCl_3$) δ 2.42 (s, 3 H, Ar CH_3), 2.82 (s, 3 H, NCH_3), 6.6–7.8 (m, 8 H, Ar H). Anal. Calcd for $C_{14}H_{14}FNOS$: C, 63.86; H, 5.36; N, 5.32. Found: C, 63.72; H, 5.53; N, 5.25.

***N*-(3-Methoxyphenyl)-4-toluenesulfinamide (8)**: NMR ($CDCl_3$) δ 2.42 (s, 3 H, Ar CH_3), 3.85 (s, 3 H, OCH_3), 6.4 (br s, 1 H, NH), 6.5–6.8 (m, 3 H, Ar H), 7.0–7.8 (m, 5 H, Ar H). Anal. Calcd for $C_{14}H_{15}NO_2S$: C, 64.34; H, 5.79; N, 5.36. Found: C, 64.07; H, 5.68; N, 5.28.

***N*-(3-Methoxyphenyl)-*N*-methylmethanesulfinamide (10)** was an unstable, colorless oil: NMR (CCl_4) δ 2.57 (s, 3 H, SCH_3), 2.63 (s, 3 H, NCH_3), 3.80 (s, 3 H, OCH_3), 6.4–7.5 (m, 4 H, Ar H).

Treatment of Sulfinamide 5 with Various Bases. Sulfinamide **5** (491 mg, 2.00 mmol) was dissolved in 20 mL of THF, and the solution was cooled to −78 °C under nitrogen. During 1 min 2 mL of 2.0 N *n*-BuLi in hexane was added dropwise via a syringe. The temperature rose to −45 °C and the solution became orange. After reaction for 2 h at −78 °C and an additional 2 h at room temperature, the reaction mixture was quenched with 5 mL of H_2O. Extraction three times with 20-mL portions of ether, drying over $MgSO_4$, and evaporation of the solvents on a rotary evaporator gave a yellow oil. Isolation of the basic fraction from this oil gave a quantitative yield of *N*-methylaniline. The nonbasic fraction was identical with *n*-butyl *p*-tolyl sulfoxide as shown by comparison with an authentic sample. The experiment was repeated with *t*-BuLi as a base, and again a quantitative yield of *N*-methylaniline was obtained and *tert*-butyl *p*-tolyl sulfoxide was formed.

When lithium dicyclohexylamide was used as a base, NMR and TLC (SiO_2, 5% EtOAc, 95% CH_2Cl_2) showed that *N*-methylaniline (R_f 0.76) and *N*-dicyclohexyl-*p*-toluenesulfinamide (R_f 0.39) were the products formed. This sulfinamide was independently synthesized in 67% yield from the reaction between *p*-toluenesulfinyl chloride and 2 molar equiv of dicyclohexylamine in CCl_4 at room temperature for 1 h, mp 135.5–136.5 °C (lit.[32] mp 136–137 °C).

Synthesis and Rearrangement of Optically Active (*R*)-*N*-(3-Methoxyphenyl)-*N*-methyl-4-toluenesulfinamides (2). A solution of 1.75 mL (5 mmol) of MeMgBr, 2.85 M in ether (Aldrich), was added dropwise during 5 min under nitrogen to a solution of 616 mg (5mmol) of freshly distilled *N*-methyl-*m*-anisidine in 15 mL of anhydrous ether. A vigorous gas evolution was observed. This solution was then added via a syringe to an ice-cooled solution of 1.373 g (5 mmol) of (−)-(*S*)-menthyl-*p*-toluenesulfinate, $[\alpha]^{23}_D$ − 119.5° (*c* 2.0, acetone), in 25 mL of dry ether. The reaction mixture was stirred at 0 °C for 2 h and then quenched with 50 mL of a 1:9 mixture of ice water and CH_2Cl_2. The organic phase was quickly separated and dryed with $MgSO_4$ and then concentrated on a rotary evaporator ($T \leq 25$ °C) to give a yellow oil. ^1H NMR showed the expected sulfinamide, which, without further purification, was rearranged as described below to the amino sulfoxides **14** and **15** in a ratio of 3:1, respectively. The total yields of the two sulfoxides was 20%. Neither of the two sulfoxides showed any optical activity.

