mass spectrum m/e (rel intensity, fragment) 234 (46, M^+), 189 (4, $M^+ - OEt$), 161 (3, $M^+ - CO_2Et$), 135 (100, $C_6H_5CNS^+$), 103 (32, $C_6H_5CN^+$), 77 (16, $C_6H_5^+$).

Anal. Calcd for $C_{11}H_{10}N_2O_2S$: C, 56.40; H, 4.30. Found: C, 56.21; H, 4.45.

Ethyl 3-(α,α,α-Trifluoro-*m*-tolyl)-1,2,4-thiadiazole-5-carboxylate (5b). Use of a similar procedure to that above (92.5-hr reaction time) gave product thiadiazole in 76% yield (isolated product) as a white solid, mp 79–80.5° (from heptane), ir ($CHCl_3$) 5.72, 5.80 μ.

Anal. Calcd for $C_{12}H_9F_3N_2O_2S$: C, 47.68; H, 3.00. Found: C, 47.86; H, 2.84.

Ethyl 3-(3,5-Dimethoxyphenyl)-1,2,4-thiadiazole-5-carboxylate (5c). Use of a similar procedure to that above (92.5-hr reaction time) gave product thiadiazole in 94% yield (isolated) as a white solid, mp 125–126.5° (from dodecane), ir ($CHCl_3$) 5.72, 5.80 μ.

Anal. Calcd for $C_{13}H_{14}N_2O_4S$: C, 53.05; H, 4.79. Found: C, 53.19; H, 4.90.

3-Phenyl-1,2,4-thiadiazole (6). A mixture of 8 g (0.034 mol) of ethyl 3-phenyl-1,2,4-thiadiazole-5-carboxylate, 1.5 g (0.037 mol) of sodium hydroxide, 10 ml of ethanol, and 60 ml of water was heated with stirring on a steam bath for 1 hr. The resultant solution was allowed to cool and was acidified with 3.5 ml (0.042 mol) of concentrated hydrochloric acid. The resultant mixture, containing granular solid carboxylic acid, was heated on a steam bath until decarboxylation was complete. The mixture was cooled and extracted with ether. The ether layer was dried ($MgSO_4$) and concentrated under vacuum to give 5.5 g (99%) of colorless oil. Distillation of this material gave a single fraction, bp 76.5° (0.5 mm) [lit.[9] bp 78–80° (0.3 mm)], nmr ($CDCl_3$) δ 9.90 (s, 1, 5-H), 8.37 (m, 2, ArH), 7.48 (m, 3, ArH).

Anal. Calcd for $C_8H_6N_2S$: C, 59.23; H, 3.74; N, 17.27; S, 19.76. Found: C, 59.03; H, 3.84; N, 17.23; S, 19.91.

Registry No.—**1**, R = Me, 17452-74-3; **1**, R = Ph, 5852-49-3; **3**, R = R′ = Ph, 4115-15-5; **3**, R = Ph, R′ = p-ClC_6H_4, 50483-71-1; **3**, R = *p*-ClC_6H_4, R′ = Ph, 50483-72-2; **3**, R = R′ = *p*-ClC_6H_4, 4115-17-7; **3**, R = Ph, R′ = *p*-MeC_6H_4; 50483-74-4; **3**, R = *p*-MeC_6H_4, R′ = Ph, 50483-75-5; **3**, R = R′ = *p*-MeC_6H_4, 17590-34-0; **3**, R = Me, R′ = Ph, 50483-77-7; **4**, R = *p*-ClC_6H_4, R′ = CH_2CO_2Et, 50483-78-8; **5a**, 50483-79-9; **5b**, 50483-80-2; **5c**, 50483-81-3; **6**, 50483-82-4.

