intensity) 212 (0.22), 210 (0.79), 156 (1.68), 154 (5.53), 1.05 (100), 77 (27.7).

2-Chloro-2-methyl-1-phenyl-1-propanone. Reaction of isobutyrophenone with lithium hexamethyldisilazane in THF (53%)-hexane (34%)-HMPA (13%) with $Me_2C(NO_2)Cl$ for 1 h at 25 °C gave 78% of the chloro ketone analyzed by the ^1H NMR singlet at δ 1.90 and identified by comparison of the ^1H NMR spectra and gas chromatography retention time with those of an authentic sample.

Reaction of $PhC(OLi)=CHCH_3$ with $Me_2C(NO_2)_2$ and $Me_2C(NO_2)SO_2PhMe$-*p*. In addition to **1c** and **3c** significant amounts of **5c** (X = NO_2) and **5d** (X = *p*-$MePhSO_2$) were formed. These products were identified by GC/MS and analyzed by ^1H NMR. For $PhCOCH(Me)NO_2$ analysis was based on the signal at δ 6.33 (q, J = 7 Hz, 1 H) in $CDCl_3$, while for $PhCOCH(Me)SO_2PhMe$-*p* analysis was based on signals at δ 1.54 (d, J = 7 Hz, 3 H), 2.34 (s, 3 H), 5.27 (q, J = 7 Hz, 1 H) in $CDCl_3$ and the GC/mass spectrum, m/e 288 (M^+), 155 (*p*-$MePhSO_2$), 139 ($C_6H_4SO_2$), 133 (PhCOCHMe).

Registry No. **1c**, 78706-73-7; **1d**, 81096-19-7; **1e**, 81096-20-0; **1f**, 81096-21-1; **1g**, 81096-22-2; **1h**, 81096-23-3; **1i**, 81096-24-4; **1j**, 81096-25-5; **1k**, 81096-26-6; **1l**, 78706-74-8; **1m**, 78706-75-9; **1n**, 81096-27-7; **2a**, 5650-07-7; **2b**, 56985-25-2; **2c**, 52776-41-7; **2f**, 81096-28-8; **2g**, 81096-29-9; **2h**, 81096-30-2; **2i**, 81096-31-3; **2j**, 81096-32-4; **2k**, 81096-33-5; **2l**, 81096-34-6; **3c** (isomer 1), 81096-35-7; **3c** (isomer 2), 73893-85-3; **3d**, 81096-36-8; **3f** (isomer 1), 81096-37-9; **3f** (isomer 2), 81096-38-0; **3g** (isomer 1), 81096-39-1; **3g** (isomer 2), 81096-40-4; **3h**, 81096-41-5; **3i**, 81096-42-6; **3j**, 81120-65-2; **3l** (isomer 1), 81096-43-7; **3l** (isomer 2), 81096-44-8; **3m** (isomer 1), 81096-45-9; **3m** (isomer 2), 81120-49-2; **3n**, 81096-46-0; (±)-**3a**, 81176-44-5; **4**, 81096-47-1; **5a**, 71491-53-7; **5b**, 7473-99-6; **5c**, 14897-67-7; **5d**, 14195-15-4; **6**, 3964-18-9; **8**, 81096-48-2; **2'**, 81096-49-3; **9a**, 81096-50-6; **9b**, 74074-96-7; **9c**, 81096-51-7; **10a**, 5706-00-3; **10b**, 73652-79-6; **10c**, 81096-52-8; **11c**, 81096-53-9; $PhC(OLi)=CH_2$, 55905-98-1; PhC(OLi)=CHOMe, 81096-54-0; PhC(OLi)=CHMe, 70887-62-6; *p*-$MeOC_6H_4C(OLi)$=CHMe, 81096-55-1; *m*-$NEt_2C_6H_4C(OLi)$=CHMe, 81096-56-2; *p*-$MeC_6H_4C(OLi)$=CHMe, 81096-57-3; *p*-$ClC_6H_4C(OLi)$=CHMe, 81096-58-4; *m*-$ClC_6H_4C(OLi)$=CHMe, 81096-59-5; *p*-$BrC_6H_4C(OLi)$=CHMe, 81096-60-8; *p*-$CNC_6H_4C(OLi)$=CHMe, 81096-61-9; *m*-$NO_2C_6H_4C(OLi)$=CHMe, 81096-62-0; PhC(OLi)=CHEt, 62416-33-5; PhC(OLi)=CHBu, 81096-63-1; PhC(OLi)=CH-*i*-Pr, 78706-71-5; PhC(OLi)=CH-*t*-Bu, 81096-64-2; PhC(OLi)=CHPh, 76639-00-4; 2-chloro-2-nitropropane, 594-71-8; 2,2-dinitropropane, 595-49-3; 2-(*p*-tolylsulfonyl)-2-nitropropane, 21272-86-6; 1-chlorol-nitrocyclohexane, 873-92-7; 3,3-dimethy-2-butanone lithium enolate, 70367-67-8; 2-chloro-3-methyl-1-phenyl-1-butanone, 78706-77-1; 2-chloro-3,3-dimethyl-1-phenyl-1-butanone, 71491-53-7; 2-chloro-2-methyl-1-phenyl-1-propanone, 7473-99-6; isobutyrophenone, 611-70-1.

Substitution at Tetracoordinate Sulfur(VI). Rearrangement of 2-Aminoaryl Arenesulfonates to *N*-(2-Hydroxyaryl)arenesulfonamides[1]

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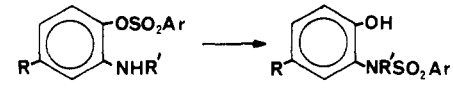
A series of eight 2-aminoaryl arenesulfonates upon treatment by strong bases rearranged intramolecularly to their corresponding *N*-(2-hydroxyaryl)arenesulfonamides as did the related tosylates derived from 2-amino-3-hydroxypyridine, 1-amino-2-naphthol, and 1-amino-8-naphthol. Two mechanisms for these rearrangements were considered likely. The first involves endocyclic nucleophilic attack by nitrogen on sulfonyl sulfur with consequent S–O bond cleavage. The other involves a 1,4-elimination reaction yielding an *o*-quinonimine–sulfinate pair which collapses to the product. Attempts to distinguish between these two alternatives were not conclusive.

