Intermediacy of *o*-Sulfonylium Arenide Ylides in the Reactions of Arenesulfonyl Derivatives with Strong Bases: Insight into the Puzzling Rearrangement of *N*-Arylarenesulfonamides into 2-Aminodiaryl Sulfones[1]

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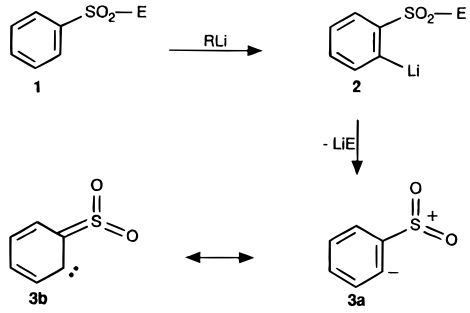
Benzenesulfonyl derivatives, $PhSO_2E$, such as benzenesulfonyl fluoride, phenyl benzenesulfonate, and *N*-methyl-*N*-phenylbenzenesulfonamide, have been found to undergo *ortho*-lithiation with lithium 2,2,6,6-tetramethylpiperidide (LTMP) in THF at −78 °C. The resulting lithio derivatives undergo 1,3-elimination of LiE to form the transient *o*-sulfonylium benzenide. The latter ylide, which may be stabilized by its carbenoid character and its complexation with LiE, can be trapped by benzophenone acting as a 1,3-dipolarophile to form the adduct, 3,3-diphenyl-1,2-benzoxathiole 1,1-dioxide. The alternative formation of the latter cyclic sulfonate by reaction of the initially formed *o*-lithio derivative with benzophenone and by subsequent cyclization was shown *not* to occur. If not trapped with benzophenone, such an ylide decomposes partly into SO_2 and benzyne and then undergoes self-condensation to yield poly(phenylene-*o*,*o*′-biphenylene sulfones). *o*-Sulfonylium benzenide also can be captured by lithium alkoxides, either present adventitously or intentionally added, to generate the corresponding alkyl benzenesulfonate. However, such alkoxides, unaided by LTMP, are themselves unable to extract an *ortho*-proton from benzenesulfonyl fluoride or from *N*-methyl-*N*-phenylbenzenesulfonamide to yield the corresponding *o*-lithio derivative. With benzenesulfonyl fluoride the lithium alkoxide can also form the sulfonate ester by direct substitution at the sulfonyl group. The Closson−Hellwinkel rearrangement of *N*-methyl-*N*-phenylbenzenesulfonamide into *o*-(methylamino)diphenyl sulfone by RLi or LTMP is reinterpreted as proceeding by way of the 2-lithio- or 2,6-dilithiobenzenesulfonyl derivative which eliminates lithium *N*-methylanilide to form the *o*-sulfonylium benzenide or its 6-lithio derivative. Attack of the latter ylide, acting as an electrophile, upon the *ortho*-position of the presumably complexed LiNMePh then consummates the rearrangement.

A broad variety of benzenesulfonyl derivatives ($PhSO_2E$, **1**) undergo useful reactions with organolithium reagents, some of which have proved to be of value in synthesis or in mechanistic studies. The fluoride derivative (**1a**, E = F) reacts with RLi to produce the sulfone, $PhSO_2R$, in excellent yield;[2] the methyl member (**1b**, E = Me) yields the useful reagent $PhSO_2CHLi_2$,[3] and the phenyl sulfone (**1c**, E = Ph) can be readily mono- or dilithiated at the *o*-position or the *o*,*o*′-positions, respectively.[4] The mechanistic questions raised by the action of RLi on such sulfonyl derivatives are no less interesting and appealing. Thus, although **1c** undergoes the aforementioned *o*-lithiation with Bu^nLi upon short reaction time, prolonged reaction converts this sulfone into dibenzothiophene.[5] Similarly, treatment of the sulfonate ester (**1d**, E = OPh) unleashes a complex array of reactions attributable to the generation of benzyne via an *o*-lithio intermediate derived from the benzenesulfonyl moiety.[6] Finally, the reaction of *N*-arylsulfonamides (**1e**; E = NPhR) with RLi causes a profound and ill-understood rearrangement

Scheme 1



leading to a 2-aminodiaryl sulfone in yields of 50−90% (*cf.*, *e.g.*, **1e** → **9** in eq 2).[7,8]

In all of these reactions with RLi, with the exception of that with methyl phenyl sulfone (**1b**), the fastest initial reaction is undoubtedly *ortho*-lithiation to produce **2** (Scheme 1). With this experimentally verified fact, we were interested in the possibility that the observed reactions of RLi with **1a**, **1c**, **1d**, and **1e** might not have resulted from the direct attack of RLi on the SO_2E group in **1** but might instead have proceeded either via **2** or, more intriguingly, via *o*-sulfonylium benzenide (**3**), accessible from **2** by a 1,3-elimination. Intermediate **3** might be relatively stabilized by π-electron delocalization as depicted in its zwitterionic or ylide structure **3a** and its carbene resonance form **3b**.[9]

[⊗] Abstract published in *Advance ACS Abstracts,* February 1, 1996.

(1) Sulfone Reagents in Organic Synthesis. 9. Part 8: Eisch, J.J.; Hallenbeck, L. E.; Lucarelli, M. A. *J. Org. Chem.* **1991**, *56*, 4095.

(2) Frye, L. L.; Sullivan, E. L.; Cusack, K. P.; Funaro, J. M. *J. Org. Chem.* **1992**, *57*, 697.

(3) Eisch, J. J.; Dua, S. A.; Behrooz, M. *J. Org. Chem.* **1985**, *50*, 3674.

(4) Truce, W. E.; Amos, M. F. *J. Am. Chem. Soc.* **1951**, *73*, 3013.

(5) Eisch, J. J.; Behrooz, M.; Galle, J. E. *Tetrahedron Lett.* **1984**, *25*, 4851.

(6) Fleming, I.; Mah, T. *J. Chem. Soc., Perkin Trans. 1* **1976**, 1599.

(7) Shafer, S. J.; Closson, W. D. *J. Org. Chem.* **1975**, *40*, 889.

(8) Hellwinkel, D.; Supp, M. *Tetrahedron Lett.* **1975**, 1499.