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Hypervalent Sulfur Chemistry. Evidence for Tetracoordinate Sulfur(IV) and Tricoordinate Sulfur(II) Intermediates in the Reaction of *p*-Tolyl Sulfoxide with *p*-Tolyllithium[1a]

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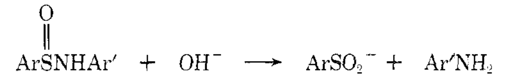
p-Tolyl sulfoxide (**1**) reacted with excess *p*-tolyllithium (**2**) to give *p*-tolyl sulfide (**3**, 66%), *p,p′*-bitolyl (**4**, 31%), and *m,p′*-bitolyl (**5**, 26%). The reaction of tri-*p*-tolysulfonium salt with **2**, which gave **3** (87%), **4**, (72%), and **5** (5%), is thought to proceed largely through a tetra-*p*-tolylsulfurane which collapses to product. A mechanism for the reaction of **1** with **2** is proposed which involves 4-toluyne formation from a tetracoodinate S(IV) precursor, tri-*p*-tolyloxysulfurane (**7**). The 4-toluyne adds **2** to give **4** and **5**. *N*-*p*-toluenesulfonyl-*S,S*-di-*p*-tolylsulfimide and **2** gave **3** (80%), **4** (66%), **5** (1–2%), and *p*-toluenesulfonamide (60%), while methoxydi-*p*-tolylsulfonium salt and **2** gave **3**, **4**, and **5** in the ratio of 135:96:1. These two reactions are proposed to proceed largely through tetra-*p*-tolylsulfurane which collapses to **3** and **4**; very little 4-toluyne is involved as an intermediate. Methyl *p*-toluenesulfinate and **2** gave **3** (77%), **4** (37%), and **5** (32%). The reaction is thought to proceed *via* formation of **1** which then reacts *via* **7**. Mesityl sulfoxide and mesityllithium gave 2,4,4′,6,6′pentamethyl-2′-(2,4,6-trimethylphenylmethyl)diphenyl sulfide (16%) but no mesityl sulfide or bimesityl.

Hypervalent sulfur chemistry,[2] the chemistry of nonoctet sulfur compounds such as sulfonium ylides, sulfoxides, and sulfuranes in which the sulfur participates in the reaction, has been of great synthetic utility and theoretical interest and consequently much studied during the past decade. In nucleophilic substitution at tricoordinate sulfur(IV),[3] *e.g.*, sulfinyl sulfur, the presence or absence of tetracoordinate S(IV) intermediates, conveniently named sulfuranes, formed by bonding of the nucleophile to sulfur, has occupied the attention of many workers. In principle, these intermediates can exist, since stable sulfuranes, such as SF_4, are known. In practice, their detection has often proved difficult. Kinetic studies have not unequivocally demonstrated their presence even though efforts have been made to detect them in various reactions (eq 1[4] and 2[5]).

$$ArSOCH_3 + CD_3OH \longrightarrow Ar\overset{\overset{\displaystyle O}{\|}}{S}OCD_3 + CH_3OH \qquad (1)$$

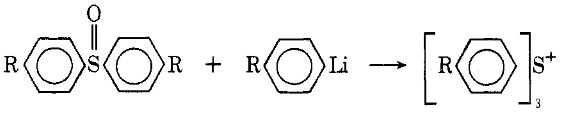


$$Ar\overset{\overset{\displaystyle O}{\|}}{S}NHAr' + OH^- \longrightarrow ArSO_2^- + Ar'NH_2 \qquad (2)$$

Stable sulfuranes usually have four electronegative atoms such as F, Cl, O, or N around sulfur, but recently examples having two carbon atoms as ligands have been synthesized.[6-8] The carbon atoms were shown in one case to be equatorial by X-ray analysis.[6] The two remaining ligands were still electronegative atoms, in these cases oxygen and fluorine. No sulfurane having four carbon atoms around sulfur has been isolated, but, based on nmr evidence, tetrakis(pentafluorophenyl)sulfurane[9] is said to be stable at temperatures below *ca.* 0°. Apparently, sulfuranes without two electronegative substituents are thermally unstable. Nevertheless, there is often good reason, besides argument by analogy, to believe that they exist as intermediates in various reactions. This paper reports on one of these reactions.

When an ethereal solution of phenyl sulfoxide was treated with phenyllithium, phenyl sulfide (87% yield) and biphenyl (65% yield) were obtained.[10] The analogous reaction of *p*-tolyl sulfoxide (**1**) with *p*-tolyllithium (**2**) yielded *p*-tolyl sulfide (**3**, 66%), *p,p'*-bitolyl (**4**, 31%), and *m,p'*-bitolyl (**5**, 26%).[3]

These reactions were originally assumed to proceed through an initial formation of a triarylsulfonium ion followed by ortho proton abstraction and elimination to give a diaryl sulfide and an aryne. Addition of aryllithium to the aryne followed by protonation of the *o*-lithiobiaryl upon aqueous work-up of the reaction mixture then would give the biaryls (eq 3–5).