Nucleophilic substitution at tetracoordinate hexavalent sulfur (sulfonyl sulfur) is a well-known reaction process. Inversion of configuration at the sulfur atom has been observed in examples subjected to stereochemical analysis.[3-6] These inversion reactions may follow an S_N2-like pathway via a trigonally bipyramidal transition state with the nucleophile (Nu), sulfur atom, and leaving group (L) approximately colinear, but other stereochemical situations are conceivable; e.g., the Nu and L could both be equatorial.

To see if approximate colinearity of Nu, S, and L is actually necessary in order for nucleophilic substitution at sulfur to occur, we are probing the effect of large deviations of the Nu–S–L angle from 180° on the course of substitution reactions. That is, we are synthesizing molecules which appear capable of undergoing endocyclic nucleophilic substitution at sulfur and then determining whether or not they undergo the desired reactions. This article describes one such set of molecules, the 2-aminoaryl arenesulfonates (**1a–8a**), and their base-induced rearrangement to *N*-(2-hydroxylaryl)arenesulfonamides (**1b-8b**, eq 1). As will be seen, it is not clear whether or not these rearrangements occur by nucleophilic substitution at sulfur.



a b (1)

1a,b, Ar = 4-$CH_3C_6H_4$; R = H; R' = H
2a,b, Ar = 4-$CH_3OC_6H_4$; R = H; R' = H
3a,b, Ar = 4-*t*-$C_4H_9C_6H_4$; R = H; R' = H
4a,b, Ar = 4-$CH_3C_6H_4$; R = CH_3; R' = H
5a,b, Ar = 4-$CH_3OC_6H_4$; R = CH_3; R' = H
6a,b, Ar = 4-*t*-$C_4H_9C_6H_4$; R = CH_3; R' = H
7a,b, Ar = 4-$CH_3C_6H_4$; R = H; R' = CH_3
8a,b, Ar = 2,4,6-$(CH_3)_3C_6H_2$; R = CH_3; R' = H

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 (**9a**) in contrast to exocyclic reactions (**9b**) where ring formation occurs and L is lost.

9a 9b

(1) This paper is based upon work supported in part by the National Science Foundation (Grants CHE-7601977 and CHE 790693).
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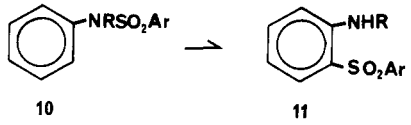
Table I. Sulfonate and Sulfonamide Melting Points and Yields of Rearrangement Products

sulfonate[a]	mp, °C	sulfonamide[a]	mp, °C	yield, %
1a	99-100[b]	1b	138-139[c]	95
2a	93-94, 135-136 (NHAC)	2b	118-119, 113-114 (OTS)	64
3a	63-64, 131 (NHAC)	3b	184.5-185	55
4a	76-78[d]	4b	147-148	50
5a	79-82, 133-134 (NHAC)	5b	102-104, 122-123 (OAC)	55
6a	114-116	6b	138.5-139.5	30
7a	66-67	7b	125-126[e]	43
8a	83-84	8b	129-130, 135 (OAC)	10
14a	131-132	14b	162-165	70
15a	160-161	15b	175-176	33
16a	160-161	16b	180-181	20
17a	105-107[f]	17b	119-120	17

[a] Satisfactory analyses (0.4% for C, H, and N) were obtained on either the parent compounds or, if listed, on their acetyl or tosyl derivatives. [b] Lit.[14] mp 100-101 °C. [c] Lit.[14] mp 138-139 °C. [d] Lit. mp 78 °C (Geigy, J. R. German Patent 201 377; *Chem. Zentralbl.* **1908**, *79II*, 999). [e] Lit. mp 127-128 °C (Hewitt, L. F.; King, H.; Murch, W. O. *J. Chem. Soc.* **1926**, 1355-1370). [f] Lit. mp 107-108 °C (King, F. E.; Clark-Lewis, J. W. *J. Chem. Soc.* **1951**, 3080-3085).

Wudl and Lee showed that a sulfinate ester with an amino group β to the alkoxy oxygen could rearrange to the sulfinamide with retention at sulfur; that is, tricoordinate tetravalent sulfur was capable of undergoing endocyclic nucleophilic substitution.[7] Closson and Hellwinkel and their co-workers found that *N*-aryl-*N*-alkyl- and *N*,*N*-diarylarenesulfonamides (**10**) rearranged intramolecularly to *o*-aminoarylaryl sulfones (**11**) when treated with certain bases which generated nucleophilic centers ortho to the nitrogen in the starting material (eq 2).[8,9] These reactions



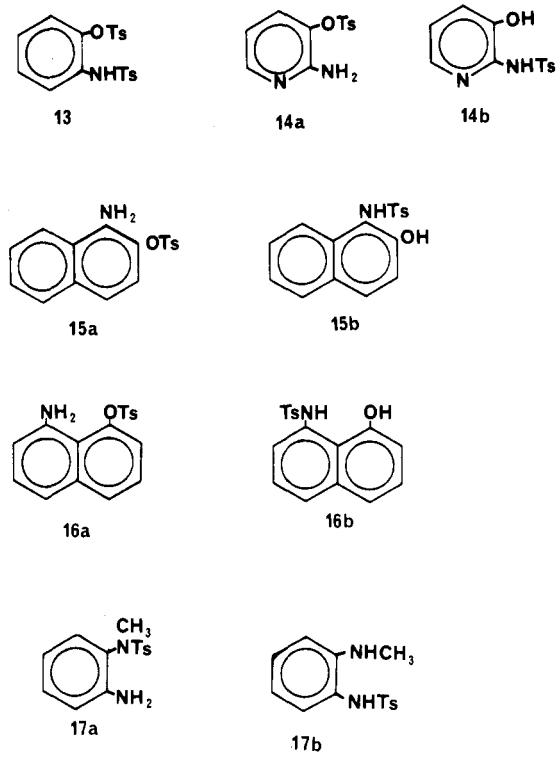
10 11 (2)

showed that sulfonyl sulfur was apparently also capable of undergoing endocyclic nucleophilic substitution. An attempt at demonstrating this process at dicoordinate divalent sulfur (sulfide sulfur) was inconclusive.[10] Methyl carbon seems not able to undergo endocyclic substitution in six-membered cyclic transition states.[11]