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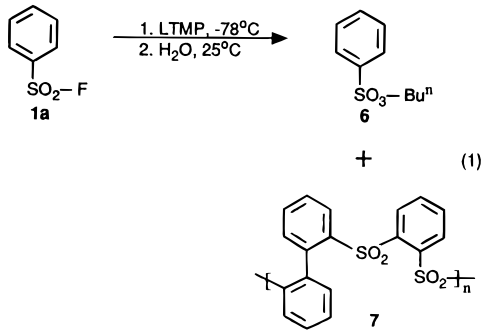
In order to test for the crucial intermediacy of **2** or **3** in these reactions of sulfonyl derivatives with RLi, we treated the individual benzenesulfonyl fluoride (**1a**), phenyl benzenesulfonate (**1d**), and *N*-methyl-*N*-phenylbenzenesulfonamide (**1e**) at low temperatures in THF solution with the strong but sterically hindered lithium 2,2,6,6-tetramethylpiperidide (LTMP, **4**).[10a] The use of LTMP was intended to effect nucleophilic attack on the *ortho*-hydrogen in **1a**, **1d**, and **1e** but not on the less accessible sulfonyl group. The resulting lithium derivatives were either hydrolyzed directly or treated with benzophenone (**5**) or methyl iodide as a trapping agent prior to hydrolysis. Through a critical analysis of the various reaction products, we have attempted to adduce evidence concerning the relative importance of intermediates **2** and **3** in these organolithium reactions and specifically in the unusual Closson−Hellwinkel rearrangement of *N*-arylarenesulfonamides.[11]

Results

Lithiation of Benzenesulfonyl Derivatives 1a, 1d, and 1e in THF by LTMP followed by Hydrolysis. The lithiation of each of these sulfonyl derivatives by LTMP (**4**) at −78 °C and subsequent hydrolysis at 20 °C yielded interesting, ether-soluble organic products, but the overall yield of such products ranged between 15 and 45% of the theoretical. The balance of the starting material was converted in varying amounts into benzenesulfonic acid and benzyne precursors, as is shown by the following reaction of LTMP with benzenesulfonyl fluoride (**1a**) in THF. The organic layer obtained upon hydrolysis contained 6% of *n*-butyl benzenesulfonate (**6**), 23% of recovered **1a**, and 20% of a suspended solid (**7**) that by IR and MS criteria is considered an *o*-phenylene−*o*,*o*′-biphenylene sulfone polymer (eq 1). The presence of

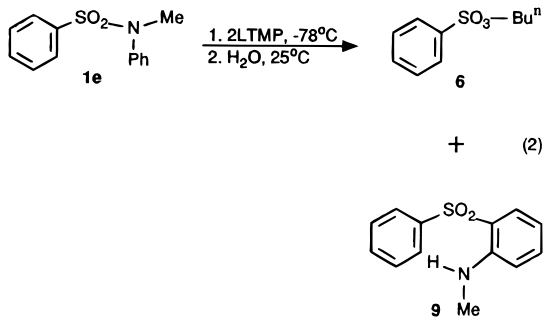


mass peaks corresponding to the phenylsulfonyl and the biphenylenesulfonyl fragments corroborate this conclusion. The aqueous layer, upon acidification, evolved SO_2 gas, and the remaining solution was boiled to dispel all such gas. Addition of aqueous $BaCl_2$ to the solution gave a colorless precipitate that was shown to be barium benzenesulfonate.

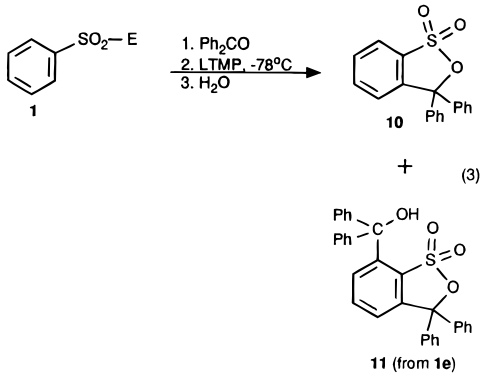
The sulfonate ester 6 was shown to have arisen from adventitious lithium *n*-butoxide present in the *n*-butyllithium used to generate **4** from 2,2,6,6-tetramethylpiperidide. When LTMP was prepared by treating 2,2,6,6-tetramethylpiperidide with methyllithium in diethyl ether solution, the reaction of **1a** with LTMP led only to ethyl benzenesulfonate (**8**). Apparently, **8** was formed from the reaction of LTMP with diethyl ether to form ethylene and lithium ethoxide, a known reaction,[10b] and the reaction of this alkoxide with **1a** or a derivative of **1a** (*cf. infra*).

A similar reaction of phenyl benzenesulfonate (**1d**) with 2 equiv of LTMP in THF gave 2% of isolated **6**, as well as the wide variety of products previously reported for this reaction.[6]

Finally, the treatment of *N*-methyl-*N*-phenylbenzenesulfonamide (**1e**) with 2 equiv of LTMP in THF under like conditions yielded 5% of **6** with 5% of the rearranged product, **9**, as well as considerable amounts of recovered **1e** (eq 2).



Lithiation of Benzenesulfonyl Derivatives 1a, 1d, and 1e by LTMP in THF in the Presence of Benzophenone. In order to trap organometallic intermediate **2** or zwitterionic **3** (*cf.* **3a**) in a dipolar addition reaction with a dipolarophile,[12] the foregoing lithiations with LTMP were again carried out in the presence of benzophenone. In every case, the trapping product, 3,3-diphenyl-1,2-benzoxathiole 1,1-dioxide (**10**), could be isolated but in varying yield: fluoride **1a**, 13%; sulfonate ester **1d**, 8%; and sulfonamide, **1e**, 5% (eq 3). In the case of **1e**, 2% of an adduct (**11**) apparently formed from the 2,6-dilithio derivative of **1e**, and 2 equiv of benzophenone was also isolated.