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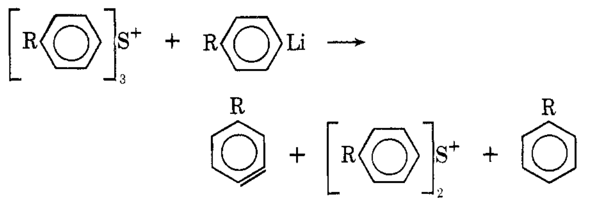

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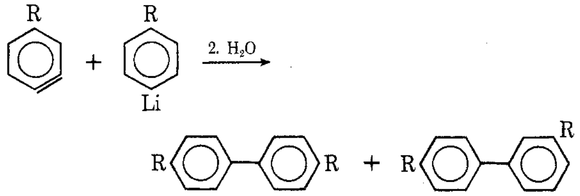


(5)

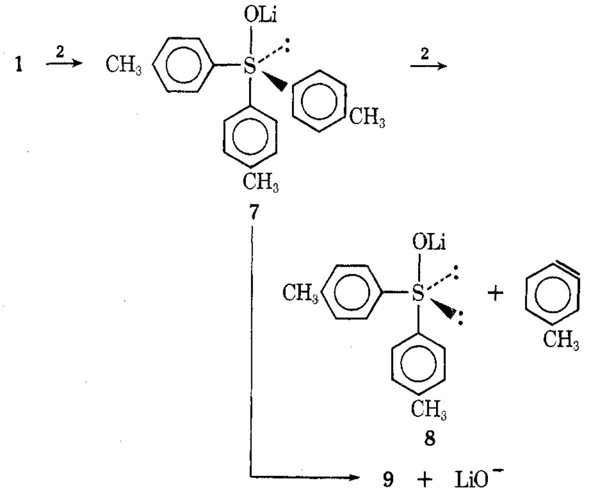
The first reaction is analogous to the formation of triphenylsulfonium ion from phenyl sulfoxide and phenylmagnesium bromide in refluxing benzene.[11] Franzen showed, as Wittig had earlier, that aryl sulfides and biaryls are formed from triarylsulfonium salts upon their reaction with aryllithiums.[12] Thus eq 3–5 seemed like a reasonable pathway to the products.

Franzen suggested, however, that two mechanisms were operative in the reaction of triarylsulfonium salts with aryllithiums. The major process, originally proposed by Wittig,[13] involved formation of a tetraaryl sulfur, a sulfurane, which was thermally unstable and collapsed rapidly to sulfide and a biaryl. The other process involved an aryne (eq 4 and 5) and was believed to be minor based on the low yield of acid formed upon carbonation of the *o*-lithiobiaryl. Our original note presented evidence for benzyne in the phenyl sulfoxide reaction through trapping by lithium thiophenoxide—the yield of phenyl sulfide increased to greater than 100% based on the triphenylsulfonium salt—and by isolation of *o*-phenylbenzoic acid formed by the carbonation of *o*-lithiobiphenyl.[10]

Doubt that a triarylsulfonium cation could be an intermediate arose when Trost and coworkers[14] showed that the reaction of tri-*p*-tolylsulfonium tetrafluoroborate (**6**) with *p*-tolyllithium in tetrahydrofuran at −78° gave only *p*-tolyl sulfide and *p,p'*-bitolyl. No *m,p'*-bitolyl, which would have been formed from 4-toluyne, was detected by ir analysis of the reaction mixture. This aryne is known to form a 50:50 mixture of **4** and **5** upon reaction with *p*-tolyllithium in ether.[15] At about the same time, Oae and Khim[16] reported evidence for aryne formation in the reaction of tri-*p*-tolysulfonium salt with phenyllithium in refluxing ether. Thus, the situation was confused by the appearance of seemingly contradictory results, although differing solvent and temperature conditions may account for this.