Results and Discussion

Treatment of sulfonate **1a** with *n*-butyllithium (*n*-BuLi) in tetrahydrofuran (THF) or ether yielded sulfonamide **1b**. The NMR spectra of reaction mixtures revealed clean reactions with a maximum yield of sulfonamide obtained when about 4 equiv of base was used. It was possible to isolate sulfonamide **1b** in 95% yield. The reaction was not reversible, for **1b** gave no **1a** upon treatment with *n*-BuLi. The following bases were also used to carry out the rearrangement and gave the yields shown in parentheses: methyllithium (75%), lithium diisopropylamide (65%), sodium hydride (25%), lithium hydride (0%), phenyllithium (0%). The lower yields with lithium and sodium hydrides are probably due to the low solubility of the bases. Phenyllithium gave phenyl *p*-tolyl sulfone presumably by nucleophilic substitution at sulfur. LDA is considerably more basic than aniline (pK = 33.1 vs. 23.4) in THF and should readily deprotonate the amino groups of the startng

Chart I



sulfonates just as the alkyllithiums do.[12] Kurita showed earlier that pyridine in boiling ethanol did not cause the rearrangement and that methanolic potassium hydroxide simply saponified the ester.[13] Similarly, Raiford found **1a** and related sulfonates exhibited no tendency to rearrange.[14]

Other 2-aminoaryl arenesulfonates (**2a**–**8a**) also underwent the *n*-butyllithium-induced rearrangement (Table I). The rearrangement of **8a** to **8b**, which proceeded in low yield, is noteworthy since Closson observed that *N*-methyl-*N*-phenyl-2,4,6-trimethylbenzenesulfonamide did not rearrange but gave only unidentified cleavage products. A small amount of 2,2′-dihydroxy-5,5′-dimethylazobenzene (**12**) was also isolated in the reaction of **8a** with *n*-BuLi.

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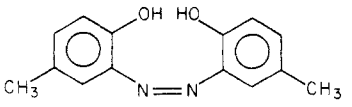


12

The reaction products of **1a** and **6a** with *n*-BuLi were carefully checked for the presence of azobenzenes. In the case of **6a**, some **12** was isolated. For **1a**, however, no 2,2′-dihydroxyazobenzene was formed as a minor product, but a small amount of *n*-butyl *p*-tolyl sulfone was isolated. Presumably this arises from nucleophilic attack of *n*-BuLi on the sulfonyl sulfur.

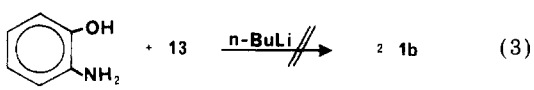
A methyl group on nitrogen did not prevent the reaction from occurring since 2-(methylamino)phenyl 4-toluenesulfonate (**7a**) rearranged to the expected *N*-methyl-*N*-(2-hydroxyphenyl)-4-toluenesulfonamide (**7b**). This shows that the formation of an *N*-lithio salt of a primary sulfonamide is not necessary to drive the reaction to completion. The ditosyl compound **13** (Chart I) with one tosyl group on oxygen and one on nitrogen was recovered unchanged after treatment with *n*-BuLi.

In addition, tosylates **14a–16a** rearranged to their corresponding sulfonamides **14b–16b** when treated with *n*-BuLi in THF. The rearrangement of **14a** was particularly clean compared to the rearrangements of **15a** and **16a** which gave some dark-colored byproducts and led to lower isolated yields of sulfonamides. Rearrangement of sulfonamide **17a** to **17b** proceeded in low isolated yield, the reaction mixture contained a considerable amount of dark-colored byproducts.

When sulfonate **1a** was heated at 200 °C for 30 mins or under reflux (162 °C) in diglyme for 6 h, no sulfonamide **1b** was detected by TLC in either case. Evidently, a thermally induced [1,4] sigmatropic rearrangement did not take place. We see no reason why deprotonation at 0 °C or below should facilitate reaction via such a process and therefore conclude a sigmatropic rearrangement is not taking place.

Endocyclic reactions are by definition intramolecular, so if the rearrangements under discussion are truly endocyclic, their intramolecularity must be demonstrated. This was attempted in two ways.

If the reaction (eq 1) proceeded by intermolecular nucleophilic substitution, an anion derived by deprotonation of the nitrogen of **1a** would attack the sulfonate sulfur atom of a second molecule of **1a**, thus forming a molecule of *o*-aminophenol and one of the ditosyl compound **13** (both in some anionic form, since the reaction mixture contains *n*-BuLi). The *o*-aminophenol (anionic form) could then react with **13** to form two molecules of the final product, sulfonamide **1b**. No *o*-aminophenol or ditosyl **13** were detected as products of the reaction nor did an equimolar mixture of the two react with one another in the presence of *n*-BuLi under the reaction conditions. Anionic forms of *o*-aminophenol and **13** are ruled out as intermediates, since they neither accumulate in the reaction mixture nor react further to product; the process depicted by eq 3 does not take place.