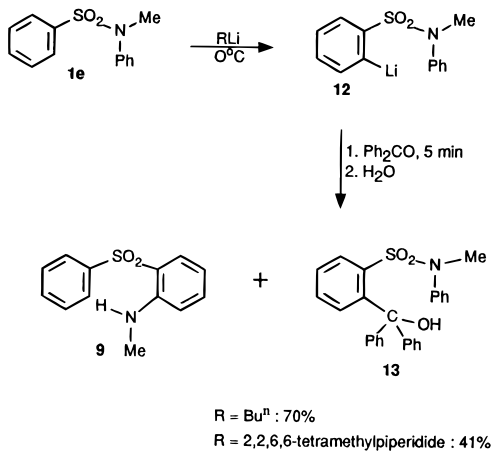
(9) Both resonance structures **3a** and **3b** should make significant contributions to the stabilization of **3**: the carbanionic center in **3a** is greatly stabilized by the potent electron-attracting SO_2^+ center; structure **3b** has no charge separation because S 3d-orbitals can be involved in bonding. *Cf.* Block, E. *Reactions of Organosulfur Compounds*; Academic Press: New York, 1978; pp 18−21.

(10) (a) Rathke, M. W.; Kow, R. *J. Am. Chem. Soc.* **1972**, *94*, 6854. (b) Ziegler, K.; Gellert, H. G. *Justus Liebigs Ann. Chem.* **1950**, *567*, 185.

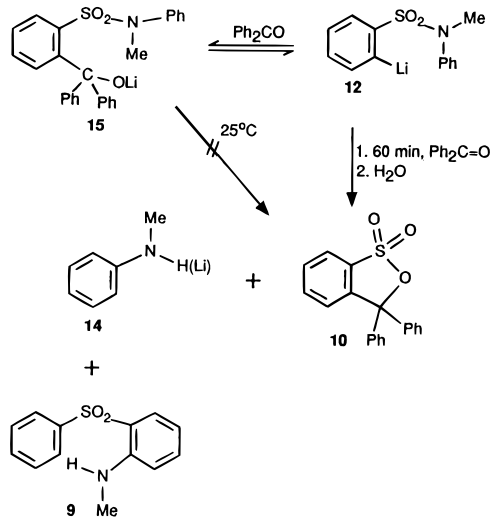
(11) Since this unusual base-promoted rearrangement of *N*-arylarenesulfamides into 2-aminodiaryl sulfones was reported independently and essentially simultaneously by the research groups of the late Professor William Closson (ref 7) and of Professor Dieter Hellwinkel (ref 8), it can be fittingly termed the Closson−Hellwinkel rearrangement. Furthermore, this author wishes to dedicate this article to the memory of Professor Closson (1934−1994), my highly esteemed colleague in the SUNY system.

(12) For a thorough discussion, *cf. 1,3-Dipolar Cycloaddition Chemistry*; Padwa, A., Ed.; John Wiley & Sons: New York, 1984; Vols. 1−2.

Scheme 2



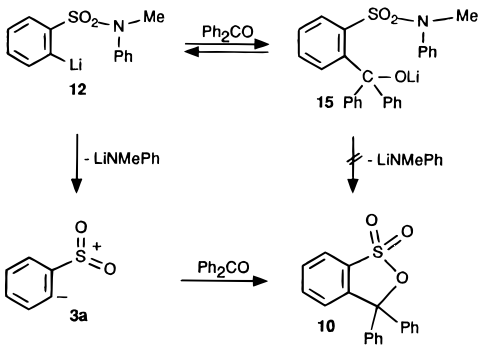
Scheme 3



Interception of the Initial *o*-Lithio Derivative from *N*-Methyl-*N*-phenylbenzenesulfonamide (1e). Treatment of sulfonamide **1e** with 1 equiv of either Bu^n-Li or LTMP in THF at 0 °C for 5 min and then with benzophenone led, upon hydrolysis to α,α-diphenyl-*o*-(*N*-methyl-*N*-phenylsulfonamyl)benzyl alcohol (**13**) as the preponderant product (>70%). The rearrangement product of **1e**, namely, **9**, was formed in about 1% yield (Scheme 2). Particularly sought for but not found was any trace of cyclic sulfonate **10**. These results demonstrate that the *o*-lithio derivative **12** is the initial result of such lithiations and that it is the precursor of both **13** and the rearrangement product **9**.

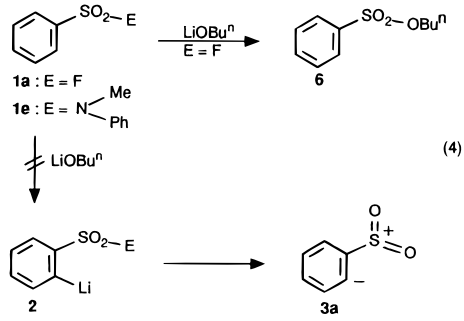
When the reaction of **1e** with Bu^{n}Li was conducted at 20 °C, the benzophenone then added, and the solution allowed to stand 60 min before hydrolysis, the amount of isolated **13** was about 1% and the rearrangement product **9** was 4%. In addition, however, new products were isolated: *N*-methylaniline (**14**) in 5% yield (because of its volatility, a minimum yield) and cyclic sulfonate **10** in 3% yield. These experiments with Bu^{n}Li at 0 °C and at 20 °C support the view that **12** reacts reversibly at 20 °C with benzophenone to form **15** (Scheme 3). The equilibrium is apparently driven to the right by competing reactions that consume **12** and lead to **10**, **14**, and increased amounts of **9**. The direct formation of the lithium salt of **14** and of **10** from **15** is rendered unlikely from the failure to observe the formation of **10** from **15** after 18 h at 25 °C (*cf. infra*).

Scheme 4



Testing the Origin of Cyclic Sulfonate 10 Formed in Lithiations of Sulfonamide 1e Performed in the Presence of Benzophenone. In employing benzophenone as a chemical trapping agent for intermediates formed in the lithiations of **1a**, **1d**, and **1e**, the assumption has been that the formation of cyclic sulfonate **10** would be a diagnostic sign that zwitterionic **3** had been trapped in a dipolar addition reaction. That the *o*-lithio derivative **2** (or specifically **12**) were the only important intermediate would be evident if only the simple alcoholate were instead to form (*e.g.*, **15**). To strengthen the reliability of such deductions, it remained to be tested whether **10** might arise, not from **3**, but from **15** (Scheme 4) by loss of lithium *N*-methylanilide. Accordingly, carbinol **13** was treated with 1 equiv of LTMP at −78 °C for 3 h to generate **15** and the solution then allowed to stand at 25 °C for 18 h. Hydrolysis and chromatographic analysis revealed no trace of **10** but only *N*-methylaniline (at least 28%) and sulfonamide **1e**. The isolation of such a large proportion of *N*-methylaniline again speaks for the reversible dissociation of **15** at 25 °C into **12** and benzophenone and for the further decomposition of **12** into **3a** and its degradation products (**6**, **7**, or **24** in Scheme 6). Apparently, the low concentration of the benzophenone concomitantly generated from **15** prevents its competing successfully for **3a** and thereby forming **10**. Furthermore, the large proportion of *N*-methylaniline formed in this experiment and the absence of any of the cyclic sulfone **10** again argue against slow cyclization of **15** into **10** with the elimination of *N*-methylaniline. Were this course of reaction to have occurred, then an equimolar mixture of the amine and **10** would have been formed. Thus, there is decidedly no indication that the cyclization of **15** into **10** takes place at 25 °C.