ESR Experiment. α-Phenyl-*N*-*tert*-butylnitrone (1.1 equiv) was added to an 0.01 M solution of sulfinamide **2** in freshly distilled benzene under nitrogen, and the resulting mixture was examined for free radicals with a Varian F-9 spectrometer. Except for signals from minor impurities, no ESR absorptions were observed. The following operating conditions were used: rectangular cavity; power, 10 mW; modulation amplitude, 2G at 100 KHz; X-band frequency, 9.5 GHz; field sweep, 200 G centered at g = 2; scan time, 8 min; gain, nominally 10^2–10^3.

Crossover Experiment. Equimolar amounts of **2** and **2-*d***were dissolved in dry $CHCl_3$ and treated with dry HCl as described below. Workup gave the two isomeric amino sulfoxides **14** and **15**, which were separately investigated for the content of isotopomers by mass spectroscopy.

Acid-Catalyzed Rearrangement of Sulfinamides to Amino Sulfoxides. General Procedures. The sulfinamide (1 g) was dissolved in 10 mL of $CHCl_3$, freshly distilled from CaH_2, and dry HCl gas was bubbled slowly through the solution for 15 s. The solution was stored under nitrogen at room temperature in

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the dark, and the reactions were monitored by TLC. Spots for starting sulfinanilides and their hydrolysis products—the anilines and sulfinic acid—were observed together with spots for the amino sulfoxides if the rearrangement occurred. The latter compounds were isolated by flash chromatography and recrystallization. Yields and melting points are listed in Table II. Except for **9** and **10**, which gave complex reaction mixtures, the TLC analyses revealed only traces of other products.

4-(Dimethylamino)-2-(methylamino)-4′-methyldiphenyl sulfoxide (16) was purified by recrystallization from $CHCl_3$–ether: NMR ($CDCl_3$) δ 2.35 (s, 3 H, Ar CH_3), 2.68 (s, 3 H, NCH_3), 3.00 (s, 6 H, $N(CH_3)_2$), 5.5 (br s, 1 H, NH) 5.80 (d, 1 H, Ar H_1, J_{12}(meta) = 2.4 Hz), 6.57 (dd, 1 H, Ar H_2, J_{12}(meta) = 2.4 Hz and J_{23}(ortho) = 8.4 Hz), 7.30 (d, 1 H, Ar H_3, J_{23}(ortho) = 8.4 Hz), 7.4 (AA′BB′, 4 H, Ar H); ^{13}C NMR ($CDCl_3$) δ 21.2, 29.7, 40.1, 93.7, 99.6, 110.0, 124.8, 129.4, 130.8, 139.6, 141.6, 151.1, 154.3; IR ($CHCl_3$) 3355 cm^{-1} (br, NH hydrogen bonded). Anal. Calcd for $C_{16}H_{20}N_2OS$: C, 66.63; H, 6.99; N, 9.71. Found: C, 66.60; H, 7.05; N, 9.69.

2-Methoxy-4-(methylamino)-4′-methyldiphenyl sulfoxide (14) was purified by flash chromatography and recrystallization from $CHCl_3$–ether: TLC R_f (SiO_2, 20% EtOAc, 80% CH_2Cl_2) 0.19; NMR ($CDCl_3$) δ 2.35 (s, 3 H, Ar CH_3), 2.65 (s, 3 H, NCH_3), 3.77 (s, 3 H, OCH_3), 4.3 (br s, 1 H, NH), 6.05 (d, 1 H, Ar H_1, J_{12}(meta) = 2, 4 Hz), 6.28 (dd, 1 H, Ar H_2, J_{12}(meta) = 2.4 Hz and J_{23}(ortho) = 8.4 Hz), 7.50 (d, 1 H, Ar H_3, J_{23}(ortho) = 8, 4 Hz), 7.40 (AA′BB′, 4 H, Ar H); ^{13}C NMR ($CDCl_3$) δ 21.3, 30.3, 55.5, 95.0, 105.0, 119.7, 125.0, 127.2, 129.5, 140.5, 143.2, 153.5, 158.1; IR ($CHCl_3$) 3462 (sharp, NH free), 3322 cm^{-1} (br, disappears upon dilution, NH hydrogen bonded). Anal. Calcd for $C_{15}H_{17}NO_2S$: C, 65.42; H, 6.22; N, 5.09. Found: C, 65.34; H, 6.13; N, 5.04.