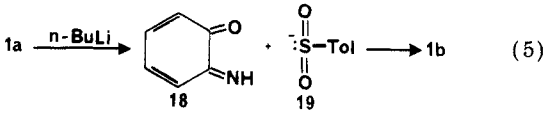


(3)

Second, a crossover experiment was carried out by using a mixture of sulfonates **2a** and **6a**. Only sulfonamides **2b** and **6b**, the products expected from intramolecular reactions, were formed; none of the products expected from intermolecular processes, **3b** or **5b**, could be detected by proton NMR or TLC. On the assumption that the rates of rearrangement of **2a** to **2b** and of **6a** to **6b** are not very different (eq 4), this crossover experiment rules out an intermolecular process.

$$\mathbf{2a} + \mathbf{6a} \xrightarrow{n\text{-BuLi}} \mathbf{2b} + \mathbf{6b} \qquad (4)$$

Even though the rearrangement appears to be intramolecular, it may not be an example of nucleophilic substitution at sulfur. An alternative mechanism involving a base-induced 1,4-elimination with consequent formation of an *o*-quinonimine (**18**) and *p*-toluenesulfinate anion (**19**) is conceivable (eq 5). The ion–molecule pair could re-

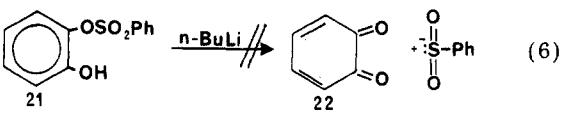


(5)

18 19

combine within a solvent cage to give the observed products. Changing the solvent/base combination from THF/*n*-BuLi or diethyl ether/*n*-BuLi to THF, NH_3/$LiNH_2$ or Me_2SO/$NaCH_2SOCH_3$ did not change the outcome of the reaction, however, although the yields of products decreased.

o-Quinonimine (**18**) has never been isolated although N-substituted and more complicated quinonimines such as 1,2-naphthoquinon-1-imine and *N*-benzenesulfonyl-1,2-naphthoquinon-1-imine are known.[15] Usually such compounds are formed by oxidation of *o*-aminophenols. We were unable to find any literature example of *o*- or *p*-quinonimine formation through an elimination reaction of the type shown in eq 5.[15] In fact, basic hydrolysis of the dibenzenesulfonate of catechol (**20**) can be stopped at the monosulfonate **21**.[16] No *o*-quinone (**22**) is formed (eq 6) from the intermediate anion with consequent loss of the



(6)

21 22

aromatic resonance energy. When we treated phenol **21** with *n*-BuLi in THF, no apparent reaction took place. The solution remained colorless. No *o*-quinone, which might have escaped from a solvent cage, was detected by TLC or by its bright red color. In addition, as mentioned earlier, **13**, the *O*-tosyl-*N*-tosyl derivative of *o*-aminophenol, was stable to *n*-BuLi. Elimination would have given *N*-tosyl-*o*-quinonimine which is probably more stable than **18**. Also, it is not clear that **18**, if formed, would add sulfinate **19** at nitrogen to give sulfonamide **1b** (eq 5). ***o*-Quinone (22)** adds benzenesulfinate anion at ring carbons via 1,4- (in water) or 1,6- (in THF) addition.[17–19] But in an analogous molecule (**23**) heavily biased toward addition at nitrogen, N-addition of arenesulfinate anion in aqueous solution occured, and this addition was favored markedly over ring addition as the pH was increased from 5 to 9 (eq 7).[20]

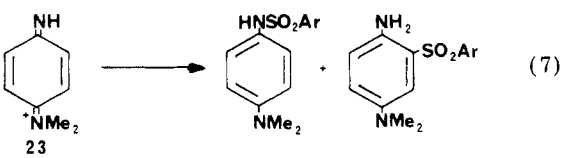


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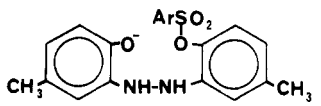
Table II. NMR Chemical Shifts

compd	shift, δ			
	Ar R	NH_n	OH	Ar H
1a	2.50 (s, 3)[a]	3.85 (br s, 2)		6.6-8.0 (m, 8)
1b	2.41 (s, 3)[a]			6.8-7.9 (m, 10)[b]
2a	3.90 (s, 3)[c]	3.8 (br s, 2)		6.5-8.0 (m, 8)
2b	3.80 (s, 3)[c]			6.8-7.8 (m, 10)[b]
3a	1.36 (s, 9)[d]	3.78 (s, 2)		6.5-7.1 (m, 4), 7.5-8.0 (q, 4)
3b	1.36 (s, 9)[d]			6.4-8.0 (m, 10)[b]
4a	2.20 (s, 3),[a] 2.42 (s, 3)[a]	3.80 (s, 2)		6.3-6.8 (m, 3), 7.3-7.9 (q, 4)
4b	2.16 (s, 3),[a] 2.41 (s, 3)[a]	6.2 (br s, 1)		6.5-7.8 (m, 8)[e]
5a	2.21 (s, 3),[a] 3.91 (s, 3)[c]	3.80 (br s, 2)		6.4-8.0 (m, 7)
5b	2.20 (s, 3),[a] 3.90 (s, 3)[c]			6.8-8.0 (m, 10)[b]
6a	1.36 (s, 9),[d] 2.22 (s, 3)[a]	3.82 (br s, 2)		6.4-6.9 (m, 3), 7.6-8.1 (q, 4)
6b	1.32 (s, 9),[d] 2.12 (s, 3)[a]	6.28 (br s, 1)	6.65 (s, 1)	6.6-7.0 (m, 3), 7.5-7.9 (q, 4)
8a	2.14 (s, 3),[a] 2.24 (s, 3),[a] 2.52 (s, 6)[a]	3.68 (s, 2)		6.15 (s, 2), 6.41 (s, 1), 6.83 (s, 2)
8b	2.1 (s, 3),[a] 2.25 (s, 3),[a] 2.50 (s, 6)[a]	6.55 (s, 1)	6.40 (s, 1)	6.65 (s, 1), 6.8 (s, 2), 6.9 (s, 2)
14a	2.5 (s, 3)[a]	4.7 (br s, 2)		6.4-8.0 (m, 7)
14b	2.4 (s, 3)[a]		8.5 (br s, 1)	6.5-8.0 (m, 7)
15a	2.43 (s, 3)[a]	4.3 (br s, 2)		7.0-8.0 (m, 10)
15b	2.4 (s, 3)[a]	6.55 (br s, 1)		7.0-7.8 (m, 11)[e]
17a	2.5 (s, 3), 3.2 (s, 3)[f]	4.3 (br s, 2)		6.4-7.8 (m, 8)

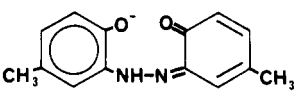
[a] $ArCH_3$. [b] Both NH and OH resonate in this region. [c] $ArOCH_3$. [d] $ArC(CH_3)_3$. [e] OH resonates in this region. [f] $ArNCH_3$.