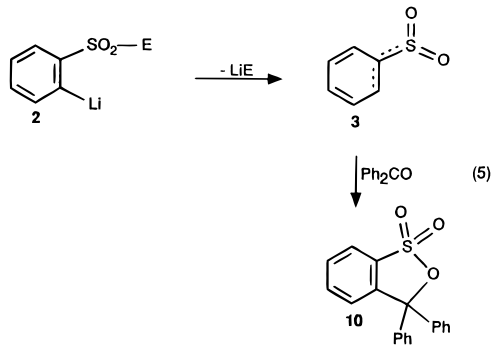
Action of Lithium *n*-Butoxide on Benzenesulfonyl Fluoride (1a) and on *N*-Methyl-*N*-phenylbenzenesulfonamide (1e). The reaction of **1a** with lithium *n*-butoxide in THF gave over a 60% yield of sulfonate ester **6**. Because no *o*-methyl derivative of **1a** was detected in a similar reaction carried out in the presence of methyl iodide, it can be concluded that **2** (E = F) and **3a** are not essential intermediates in the formation of **6** from **1a**. Rather, lithium *n*-butoxide must form **6** by direct attack at the sulfonyl center of **1a**. Further corroboration that intermediate **3a** was not involved in this reaction comes from the reaction of **1a** with lithium *n*-butoxide in the presence of benzophenone. None of the cyclic ester **10**, the normal trapping product of **3a** with this ketone, could be detected in the reaction mixture (eq 4).



In the case of the attempted reaction of sulfonamide **1e** with lithium *n*-butoxide, none of ester **6** was formed. This finding shows the inability of this alkoxide to attack the sulfonyl group of **1e** directly (eq 4).

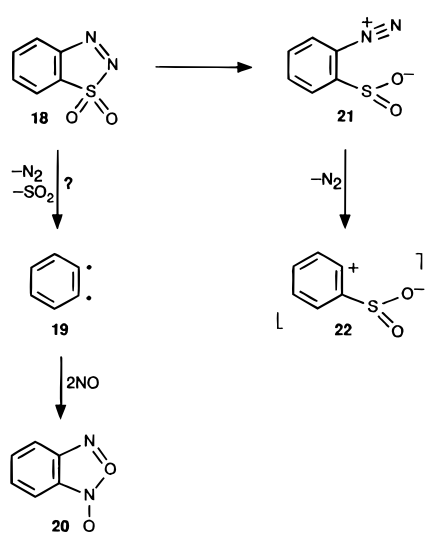
Discussion

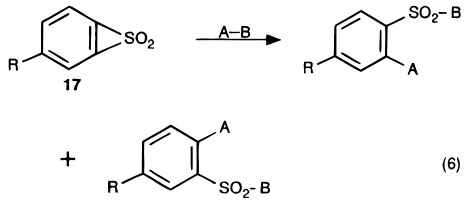
From the foregoing observations, it is clear that the fastest reaction with sulfonyl fluoride **1a**, phenylsulfonate ester **1d**, or sulfonamide **1e** and either alkyllithium or lithium amide bases is the formation of the *o*-lithio derivative **2**. The question whether **2** is the only significant intermediate in such reactions has been answered by the benzophenone-trapping experiments. The isolation of cyclic sulfonate **10** from such reactions is unequivocal proof that zwitterionic or carbene-like (**3a** ↔ **3b**) *o*-sulfonylium benzenide (**3**) has been trapped in a 1,3-dipolar cycloaddition with benzophenone (eq 5). The alternative possibility that **10** could have arisen from a benzophenone adduct of **2** has been ruled out by a direct test (Scheme 4).



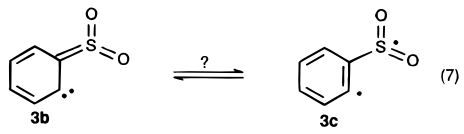
The nature of **3** is not yet completely defined. First, it is not known whether **3** is completely separated from the eliminated lithium salt, LiE, or whether the salt remains complexed with **3** (if then, most likely to oxygen of the SO_2 group; *cf. infra*).[13] One can rule out, however, that such an intermediate would have taken on any episulfone character, as in **17**. In this case, a substituted benzene ring would of necessity lead to *meta*- and *para*-substituted isomers in subsequent sulfone ring-opening reactions (eq 6), but such is not the case. Both in the formation of sulfones from alkyllithiums and substituted sulfonyl fluorides[2] and in the Closson–Hellwinkel rearrangement of substituted sulfonamides,[7] no such isomeric mixtures arise.

Scheme 5





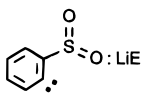
A further, yet to be determined, aspect of **3** is whether it exists as a singlet (**3b**) or as a triplet (**3c**) (eq 7). From



the generation of **3** by thermal means at lower temperatures, one might expect **3b** to arise. Were **3c** to exist, it would be expected to lose SO_2 very readily, as in the metal-catalyzed decomposition of sulfonyl halides.[14] Furthermore, the arylic radical character of **3c** should lead to rapid H-atom abstraction from the THF solvent. Although there is evidence of some SO_2 loss in the present reactions, it is not a dominant pathway.