When we treated a slurry of tri-*p*-tolylsulfonium bromide with *p*-tolyllithium in ether we obtained *p*-tolyl sulfide (87%), *p,p'*-bitolyl (72%), and *m,p'*-bitolyl (5%) in close agreement with the results of Trost. One might question the origin of the small amount of **5**. In our case, the *p*-tolyllithium was prepared from *n*-butyllithium and *p*-bromotoluene in benzene, a technique which leads to the formation of benzene-insoluble *p*-tolyllithium. Some **4** and **5** were also formed, most of these were removed from the organolithium reagent as it was used in the various reactions, and our results have been corrected for these small amounts. However, the essential point remains that tri-*p*-tolysulfonium salt under our conditions gave very little 4-toluyne; most of the reaction seems to follow another pathway, presumably the one involving a tetratolyl sulfurane for which Trost has presented a good argument.[13] Recently, Jacobus[17] has reinforced the case for a sulfurane.

An explanation for the formation of *m,p'*-bitolyl in the sulfoxide reaction which does not involve a sulfonium salt intermediate must now be forthcoming and a possibility is given by eq 6 and 7.



(6)

(7)

The initially formed adduct, **7**, is postulated to react in two ways. One (eq 6) is the reaction with *p*-tolyllithium to give 4-toluyne, which reacts as in eq 5, and the rather novel tricoordinate S(II) species, **8**, which loses lithium oxide to give **3**. The other pathway leads to tri-*p*-tolylsulfonium ion (**9**), which goes on principally to a tetraaryl sulfurane, but which may also have a small 4-toluyne-forming component (eq 7).

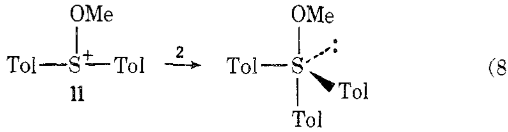
A test for this hypothesis was made by treating *N*-*p*-toluenesulfonyl-*S,S*-di-*p*-tolylsulfimide (**10**) with *p*-tolyllithium. The toluenesulfonamide anion would be expected to be a better leaving group than the oxyanion, assumed to be the leaving group in **7**; so the rate of tritolylsulfonium salt formation should be increased relative to the formation of an intermediate resembling **8**. Thus, the yield of **5** should decrease as a consequence of the decrease in 4-toluyne production, while that of **4** should increase. This was found to be so. The yield of **5** was 1–2% while that of **4** was 66%. *p*-Tolyl sulfide (72–82%) and *p*-toluenesulfonamide (58–65%) were also produced.

Table I
Pmr Parameters of Compounds 14a and 14b[a]

Compd	H_6^1	H_3^2	H_3^3	H_3^4	H_6^5	H_3^6	H_1^7	H_1^8	H_1^9	H_2^{10}	H_2^{11}	H_1^{12}
14[b]	2.24				1.99	2.13	3.98		6.09	6.79		
14b	1.97	2.14	2.31		2.50	2.65	4.04	4.15	6.38	6.99		
LIS (**14b**)[c]	−1.13	−0.83	−0.55	−0.30	−3.9	−5.0	−3.9	−5.8	−1.57	−0.50	−1.36	−1.63

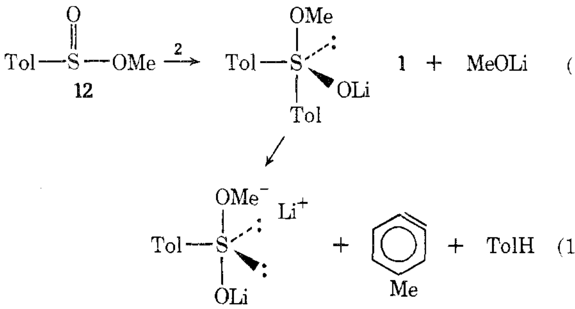
[a] All measurements were performed on a Jeolco HA-100 instrument in $CDCl_3$ solutions (~0.2 *M*) at ordinary probe temperature. Chemical shifts are given in parts per million downfield from internal tetramethylsilane. [b] Assignments of H^1–H^6 are based on comparison with the $ArCH_3$ groups of mesitylene (δ 2.22), of ditolylmethane (2.27), and of mesityl sulfide [2.17 (ortho) and 2.22 (para)]. [c] Lanthanide-induced chemical shifts were extrapolated to 100 mol % $Eu(fod)_3$ from observed shifts at 0, 14.3, 28.5, 43, and 57 mol % by the method of least squares (correlation coefficients >0.993) and are presented as $\Delta[Eu(fod)_3]$ values in parts per million: P. V. Demarco, T. K. Elzey, R. B. Lewis, and E. Wenkert, *J. Amer. Chem. Soc.*, **92**, 5734 (1970).