We tried to trap any quinonimine by treating the mesitylenesulfonate **8a** with *n*-BuLi in the presence of *p*-toluenesulfinate anion (**19**). Recall that sulfonate **8a** gave low yields of the expected sulfonamide **8b**. If the elimination mechanism (eq 5) were being followed, it seemed likely that steric hindrance to recombination of the ion–molecule pair might have been responsible for the low yield. But added anion **19** should react with a quinonimine intermediate. However, no sulfonamide **4b**, which should have resulted, was detected by TLC. On the other hand, **19** is not very soluble in THF and may not efficiently trap any quinonimine.

The formation of azobenzene **12** in the reactions of **6a** and **8a** with *n*-BuLi may well be evidence of a quinonimine. Its formation might occur via addition of the anilide anion to the quinonine to give intermediate **24**. Two



24



25

proton abstractions would give **25** first and then the dianion of **12**. Furthermore, **12** was not formed from either **6b** or **8b**. This was confirmed by treating **6b** and **8b** individually with *n*-BuLi; no **12** was detected. Why **12** was formed from **6a** and **8a** but an analogous azobenzene was not formed from **1a** is not clear.

Several other reactions were carried out which bear on the mechanism of the rearrangement. First, a mixture of *p*-toluidine (**26**) and phenyl *p*-toluenesulfonate (**27**) was treated with *n*-BuLi in THF. No formation of *N*-*p*-tolyl-*p*-toluenesulfonamide (**28**) took place; instead, a complex mixture of products was formed. This result is consistent with an elimination mechanism. It may also agree with the endocyclic mechanism. Trigonally bipyramidal sulfuranes are stabilized by ring formation, and the same may hold true here; i.e., ring formation may facilitate an endocyclic reaction.[21] Second, 4-aminophenyl 4-toluenesulfonate (**29**) was treated with *n*-BuLi in THF. The elimination mechanism is possible, but nucleophilic substitution, in view of the results obtained with **26** and **27**, is not very likely. A complex mixture which did not contain any *N*-(4-hydroxyphenyl)-*p*-toluenesulfonamide (**30**) was obtained.

Sulfonate **16a** cannot form a quinonimine, yet it rearranged to sulfonamide **16b**. A six-membered cyclic transition state or intermediate would be involved in this reaction in contrast to the five-membered cyclic transition states or intermediates postulated for the rearrangements of the sulfonates (**1a–8a**) derived from *o*-aminophenols and the related compounds **14a** and **15a**. Neither can quinonimines be involved in the rearrangement of the sulfonamides studied by Closson and Hellwinkel and their coworkers.[8,9] Four-membered cyclic transition states or intermediates should be involved in these reactions.

It appears that the rearrangement of **16a** which we studied as well as those studied by Closson and Hellwinkel are at present best explained as examples of endocyclic nucleophilic substitution at tetracoordinate hexavalent sulfur (sulfonyl sulfur) which proceed through four- or six-membered cyclic transition states, depending on the structure of the starting molecule. But for the rearrangements of sulfonates derived from *o*-aminophenol and analogous compounds, it is not at all clear what mechanism they follow, be it endocyclic nucleophilic substitution, a quinonimine–sulfinate molecule–ion pair, both, or some other pathway. The nature of any intermediates and the stereochemistry of the reactions in all cases remain to be clarified.[22]

Experimental Section

Melting points determined in capillary tubes are uncorrected. Microanalysis were performed by D. Cardin using a Perkin-Elmer 240B elemental analyzer. Satisfactory elemental analyses were obtained for **2a,b–6a,b**, **7a**, **8a,b**, **14a,b–16a,b**, **17b**, and **31**. NMR spectra were determined on $CDCl_3$ solutions by using JEOL FX90Q, JEOL MN-100, Varian EM-360, and Varian A-60 spec-

(20) Finley, K. T.; Kaiser, R. S.; Reeves, R. L.; Werimont, G. *J. Org. Chem.* **1969**, *34*, 2083–2090.
(21) Perozzi, E. F.; Martin, J. C. *J. Am. Chem. Soc.* **1979**, *101*, 1155–1159.
(22) A referee has suggested that treatment of the sulfamate derived from *N*-methyl-*o*-aminophenol with *p*-tolyllithium would generate the intermediate presumed to be formed in an endocyclic substitution process involving **7a**.

trometers (chemical shifts are reported in parts per million downfield from Me_4Si and are given, in part, in Table II). IR spectra were determined on Perkin-Elmer 337 and 283B spectrophotometers. Mass spectra were determined on a Hitachi Perkin-Elmer RMU-6E spectrometer. The rearrangement reactions were carried out under nitrogen atmospheres. In some cases, the oxygen content of the nitrogen was further reduced by passing the gas over Ridox (Fisher). THF was distilled from sodium benzophenone ketyl. *n*-Butyllithium was a 1.6 M solution in hexane (Alfa). Methyllithium was a 1.4 M solution in ether.

2-Aminophenyl 4-Toluenesulfonate (1a) was prepared according to the procedure of Kurita[13] by treating a stirred, ice-cold suspension of 2-aminophenol (1.09 g, 10.0 mmol) in 20 mL of CH_2Cl_2 with triethylamine (1.01 g, 10.0 mmol) and *p*-toluenesulfonyl chloride (1.91 g, 10.0 mmol). After being stirred for 1 h at room temperature, the mixture was washed with 15 mL of water. The organic layer was removed, dried over magnesium sulfate, filtered, and concentrated in vacuo to give 2-aminophenyl 4-toluenesulfonate (**1a**; 2.84 g, 1.08 mmol) in 94% yield; It was recrystallized from benzene–hexane. Sulfonates **2a–8a**, **14a**, and **15a** were prepared in a similar way. *N*-Acyl derivatives of **2a**, **3a**, and **5a** were prepared by heating under reflux for 30 min a mixture of the sulfonates (5 mmol), acetic anhydride (0.5 mL), acetic acid (0.5 mL), and zinc dust (5 mg).