The reported thermal decomposition of 1,2,3-benzothiodiazole 1,1-dioxide (**18**) into benzyne, SO_2, and N_2 would at first glance appear to be relevant to the present discussion of the possible electronic states of **3**.[15] In that study, Wittig and Hoffmann attempted to find evidence for the *o*-phenylene biradical (**19**) by trapping it with NO as the benzofuroxane (**20**). Failing to find any **20**, they suggested that the benzyne was rather formed by the heterolysis of the S–N bond leading to intermediate **21** (Scheme 5). By comparing **21** with the present proposed ylide **3a**, it is immediately evident that loss of N_2 from **21** would yield an isomeric *(not resonance) structure of*

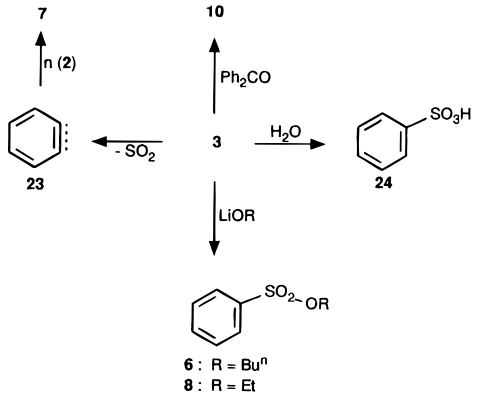
(13) As in the eliminations of lithium halides from halomethyllithiums or from (*o*-halophenyl)lithiums to liberate carbenes or benzynes, respectively, it remains unknown whether "free" **3** is generated or whether the LiE (E = F, OPh or NMePh) remain complexed with **3** in some fashion, possibly by O-coordination at the sulfonylium center, *e.g.*, in **3b** form



(*cf.* the structure of a carbanions α to sulfone centers, as reviewed in: Boche, G. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 277. For this situation, one would follow the usage honored in carbene chemistry and term intermediate **3b** as a carbenoid, meaning that structure **3** is complexed with LiE.

(14) Blum, J. *Tetrahedron Lett.* **1966**, *3041*.
(15) Witting, G.; Hoffmann, R. W. *Chem. Ber.* **1962**, *95*, 2718.

Scheme 6



3a but of opposite polarity (**22**).[16] From these considerations, we conclude that thermal lability of **18** does not give us any reliable insight into the thermal stability of **3a**.

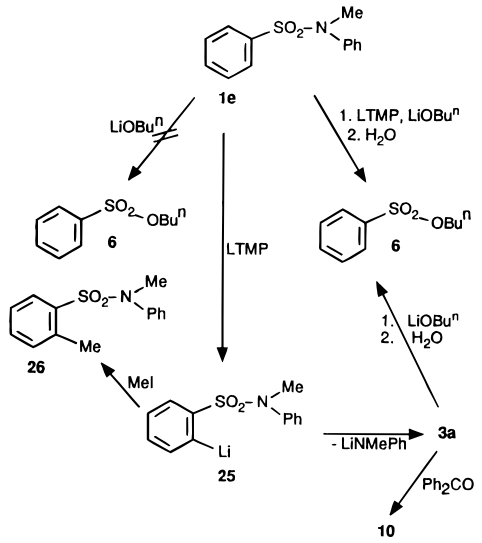
The principal reactions exhibited by **3** are in better accord with its singlet character (**3b**) (Scheme 6). Thermal loss of SO_2 by **3** would yield benzyne (**23**), which if captured by several equivalents of **2** would lead to the *o*-phenylene sulfone polymer **7**. Capture of **3** by H_2O or by LiOR would yield the sulfonic acid **24** and the sulfonate ester **6** or **8**, respectively.

However, the formation of alkyl benzenesulfonates as minor products from the individual reactions of fluoride **1a**, phenyl sulfonate ester **1d**, and sulfonamide **1e** with LTMP in ethereal media would alternatively seem readily explicable in terms of a direct attack by lithium alkoxide at the sulfonyl center in **2** with displacement of anion E. Although this route to the sulfonate esters cannot be ruled out for the reactions of **1a** and **1d** with LiOR in the presence of LTMP, such a straightforward explanation cannot apply to the reaction of amide **1e** with $LiOBu^n$. A control experiment of **1e** with only $LiOBu^n$ in THF does not yield sulfonate ester **6**. Only when LTMP is also present in the reaction mixture does **6** form. Under these conditions, *o*-lithiation occurs as is evident by the trapping of **25** by methyl iodide (**26**). Also under these conditions, **25** decomposes into **3a**, which is proved by capturing **3a** with benzophenone as **10**. Thus, in this instance, **6** is most likely formed by the trapping of **3a** by $LiOBu^n$ (Scheme 7).

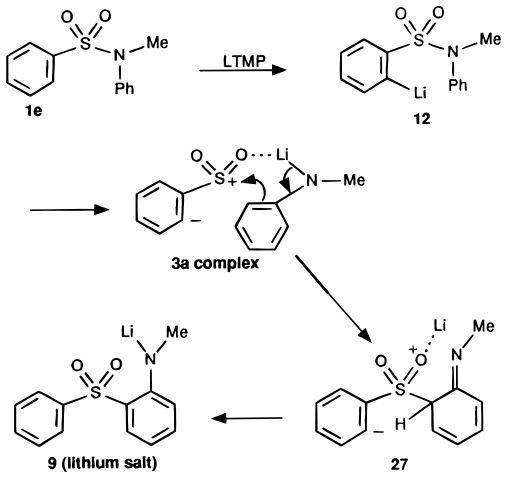
We judge that the final reaction to require **3** as a crucial intermediate is the Closson−Hellwinkel rearrangement. In considering suitable mechanisms for this reaction, it is important to note that Shafer and Closson did not observe any "cross products" when a mixture of two suitably different sulfonamides were allowed to rearrange. From this fact one can conclude that the rearrangement is most likely intramolecular.

In light of our evidence for the existence of **3** in the reactions of sulfonamide **1e** with Bu^nLi or with LTMP, we propose the following mechanism for this rearrangement (Scheme 8). After the formation of **12**, a slow 1,3-elimination of LiNMePh takes place to form **3**, but in order for that intramolecular reaction can occur, it is essential that **3** and the lithium amide remain complexed (**3a complex**). Thereupon, the sulfonylium center attacks electrophilically the β-carbon of the enaminate salt to give **27**. Simple H−Li exchange forms the final amide.

Scheme 7



Scheme 8



In conclusion then, we have demonstrated that benzenesulfonyl fluoride, phenyl benzenesulfonate, and *N*-arylbenzenesulfonamides with strong lithium bases produce a reactive *o*-sulfonylium benzenide intermediate, via *o*-lithiation and 1,3-lithium salt elimination, which is the crucial intermediate in a variety of substitution, cycloaddition, and rearrangement reactions.