A second variation in leaving group was made by treating methoxydi-*p*-tolylsulfonium fluorosulfonate (**11**) with *p*-tolyllithium (eq 8). Here again, an expected enhancement of leaving-group ability should lead to a lowered yield of toluyne-derived product. While the yields of **3**, **4**, and **5** were low, presumably due to reaction of **2** at the methyl group, the ratio of **4** to **5** was 96:1, which again supports the hypothesis of an initially formed sulfurane intermediate reacting in two ways as in eq 6 and 7.


(8)

While the presence of 4-toluyne as an intermediate seems well supported, oxyanions rather than **2** may be the bases involved in the aryne-forming elimination reaction. Intramolecular proton abstraction by oxygen in **7** or proton abstraction by lithium oxide (Li_2O or LiO^-) on **7** or the tritolysulfonium salt are conceivable alternatives. However, treatment of triphenylsulfonium bromide with a 28-fold excess of lithium oxide in an ether slurry for 9 days at room temperature gave only a trace of diphenyl sulfide. Apparently, lithium oxide was not a very effective base in catalyzing benzene formation from the sulfonium salt, if indeed that was how the diphenyl sulfide arose. Triarylsulfonium halides have been treated with a variety of nitrogen, sulfur, and oxygen bases in different solvents without any evidence of aryne formation.[18] Although the presence of **8** cannot be demonstrated with certainty and must remain speculative, the arguments supporting **7** and its further reaction along two competing pathways seem strong.

Other experiments are suggested by this hypothesis. One could react a variety of tricoordinate sulfur(IV) species with **2** to form an initial intermediate which might undergo a variety of reactions. For example, the reaction of methyl *p*-toluenesulfinate (**12**) with **2** was performed (eq 9 and 10). Duplicate runs of this reaction gave **5**, **4**, and **3** in yields of 32 and 25, 37 and 44, and 77 and 69%, respectively. These yields are essentially the same as obtained from **1**, so there seems to be no evidence for a pathway such as shown by eq 10.

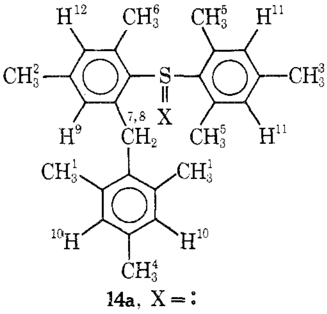

(9)

(10)

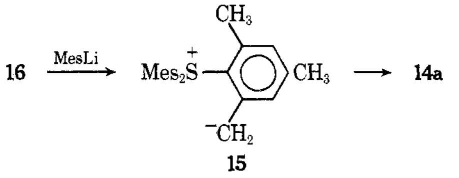
Repetition of the various reactions discussed above never gave exactly the same yields on any two occasions. This probably results from the variation in reagent concentrations from one run to the next which is consistent with partitioning of an intermediate in which one step is *first order in p-tolyllithium and the other zero order*. These variations, of course, argue against intramolecular hydride abstraction reactions, which should be independent of the concentration of **2**.

Reaction of mesityl sulfoxide (**13**) with 5 molar equiv of mesityllithium was performed. Although the aryne pathway is ruled out by the presence of ortho methyl substituents, the collapse of a tetracoordinate intermediate to bimesityl and mesityl sulfide is not. However, these two compounds were not detected in the reaction mixture. Column chromatography on alumina of the crude reaction mixture gave mesitylene, a white solid, some unidentified oils, and an emorphous solid.