***N*-(2-Hydroxyphenyl)-4-toluenesulfonamide (1b)** was prepared in 95% yield by treating *o*-aminophenol with *p*-toluenesulfonyl chloride as above except that pyridine was used in place of triethylamine.[13] Sulfonamides **2b–6b**, **8b**, **14b**, and **15b** were prepared in a similar manner. *O*-Acetyl derivatives of **5b** and **8b** were prepared by treating the respective sulfonamide (1 g) dissolved in 3 M NaOH (50 mL) with crushed ice (10–20 g) and acetic anhydride (1.5 mL). The acetates which precipitated were recrystallized from aqueous ethanol and then from benzene–hexane. The *O*-*p*-toluenesulfonate derivative of **2b** (**13**) was prepared by using *p*-toluenesulfonyl chloride and triethylamine in methylene chloride according to the procedure described above for sulfonate **1a**. Analytically pure samples of the various compounds were often successfully prepared by vacuum sublimation.

Rearrangement of 1a to 1b. Sulfonate **1a** (500 mg, 0.19 mmol) in ether (100 mL) was treated with *n*-BuLi (5.3 mL, 8.4 mmol) at 0 °C. After being stirred for 1 h at room temperature, the mixture was hydrolyzed with water. The water layer was extracted with three 50-mL portions of CH_2Cl_2. The combined organic layers were dried and concentrated to give unreacted starting material and impurities. The aqueous layer was acidified with dilute HCl and then extracted with three 50-mL portions of CH_2Cl_2. A workup as above gave **1b** which was recrystallized from CH_2Cl_2–petroleum ether. Repetition of this reaction with 1 g of **1a** led to the isolation of *n*-butyl *p*-tolyl sulfone: 50 mg (0.24 mmol, 3%); ^1H NMR δ 0.9 (t, 3, CH_3), 1.1–1.8 (m, 4, CH_2CH_2), 2.4 (s, 3 H, Ar CH_3), 3.1 (t, 2 H, CH_2SO_2), 7.5 (2 d, 4 H, Ar H); ^{13}C NMR δ 1.0, 13.5, 21.6 24.7, 56.2, 128.0, 129.9, 136.4, 144.5; IR (neat) 1260 and 1140 (SO_2) cm^{-1}; MS, *m/e* 212 (M^+). Rearrangements of sulfonates **2a** to **7a** were carried out in a similar fashion. THF was also used at times for the reaction solvent.

Treatment of 1b with *n*-BuLi in the manner described for the rearrangement of **1a** and **1b** gave only recovered **1b** (TLC, SiO_2, 5% EtOAc/95% $CHCl_3$). The NMR spectrum exhibited a single tolyl methyl resonance at δ 2.41 characteristic of **1b** and none at δ 2.50 characteristic of **1a**.

Treatment of 13 with *n*-BuLi in similar fashion gave only unreacted **13** after hydrolysis as shown by TLC (SiO_2, 5% EtOAc/95% $CHCl_3$) and NMR.

Treatment of 1a with Various Bases. (1) Phenyllithium (1.52 mmol), prepared from bromobenzene and lithium wire, and **1a** (0.10 g, 0.38 mmol) were reacted in THF (70 mL) at room temperature for 6 h. The workup gave a mixture which was analyzed by TLC. No spot for **1b** was observed, but spots with retention times characteristic of **1a**, *o*-aminophenol, and phenyl *p*-tolyl sulfone were observed as well as a fourth spot due to an unidentified substance. (2) Methyllithium treatment of **1a** in either for 0.5 h at 0 °C and 2 h at room temperature gave **1b** (75%). (3) Treatment of **1a** (500 mg, 0.19 mmol) with sodium hydride (200 mg, 8.5 mmol) in THF at 0 °C for a few minutes and then for 16 h at room temperature gave only a 25% yield of **1b** plus recovered **1a**. (4) Lithium hydride did not induce any formation of **1b** from **1a** under the conditions used for NaH. (5) Lithium diisopropylamide (8.5 mmol) was prepared in situ from *n*-BuLi and diisopropylamine in ether at 0 °C. Sulfonate **1a** (500 mg, 0.19 mmol) rearranged to **1b** (60%) when treated with the LDA solution for 0.5 h at 0 °C and then room temperature for 2 h. (6) Sulfonate **1a** (250 mg, 0.095 mmol), THF (25 mL), and liquid NH_3 (25 mL) were cooled in a dry ice–acetone bath. Methyllithium (4.26 mmol) was added, and the mixture was stirred overnight. Evaporation of the NH_3 followed by the usual workup gave **1b** in low yield. (7) The anion of dimethyl sulfoxide was prepared from Me_2SO (10 mL) and NaH (400 mg, 8.5 mmol). Sulfonate **1a** (500 mg, 0.19 mmol) in Me_2SO (10 mL) was added at room temperature. After being stirred for 4 h, the mixture was hydrolyzed and extracted with CH_2Cl_2 to give sulfonamide **1b** in low yield.

2-(Methylamino)phenyl 4-Toluenesulfonate (7a). Dimethyl sulfate (31.9 g, 0.253 mol) was added dropwise over a 5-min period to a stirred, gently boiling mixture of sulfonate **1a** (27.4 g, 0.104 mol) and 5.5 M sodium hydroxide (140 mL). Two layers formed. Stirring and heating were continued for 0.5 h. Ether extraction of the cooled mixture followed by drying and concentration of the organic layer yielded an oil which was crystallized from ethanol: 22% yield (6.43 g, 0.023 mol); NMR δ 2.40 (s, 3, Ar CH_3), 2.70 (d, 3, NCH_3), 4.0 (br s, 1, Ar NH), 6.36–6.98 (m, 4, Ar H), 7.12–7.76 (2 d, 4, Ar H); IR (KBr) 3410 (NH) cm^{-1}.