Experimental Section

General Procedures. Melting points were determined with a Thomas-Hoover Unimelt capillary melting point apparatus and are uncorrected. The IR spectra were recorded with a Perkin-Elmer instrument, Model 457, and samples were measured either as mineral oil mulls or as KBr films. The NMR spectra (^1H and ^{13}C) were recorded with a Bruker spectrometer, Model AM-360, and tetramethylsilane (TMS) was used as the internal standard. The chemical shifts are reported on the δ-scale and in parts per million (ppm) from the reference TMS signal. The mass spectra were obtained on a Finnigan TSQ 700 (triple quad) by direct probe insertion under EI conditions with methane chemiionization. Tetrahydrofuran (THF) was distilled from sodium/benzophenone ketyl prior to use. All reactions were carried out under a positive pressure of anhydrous, oxygen-free argon. Phenyl benzenesulfonate was prepared according to a published procedure.[17]

(16) It should be emphasized that **3a** and **22** are not proper resonance structures of each other since the sp^2-hybridized orbital of the *ortho*-carbon is orthogonal to the π-bonding orbitals of the benzene ring and the SO_2 group.

Lithiation Reactions of Benzenesulfonyl Fluoride (1a). Reaction with LTMP Prepared from *n*-Butyllithium in THF or from Methyllithium in Diethyl Ether. A mixture of 2,2,6,6-tetramethylpiperidine (1.40 mL, 8.3 mmol) and *n*-BuLi (5.2 mL, 8.3 mmol, 1.6 M in hexane) was prepared at room temperature in 5 mL of THF and then added dropwise to benzenesulfonyl fluoride (1 mL, 8.3 mmol) in dry THF at −78 °C. The dark-red solution was stirred for 2 h at −78 °C and then was allowed to stir at room temperature overnight, whereupon the reaction was quenched with saturated aqueous NH_4Cl solution.

The yellow solid suspended in the hydrolysate was filtered off, washed with CH_2Cl_2, and dried to afford the apparently polymeric **7** (0.21 g): mp > 320 °C; IR (mineral oil, cm^{-1}) 1150, 1320, 720; MS *m/e* 811, 667, 617, 502, 357, 325, 221, 159, 142, 146, 111, 81, 65. The IR bonds are consistent with the presence of sulfone groups on aromatic nuclei. The MS peaks are attributable to SO_2H (65), PhSOH (126), $PhSO_2H$ (142), $PhSO_3H_2$ (159), $C_6H_4(SO_2)_2OH$ (221), $(C_6H_4)_3S_2O_2H$ (325), $(C_6H_5)_3S_2O_4$ (357), and higher oligomers.

The filtrate was concentrated under reduced pressure and the residue extracted with CH_2Cl_2. The organic layer was washed with water, dried with anhydrous $MgSO_4$, filtered, and concentrated. The residue was purified by flash chromatography (silica gel, 50:1 hexanes/THF) to afford the butyl benzenesulfonate **6** (0.1 g, 5.6% yield): ^1H NMR ($CDCl_3$) δ 7.5−7.9 (m, 5H), 3.99−4.03 (t, 2H) 1.56−1.6 (m, 2H), 1.26−1.3 (m, 2H), 0.79−0.84 (m, 3H); ^{13}C NMR ($CDCl_3$) δ 135.90, 133.36, 128.91, 127.48, 70.32, 30.44, 18.23, 13.02. Benzenesulfonyl fluoride (0.3 g, 22.6%) and 2,2,6,6-tetramethylpiperidine (0.03 g, 2.5%) were also recovered.

The aqueous extract was boiled to remove any traces of organic solvent, cooled, and acidified with 1.0 N HCl.

The evolved SO_2 gas was identified by its odor, its acidic reaction to litmus, and the fact that it caused a white precipitate when led into aqueous $BaCl_2$ solution. That the precipitate was $BaSO_3$ was verified by its dissolution upon adding dilute aqueous HCl. The acidic aqueous extract was boiled to complete expulsion of the SO_2 and then cooled and treated with aqueous $BaCl_2$ solution. The colorless precipitate thereupon formed did not dissolve in aqueous HCl, and upon heating in a crucible burned to leave a residue. It is therefore concluded to be barium benzenesulfonate.

A similar reaction was carried out with the LTMP that was prepared from 2,2,6,6-tetramethylpiperidine and CH_3Li (1.4 M in Et_2O). The workup procedure was the same as that described previously; flash chromatography separation gave ethyl benzenesulfonate (**8**) in 4% yield: ^1H NMR ($CDCl_3$) δ 7.53−7.93 (m, 5H), 4.10−4.17 (q, 2H), 1.26−1.33 (t, 3H); ^{13}C NMR ($CDCl_3$) δ 136.0, 133.61, 129.19, 127.80, 66.99, 14.72.

Reaction with LTMP in the Presence of Benzophenone. The LTMP (8.3 mmol) in 5 mL of THF was added dropwise over 5 min to a rapidly stirred solution of benzenesulfonyl fluoride (1 mL, 8.3 mmol) and benzophenone (1.51 g, 8.3 mmol) in dry THF at −78 °C. The solution was stirred at −78 °C for 2 h and then was allowed to warm to room temperature slowly overnight. To the resulting red solution was added, with stirring, 10 mL of aqueous NH_4Cl solution followed by 10 mL of aqueous NH_4Cl. It was extracted with ether (3 × 50 mL), dried ($MgSO_4$), and concentrated under reduced pressure. The 3,3-diphenyl-1,2-benzoxathiole 1,1-dioxide (**10**) (0.35 g, 13%) and two other products, **6** (0.1 g, 5.6%) and **11** (0.15 g, 3.6%), were isolated by flash chromatography (silica gel, gradient elution with hexanes/THF (50:1), hexanes/CH_2Cl_2 (1:1), and then $CHCl_3$); benzophenone was also recovered (0.21 g, 14%). The novel products were identified by NMR spectroscopy and mass spectrometry. **10**: mp 161−162 °C (lit.[18] mp 163−164 °C); ^1H NMR ($CDCl_3$) δ 7.8−7.9 (m), 7.7−7.6 (m), 7.4−7.3 (m); ^{13}C NMR ($CDCl_3$) δ 141.5, 140.1, 133.5, 132.2, 130.2, 129.2, 128.6, 127.7, 125.9, 122.1, 96; IR (film, cm^{-1}) 1440, 1350, 1200, 900, 820; MS *m/e* 322 (M^+), 257.245, 239, 152, 105, 77.