4-Methoxy-2-(methylamino)-4′-methyldiphenyl sulfoxide (15) was purified by flash chromatography and recrystallization from THF: TLC R_f (SiO_2, 20% EtOAc, 80% CH_2Cl_2) 0.67; NMR ($CDCl_3$) δ 2.35 (s, 3 H, Ar CH_3), 2.65 (s, 3 H, NCH_3), 3.78 (s, 3 H, OCH_3), 6.1 (br s, 1 H, NH), 6.05 (d, 1 H, Ar H_1, J_{12}(meta) = 2.7 Hz), 6.20 (dd, 1 H, Ar H_2, J_{12}(meta) = 2.7 Hz and J_{23}(ortho) = 8.5 Hz), 7.32 (d, 1 H, Ar H_3, J_{23}(ortho) = 8.5 Hz), 7.30 (AA′BB′, 4 H, Ar H); ^{13}C NMR ($CDCl_3$) δ 21.0, 29.4, 55.0, 96.9, 100.5, 115.0, 124.5, 129.2, 130.5, 140.0, 140.6, 151.3, 164.0; IR ($CHCl_3$) 3350 cm^{-1} (broad NH hydrogen bonded). Anal. Calcd for $C_{15}H_{17}NO_2S$: C, 65.43; H, 6.22; N, 5.09. Found: C, 65.43; H, 6.36; N, 5.02.

2-Methyl-4-(methylamino)-4′-methyldiphenyl sulfoxide (17) was purified by flash chromatography and recrystallization from ether: TLC R_f (SiO_2, 20% EtOAc, 80% CH_2Cl_2) 0.33; NMR ($CDCl_3$) δ 2.31 (s, 3 H, Ar CH_3), 2.33 (s, 3 H, Ar CH_3), 2.76 (s, 3 H, NCH_3), 4.3 (br s, 1 H, NH), 6.31 (d, 1 H, Ar H_1, J_{12}(meta) = 2.3 Hz), 6.45 (dd, 1 H, Ar H_2, J_{12}(meta) = 2.3 Hz and J_{23}(ortho) = 8.5 Hz), 7.49 (d, 1 H, Ar H_3, J_{23}(ortho) = 8.5 Hz), 7.30 (AA′BB′, 4 H, Ar H); ^{13}C NMR ($CDCl_3$) δ 18.8, 21.3, 30.1, 110.6, 113.7, 125.3, 127.9, 129.5, 129.6, 138.4, 140.6, 142.5, 151.7; IR ($CHCl_3$) 3475 (sharp, NH free), 3355 cm^{-1} (br, disappears upon dilution, NH hydrogen bonded). Anal. Calcd for $C_{15}H_{17}NOS$: C, 69.46; H, 6.61; N, 5.40. Found: C, 69.32; H, 6.66; N, 5.38.

Methyl 4-(Dimethylamino)-2-(methylamino)phenyl Sulfoxide (18). Attempts to purify **18** by flash chromatography and recrystallization were unsuccessful: TLC R_f (SiO_2, 50% EtOAc, 50% $CHCl_3$) 0.26; NMR ($CDCl_3$) δ 2.85 (s, 6 H, NCH_3 and SCH_3), 2.97 (s, 6 H, $N(CH_3)_2$), 5.90 (d, 1 H, Ar H_1, J_{12}(meta) = 2.4 Hz), 6.00 (dd, 1 H, Ar H_2, J_{12}(meta) = 2.4 Hz and J_{23}(ortho) = 8.4 Hz), 6.3 (br s, 1 H, NH), 7.02 (d, 1 H, Ar H_3, J_{23}(ortho) = 8.4 Hz); IR ($CHCl_3$) 3360 cm^{-1} (br, NH hydrogen bonded).