Rearrangement of Sulfonate 7a to *N*-Methyl-*N*-(2-hydroxyphenyl)-4-toluenesulfonamide (7b). Sulfonate **7a** (2.48 g, 10.2 mmol) was treated with *n*-BuLi (6.40 mL, 10.2 mmol) in ether (150 mL) at 0 °C for 2 h. The mixture was worked up as for the rearrangement of **1a** to give sulfonamide **7b** (1.20 g, 0.43 mmol) in 43% yield from ethanol: NMR δ 2.40 (s, 3, Ar CH_3), 3.15 (s, 3, NCH_3), 6.1–7.7 (m, 9, Ar H, OH); IR (KBr) 3450 (OH) cm^{-1}.

Rearrangement of 2-Aminopyrid-3-yl 4-Toluenesulfonate (14a) to *N*-(3-Hydroxypyrid-2-yl)-4-toluenesulfonamide (14b). Sulfonate **14a** (500 mg, 0.19 mmol) in THF (50 mL) was treated with *n*-BuLi (4.75 mL, 7.6 mmol) at −68 °C for 1 h. The mixture was then brought to room temperature for 15 min, 20 mL of water was added, and the mixture was extracted once with methylene chloride to remove only **14a**. The aqueous layer was saturated with salt and extracted three times with 50-mL portions of ethyl acetate. After being dried, the organic extracts yielded sulfonamide **14b**: 350 mg (0.13 mmol, 70% yield); mp 162–163 °C (from CH_2Cl_2/peteroleum ether).

Rearrangement of 1-Aminonaphth-2-yl 4-Toluenesulfonate (15a) to *N*-(2-Hydroxynaphth-1-yl)-4-toluenesulfonamide (15b). Sulfonate **15a** (200 mg, 0.064 mmol) in THF (20 mL) was treated with *n*-BuLi (1.5 mL, 2.4 mmol) at −68 °C for 1 h. When the mixture was warmed to room temperature, the color of the solution turned from yellow to orange to dark red. Hydrolysis and workup showed (TLC) the residue to consist of **15a** and **15b** in roughly equal amounts. Preparative TLC (SiO_2, 90% CH_2Cl_2/10% EtOAc) gave **15a** (50 mg, 0.016 mmol; 25% recovery) and **15b** (50 mg, 0.016 mmol) in 33% yield; mp 175–176 °C (from $CHCl_3$/petroleum ether). Repetition of the reaction with MeLi in place of *n*-BuLi gave 10% recovered **15a** and 22% **15b**, based on recovered **15a**.

8-Aminonaphth-1-yl 4-toluenesulfonate (16a) was prepared by treating 8-amino-1-naphthol (300 mg, 0.096 mmol) with triethylamine (192 mg, 0.19 mmol) and *p*-toluenesulfonyl chloride (360 mg, 0.19 mmol) in CH_2Cl_2 as described for **1a**. Preparative TLC (SiO_2, 90% petroleum ether–10% EtOAc) gave **16a**: [100 mg (0.032 mmol, 33%); mp 160–161 °C (from $CHCl_3$–petroleum ether); NMR δ 2.3 (s, 3, $CH_3C_6H_4SO_3$), 4.7 (s, 2, NH_2), 6.5–7.9 (m, 10, Ar H); IR (Nujol) 3460 (NH_2), 3360 (NH_2) cm^{-1}] and *N*-(8-toluenesulfonoxynapthyl)-4-toluenesulfonamide (**31**): 200 mg (0.063 mmol, 44%); mp 150–151 °C (from CH_2Cl_2–petroleum ether); NMR δ 2.3 (s, 3, $CH_3C_6H_4SO_3$), 2.5 (s, 3, $CH_3C_6H_4SO_2NH$), 7.1–8.1 (m, 14, Ar H), 8.6 (br s, 1, NH); IR (Nujol) 3400 (NH) cm^{-1}.

Rearrangement of 16a to 16b. Sulfonate **16a** (100 mg, 0.032 mmol) in 25 mL of THF was treated with *n*-BuLi (0.75 mL, 1.2 mmol) at −68 °C for 1 h and then at room temperature for 20 min. The hydrolysis and workup were carried out as for **1a**. TLC indicated the presence of several products but no starting material. The major product isolated by preparative TLC (SiO_2, 15% of EtOAC/85% of petroleum ether) was **16b**: 20 mg (0.086 mmol,

20%); mp 180–181 °C (from $CHCl_3$–petroleum ether); NMR δ 2.2 (s, 3, $CH_3C_6H_4$) 6.7–7.8 (m, 12, Ar H, OH, NH); IR (Nujol) 3320 and 3280 cm^{-1}.

Rearrangement of 17a to 17b. Sulfonamide **17a** (300 mg, 0.108 mmol) in THF (50 mL) was treated with *n*-BuLi (4 mL, 6.4 mmol) at −68 °C for 2 h and then at room temperature for 0.5 h. The solution went from yellow to dark red. After hydrolysis, the major product (**17b**) was isolated by preparative TLC (SiO_2, 9:1 CH_2Cl_2/EtOAc): 50 mg (0.018 mmol, 17%); mp 119–120 °C (from EtOH); NMR δ 2.4 (s, 3, $CH_3C_6H_4$), 2.8 (s, 3, NCH_3), 6.5–7.8 (m, 10, Ar H, NH). IR (Nujol) 3420 (NH), 3260 (NH) cm^{-1}.

Attempted Thermal Rearrangement of 1a. (a) A sample of sulfonate **1a** in a melting point capillary tube was kept at 197 °C for 0.5 h during which time the clear melt became dark in color. Analysis of the melt by TLC revealed no sulfonamide **1b**. (b) A solution of sulfonate **1a** (200 mg) in diglyme (20 mL) was heated under reflux under a nitrogen atmosphere for 6 h. Upon removal of the solvent, only starting material was detected by TLC. No sulfonamide **1b** was observed.

Crossover Experiment. Sulfonates **2a** (1.5 g, 5.4 mmol) and **6a** (1.5 g, 4.7 mmol) in THF (800 mL) cooled to 0 °C were treated with *n*-BuLi (1.6 M, 26 mL, 42 mmol). After being stirred for 6 h at room temperature, the mixture was hydrolyzed with 5% HCl (100 mL), concentrated in vacuo, and extracted with ether. The ether extracts were analyzed by a combination of column chromatography, TLC, and NMR. Sulfonamides **2b** and **6b** were shown to be present whereas **3b** and **5b** were absent. There was no spot for **3b** on TLC. Sulfonamide **5b** shown to be absent by adding authentic samples to fractions from the column chromatography. A signal at δ 2.14 due to the 5′-CH_3 group of **5b** was absent in the fraction which contained **6b** (5′-Me at δ 2.08).