11: mp 183−184 °C; ^1H NMR ($CDCl_3$) δ 7.07−7.45 (m), 396 (s); ^{13}C NMR ($CDCl_3$) δ 145.28, 145.03, 143.50, 140.51, 132.44, 131.36, 129.56, 129.03, 128.54, 128.29, 128.04, 127.99, 127.84, 125.36, 93.82, 82.84; MS *m/e* 504 (M^+), 422, 345, 241, 239, 105, 77, 32.

Reaction with Lithium *n*-Butoxide in the Presence of Methyl Iodide. Admixture of dry 1-butanol (0.76 mL, 8.3 mmol) and *n*-BuLi (5.2 mL, 8.3 mmol, 1.6 M in hexane) was conducted at room temperature in 5 mL of THF to form lithium *n*-butoxide, which was then added dropwise to benzenesulfonyl fluoride (1 mL, 8.3 mmol) in dry THF at −78 °C. The reaction mixture was stirred for 10 min at −78 °C, and then 3.53 g (1.55 mL, 24.9 mmol) of methyl iodide was added. After being allowed to warm to room temperature slowly, the resulting slight yellow solution was treated with aqueous 6 N HCl and then extracted with ether. The residue were separated by means of flash chromatography (silica gel; gradient elution with hexanes, then hexanes/THF (50:1)) to give *n*-butyl benzenesulfonate (**6**) (1.10 g, 62%). The unreacted methyl iodide and benzenesulfonyl fluoride (0.26 g, 20%) were recovered. No *o*-methyl derivative of **1a** or of **6** was detected.

Reaction with Lithium *n*-Butoxide in the Presence of Benzophenone. Admixture of dry 1-butanol (0.76 mL, 8.3 mmol) and *n*-BuLi (5.2 mL, 8.3 mol, 1.6 M in hexane) was conducted at room temperature in 5 mL of THF, and the resulting lithium *n*-butoxide was then added dropwise to benzenesulfonyl fluoride (1 mL, 8.3 mmol) and benzophenone (1.51 g, 8.3 mmol) in 20 mL of THF at −78 °C. The reaction mixture was allowed to warm to room temperature slowly. The workup procedure was the same as given earlier. Flash chromatography using 1:50 (THF/hexanes) on silica gel provided butyl benzenesulfonate **6** (0.6 g, 33.7%). The benzophenone and benzenesulfonyl fluoride were also recovered. None of the cyclic ester **10** was detected among the reaction products.

Lithiation Reactions with Phenyl Benzenesulfonate (1d). The LTMP (5.3 mmol) in 5 mL of THF was added dropwise to phenyl benzenesulfonate (0.62 g, 2.65 mmol) in 10 mL of dry THF at −78 °C, whereupon the reaction mixture immediately turned yellow. Stirring was continued for 2 h at −78 °C, after which time the mixture was allowed to warm to room temperature slowly. The resulting dark-brown solution was treated with water, the THF was evaporated, and the residue was dissolved in ether and extracted by aqueous KOH.

The ether layer was dried over $MgSO_4$ and concentrated under reduced pressure. Purification by flash chromatography on silica gel afforded **6** (0.01 g, 1.8%).

The aqueous layer was acidified by 6 N HCl and extracted with ether. The extract was dried ($MgSO_4$) and evaporated to give phenol (0.01 g, 4%).

Reaction with LTMP in the Presence of Benzophenone. The LTMP (8.3 mmol) in 5 mL of THF was added dropwise to a rapidly stirred solution of phenyl benzenesulfonate (1.94 g, 8.3 mmol) and benzophenone (1.51 g, 8.3 mmol) in 10 mL of THF at −78 °C. After being stirred at −78 °C for 2 h, the solution was allowed to warm to room temperature slowly. After the usual workup procedure and purification by flash chromatography on silica gel (1:1 hexanes/CH_2Cl_2), 0.21 g (7.8%) of **10** was isolated. In addition, 0.99 g of a mixture of phenyl benzenesulfonate and benzophenone was also recovered.

Lithiation Reactions of *N*-Methyl-*N*-phenylbenzenesulfonamide (1e). Reaction with LTMP. To a solution of 1.0 g (4.05 mmol) of *N*-methyl-*N*-phenylbenzenesulfonamide in 10 mL of THF at −78 °C was added dropwise LTMP (8.10 mmol) in 5 mL of THF. The yellow solution was stirred for 2 h at −78 °C and then allowed to warm to room temperature slowly. The resulting dark-red solution was treated with water and then extracted with ether. The organic layer was dried over anhydrous $MgSO_4$ and concentrated. The residue was separated by means of flash chromatography (silica gel; gradient elution with hexanes/THF (50:1), then hexanes/CH_2Cl_2 (1:1)) to give **6** (0.04 g, 4.5%) and **9** (0.05 g, 5%). Some *N*-methyl-*N*-phenylbenzenesulfonamide was also recovered (0.05 g, 5%). **9**: mp 136−137 °C; ^1H NMR ($CDCl_3$) δ 7.89−7.83 (m), 7.53−7.38 (m), 6.74−6.72 (t), 6.64−6.62 (d), 6.39 (s,

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(18) Watanabe, H.; Schwarz, R. A.; Hauser, C. R. *Can. J. Chem.* **1969**, *47*, 1543.

1H), 2.83−2.82 (d, 3H); ^{13}C NMR ($CDCl_3$) δ 147.97, 142.06, 135.34, 132.86, 130.42, 128.93, 126.67, 121.09, 115.85, 111.74, 30.0.

Reaction with LTMP in the Presence of Benzophenone. The LTMP (8 mmol) in 5 mL of THF was added dropwise to a rapidly stirred solution of *N*-methyl-*N*-phenylbenzenesulfonamide (1.0 g, 4 mmol) maintained at −78 °C. To the reaction mixture, a solution of benzophenone (0.74 g, 4 mmol) was then added. The solution was stirred at −78 °C for 2 h, after which time it was allowed to stir at room temperature overnight. After the usual workup, 120 mg of a mixture of **9** and **10** was separated by means of silica gel flash chromatography, as well as 100 mg of a mixture of *N*-methyl-*N*-phenylbenzenesulfonamide and benzophenone. The identity of the products was confirmed by ^{1}H and ^{13}C NMR analysis.