Methyl 2-Methoxy-4-(methylamino)phenyl Sulfoxide (19). Attempts to purify **19** by flash chromatography and recrystallization were unsuccessful: TLC R_f (SiO_2, 80% EtOAc, 20% $CHCl_3$) 0.23; NMR ($CDCl_3$) δ 2.81 (s, 3 H, NCH_3), 3.11 (s, 3 H, SCH_3), 3.90 (s, 3 H, OCH_3), 4.6 (br s, 1 H, NH), 6.10 (d, 1 H, Ar H_1, J_{12}(meta) = 3.0 Hz), 6.28 (dd, 1 H, Ar H_2, J_{12}(meta) = 3.0 Hz and J_{23}(ortho) = 9.0 Hz), 7.70 (d, 1 H, Ar H_3, J_{23}(ortho) = 9.0 Hz); IR ($CHCl_3$) 3455 (sharp, NH free), 3400 cm^{-1} (br, disappears upon dilution, NH hydrogen bonded).

4-Toluene-d_7-sulfonyl Chloride (20). Ten grams (100 mmol) of toluene-d_8 (99% isotopic purity, Stohler) was dissolved in 50 mL of $CHCl_3$ and cooled under nitrogen in an ice–salt bath. Chlorosulfuric acid (50 mL) was added during 10 min at 5–10 °C. The ice–salt bath was removed and after 45 min at room temperature the mixture was poured onto 500 mL of ice. The organic layer was separated, diluted with $CHCl_3$ (50 mL), washed with water (2 × 30 mL), dried ($MgSO_4$), and evaporated ($T \leq 30$ °C) to give a colorless oil, which crystallized upon cooling to −78 °C. Addition of 200 mL of hexane, cold filtration, and drying gave 14.5 g (73%) of **20**, mp 69.5–70.5 °C (lit.[33] mp 71–72 °C).

4-Toluene-d_7-sulfinyl chloride (21) was synthesized by reduction of **20** with sodium sulfite[34] to the sodium sulfinate, followed by reaction with $SOCl_2$;[31] yield of **21** from **20**, 46%; bp 73–75 °C (1.8 mm).

3-Methoxy-*N*-methyl-*N*,2,4,6-tetradeuterioaniline (22). *N*-Methylaniline (5.9 g, 43 mmol) was dissolved in a solution of 25 mL of D_2O (99%, Stohler) and 2 mL of H_2SO_4/SO_3 (65%, Oleum).[35] The mixture was heated under reflux for 2 h, and then it was cooled and made basic with sodium carbonate. The aniline was removed by extraction with 2 × 50 mL of ether. Distillation at 77–79 °C (1.6 mm) gave 5.4 g of **22**. The deuterium incorporation in the 2-, 4-, and 6-positions of the ring was measured by ^1H NMR to be ca. 90%.

***N*-(3-Methoxy-2,4,6-trideuteriophenyl)-*N*-methylhepta-deuterio-4-toluenesulfinamide (2-d_{10}).** The synthesis of **2**-d_{10}, analogous to the synthesis of **2**, was by reaction between **21** and **22** in ether–pyridine; yield 91%, mp 41–43 °C. The total combined deuterium content in the seven positions in the toluene ring and in the 2-, 4-, and 6-positions in the aniline ring was measured by ^1H NMR to be ca. 85%.

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Registry No. **1**, 87433-14-5; **2**, 87433-15-6; **2**-d_{10}, 87433-16-7; **3**, 87433-17-8; **4**, 87433-18-9; **5**, 33692-24-9; **6**, 87433-19-0; **7**, 87433-20-3; **8**, 87433-21-4; **9**, 87433-22-5; **10**, 87433-23-6; **14**, 87433-24-7; **15**, 87433-25-8; **16**, 87433-26-9; **17**, 87433-27-0; **18**, 87433-29-2; **19**, 87433-30-5; **20**, 81255-49-4; **21**, 87433-31-6; **22**, 87433-28-1; *p*-toluenesulfinyl chloride, 98-59-9; methanesulfinyl chloride, 676-85-7; *N*-methyl-*m*-anisidine, 14318-66-2; *N*-methyl-*p*-anisidine, 5961-59-1; *N*-methylaniline, 100-61-8; 3-chloro-*N*-methylaniline, 7006-52-2; *m*-anisidine, 536-90-3; (−)-menthyl *p*-toluenesulfinate, 20752-45-8; *N*,*N*,*N*′-trimethyl-1,3-benzenediamine, 84995-19-7; *N*,3-dimethylaniline, 696-44-6; 3-fluoro-*N*-methylaniline, 1978-37-6.

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