Rearrangement of 8a to 8b. Sulfonate **8a** (2.4 g, 7.87 mmol) in THF (150 mL) was treated with *n*-BuLi (15 mL. 27 mmol) for 0.5 h at −78 °C and then for 2.5 h at room temperature. After the usual workup sulfonamide **8b** was isolated: 100 mg (0.32 mmol, 42%); mp 129–130 °C. 2,2′-Dihydroxy-5,5′dimethylazobenzene (**12**) was also isolated: 200 mg (0.83 mmol, 11%); mp 216–217 °C (lit.[23] mp 216–217 °C); MS *m/e* 242; ^1H NMR δ2.3 (s, 6, CH_3), 6.8–7.5 (ABC m, 6, Ar H), (s, 2, OH); ^{13}C NMR δ 20.4, 118.6, 130.2, 131.3, 134.5, 135.6, 151.2; IR (KBr) 3430 (OH) cm^{-1}.

(23) Schetty, G. *Helv. Chim. Acta* **1970**, *53*, 1437–1459.

Rearrangement of 8a to 8b in the Presence of Sodium *p*-Toluenesulfinate. A mixture of **8a** (250 mg, 0.82 mmol), anhydrous sodium *p*-toluenesulfinate (500 mg, 2.76 mmol), and THF (80 mL) was treated with *n*-BuLi (2.0 mL, 3.3 mmol) as above. The workup of the reaction mixture gave results as above with no evidence (TLC) for the presence of **4b**.

Treatment of 2-Hydroxyphenyl Benzenesulfonate (21) with *n*-BuLi. Sulfonate **21** (250 mg, 1 mmol) in THF (25 mL) was treated with *n*-BuLi (0.63 mL, 1.0 mmol) at −78 °C for 0.5 h and then at room temperature for 3 h. The solution remained colorless. Starting material **21**, as indicated by TLC and NMR, was recovered quantitatively upon hydrolysis of the reaction mixture.

Reaction of *p*-Toluidine (26) with Phenyl *p*-Toluenesulfonate (27). *p*-Toluidine (495 mg, 0.42 mmol) in THF (25 mL), cooled to −68 °C, was treated with MeLi (10 mL, 12.5 mmol) whereupon the solution turned pale yellow. Sulfonate **27** (1.1 g, 0.44 mmol) was added. After 1.5 h, the mixture was brought to room temperature whereupon the color turned to dark red. After 0.5 h, the mixture was hydrolyzed and worked up as usual. TLC revealed no starting material nor any *N*-(4-tolyl)-4-toluenesulfonamide. The products were not further investigated.

Reaction of 4-Aminophenyl 4-Toluenesulfonate (29) with *n*-BuLi. Sulfonate **29** (500 mg, 1.9 mmol) was treated with MeLi (5.4 mL, 7.6 mmol) in THF (100 mL) at 0 °C. Upon the usual workup, the reaction mixture became dark purple during solvent removal. Repetitions of the reaction always resulted in dark-colored materials which were not futher identified.

Acknowledgment. We thank the NSF for partial support of this research and for providing funds for the purchase of a JEOL FX90Q spectrometer (Grant No. CHE-77893). We also thank M. Turnbull for experimental assistance.

Registry No. **1a**, 1216-96-2; **1b**, 3897-39-0; **2a**, 81256-07-7; **2b**, 81256-08-8; **3a**, 81278-80-0; **3b**, 81256-09-9; **4a**, 81256-10-2; **4b**, 81256-11-3; **5a**, 81256-12-4; **5b**, 81256-13-5; **6a**, 81256-14-6; **6b**, 81256-15-7; **7a**, 81256-16-8; **7b**, 81256-17-9; **8a**, 81256-18-0; **8b**, 81256-19-1; **13**, 81256-20-4; **14a**, 30378-30-4; **14b**, 81256-21-5; **15a**, 81256-22-6; **15b**, 81256-23-7; **16a**, 81256-24-8; **16b**, 36364-83-7; **17a**, 25446-46-2; **17b**, 38163-84-7; **21**, 3839-96-1; **26**, 106-49-0; **27**, 640-60-8; **29**, 3899-93-2; 2-aminophenol, 95-55-6; 8-aminonaphthol, 2834-91-5.

Effects of Pressure and Isotopic Substitution on the Rate of Reaction of Coal with Tetralin

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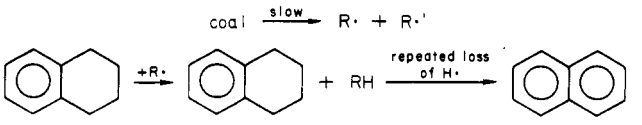
The molar activation volume for the reaction of coal with tetralin at 344 °C is −27 ± 3 mL. This result suggests a transition state which is bimolecular and possibly ionic. It is inconsistent with the hypothesis that the rate is controlled by homolysis of the coal molecule. The H/D kinetic isotope effect for the reaction of coal with tetralin containing deuterium at the α-positions is 2.1 ± 0.1 at 335 °C. This result reinforces the conclusions based on the activation volume.

Since 1967 a majority of writers on the subject of liquefaction of coal by hydrogen donor solvents have endorsed the free-radical mechanism proposed by Curran, Struck, and Gorin.[1] The rate-limiting step is assumed to be homolysis of a C–C or C–O bond followed by abstraction of hydrogen atoms from the donor. Using tetralin as an example of a donor solvent, one may represent the process as in Scheme I. Following this proposal there have been a number of studies of the free-radical decomposition of

Scheme I



(1) G. P. Curran, R. T. Struck, and E. Gorin, *Ind. Eng. Chem. Process Des. Dev.*, **6**, 166 (1967).

0022-3263/82/1947-1889$01.25/0