Reaction with LTMP in the Presence of Lithium *n*-Butoxide and Methyl Iodide. To the mixture of 1-butanol (0.37 mL, 4 mmol) and 2,2,6,6-tetramethylpiperidine (0.68 mL, 4 mmol) in 5 mL of THF was added *n*-BuLi (5 mL, 8 mmol, 1.6 M in hexane) at room temperature. The resulting lithium *n*-butoxide−LTMP mixture was transferred dropwise to the *N*-methyl-*N*-phenylbenzenesulfonamide in 30 mL of THF at −78 °C. The reaction mixture was stirred for 10 min at −78 °C, and then 0.75 mL (12 mmol) of methyl iodide was added. After the reaction mixture warmed to room temperature slowly, the workup procedure was carried out as given earlier. Flash chromatography using 1:3 (EtOAc/hexanes) on silica gel provided *N*-methyl-*N*-phenyl-*o*-toluenesulfonamide (0.10 g, 9.6%): ^{1}H NMR ($CDCl_3$) δ 7.43−7.14 (m, 9H), 3.22 (s, 3H), 2.28 (s, 3H).[19] No trace of **6** could be detected in the reaction products.

A similar interaction between **1e** and lithium *n*-butoxide in the presence of methyl iodide gave no discernible reaction; neither **6** nor the *o*-methyl derivative of **1e** were detected.

Reaction with *n*-Butyllithium at 25 °C and then with Benzophenone. To a stirred solution of 1.0 g (4 mmol) of *N*-methyl-*N*-phenylbenzenesulfonamide in 10 mL of THF at room temperature was added 2.5 mL of 1.6 M *n*-butyllithium in hexane. After 15 min, to the resulting yellow solution was added a solution of 0.73 g (4 mmol) of benzophenone in 5 mL of THF, and the stirring was continued for 1 h at room temperature. The resulting orange-red solution was treated with saturated aqueous NH_4Cl solution. After the usual workup procedure, *N*-methylaniline (170 mg 4%), **9** (40 mg, 4%), **10** (40 mg, 3.1%), and **11** (10 mg, 0.6%) were isolated by flash column chromatography (silica gel, gradient elution with hexanes/AcOEt (3:1), hexanes/AcOEt (1:1), and then AcOEt). A 100 mg mixture of the starting benzenesulfonamide and benzophenone was also recovered.

(19) Wagenaar, A.; Kirby, A. J.; Engberts, J. B. F. N. *Recl. Trav. Chim. Pays-Bas* **1985**, *104*, 203.

Reaction with *n*-Butyllithium at 0 °C and then with Benzophenone. To a stirred solution of 1.0 g (4 mmol) of *N*-methyl-*N*-phenylbenzenesulfonamide in 10 mL of dry THF at 0 °C was slowly added 2.5 mL of 1.6 M *n*-butyllithium in hexane. To the bright yellow lithiosulfonamide (**12**) was added, over 5 min, a solution of 0.73 g (4 mmol) of benzophenone in 5 mL of THF, and the stirring was continued for 5 min at 0 °C. The golden-colored solution was then treated with saturated, aqueous NH_4Cl solution.

After the usual workup, α,α-diphenyl-*o*-(*N*-methyl-*N*-phenylsulfamyl)benzyl alcohol (**13**) (1.20 g, 70% recrystallized from ethanol) and **9** (0.1 g, 1%) were isolated by flash chromatography. Benzophenone and *N*-methyl-*N*-phenylbenzenesulfonamide (100 mg) were also recovered. **13**: mp 172−173 °C; IR (Nujol, cm^{-1}) 3460 (OH), 1140, 1303 (SO_2); ^{1}H NMR δ 6.80−7.64 (19H, m), 6.46 (H, s), 3.03 (3H); ^{13}C NMR ($CDCl_3$) δ 147.60, 147.12, 141.27, 138.65, 132.74, 132.06, 131.53, 129.17, 128.02, 127.83, 127.61, 127.43, 127.30, 127.20, 82.42, 38.73. Anal. Calcd for $C_{26}H_{23}NSO_3$: C, 72.70; H, 5.40; N, 3.26; S, 7.47. Found: C, 72.33; H, 5.34, N, 3.30; S, 7.48.

Reaction with LTMP at 0 °C and then with Benzophenone. To a solution of 1.0 g (4 mmol) of *N*-methyl-*N*-phenylbenzenesulfonamide was added dropwise LTMP (4 mmol) in 5 mL of THF at 0 °C. To the orange solution was added, over 5 min, a solution of 0.73 g (4 mmol) of benzophenone in 5 mL of THF, and the stirring was continued for 5 min at 0 °C. The resulting dark-red solution was hydrolyzed with saturated, aqueous NH_4 solution, and the workup procedure was the same as described above. The α,α-diphenyl-*o*-(*N*-methyl-*N*-phenylsulfamyl)benzyl alcohol (**13**) (0.7 g, 41%) and **9** (0.1 g, 1%) were isolated. Benzophenone and *N*-methyl-*N*-phenylbenzenesulfonamide (150 mg) were also recovered.

Reaction of α,α-Diphenyl-*o*-(*N*-methyl-*N*-phenylsulfamyl)benzyl Alcohol with LTMP. To a solution of 0.43 g (1 mmol) of α,α-diphenyl-*o*-(*N*-methyl-*N*-phenylsulfamyl) benzyl alcohol in 10 mL of THF was added dropwise LTMP (1.2 mmol) in 5 mL THF at −78 °C. The orange-red solution was stirred for 3 h at −78 °C and then was allowed to warm to room temperature overnight. The resulting violet solution was treated with saturated, aqueous NH_4Cl solution and worked up in the usual manner. Purification by flash chromatography on silica gel (1:3 AcOEt/hexanes) afforded 30 mg (28%) of *N*-methylaniline and a 20 mg mixture of *N*-methyl-*N*-phenylbenzenesulfonamide (**1e**) and the starting carbinol−sulfonamide.

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