The white solid, $C_{27}H_{32}S$, was assigned the structure **14a** based on the nmr spectrum (Table I) and an osmometrically determined molecular weight of 390 (calcd, 388). Further proof of this structural assignment was gained from the oxidation with hydrogen peroxide, which gave a white, crystalline derivative, $C_{27}H_{32}OS$, assigned as the corresponding sulfoxide (**14b**). The nmr spectrum **14a** showed three different $ArCH_3$ groups and a singlet for the two methylene protons, whereas that of **14b** showed five different $ArCH_3$ groups and an AB quartet for the methylene protons which indicates the presence of a chiral center (sulfur) in **14b**. A lanthanide-induced chemical shift study using tris(7,7-dimethyl-1,1,1,2,2,3,3-heptafluoro-4,6-octanedionato)europium(III) in deuteriochloroform solution (Table I) further resolved the spectrum of **14b** to give six $ArCH_3$ signals and four (ratio 1:2:2:1 H) ArH signals. This allowed an assignment of the protons as shown and therefore confirmed the identification of the reaction product and its derivative as 2,4,4′,6,6′-pentamethyl-2′-(2,4,6-trimethylphenylmethyl)diphenyl sulfide and the corresponding sulfoxide, respectively.

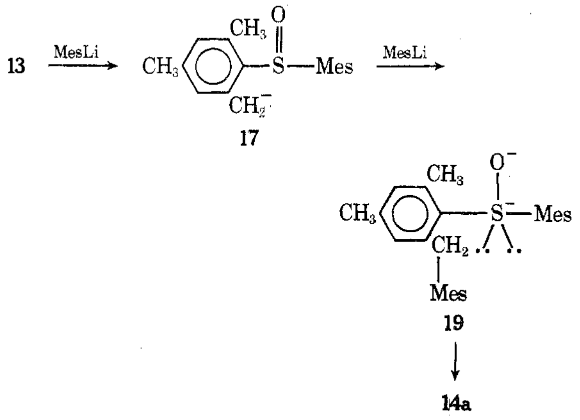

14a, X = :
b, X = O

Several reaction pathways might lead to **14a**. A Smiles rearrangement of the vinylogous ylide **15**, derived from an initially formed sulfonium salt **16**, would give **14a**. Unfortunately, we were unsuccessful in synthesizing **16** from **13** and mesitylene using phosphorus pentoxide as a catalyst or from the reaction of dimesitylethoxysulfonium tetrafluoborate with mesitylmagnesium bromide, and, thus, were unable to test for the possibility of the 1,4-sigmatropic rearrangement represented by eq 11.

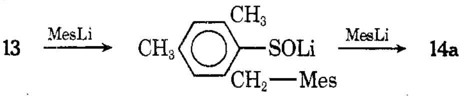

(11)

This does not mean that a trimesitylsulfonium salt is incapable of being synthesized nor that it cannot appear as an intermediate during the course of the reaction. Since lithium reagents differ somewhat from Grignard reagents in their reactions, it is possible that such a salt could have been formed and rapidly disappeared to products, thus escaping detection.

Another possible mechanism for the formation of **14a** would involve **13** directly (eq 12). This mechanism implies that the carbanion intermediate **17** is part of a π system involving an orbital on sulfur. When the mesityllithium adds to **17**, a second electron pair is localized on sulfur, resulting in the formation of a tricoordinate S(II) species **18** analogous to **8**. Loss of lithium oxide yields **14a**.


(12)

A third mechanism is suggested by the rearrangement of mesityl phenyl sulfone to lithium 2-benzyl-4,6-dimethylbenzenesulfinate when treated with *n*-butyllithium.[19] In our case, a sulfenate salt formed from **13** might lead to the product (eq 13). In any event, no products which might arise from a sulfenic acid, presumably too unstable to be isolated, were obtained.


(13)

Although the exact mechanism involved is not known, the essential point remains that no bimesityl nor mesityl sulfide were formed from mesityl sulfoxide reacting with mesityllithium.

In conclusion, it seems that tricoordinate S(IV) compounds such as aryl sulfoxides, sulfimides, or alkoxysulfonium salts react with aryllithiums to give tetracoordinate S(IV) species, *e.g.*, **7**, which, depending on the nature of the leaving group, partition between two paths (eq 6 and 7). One pathway leads to a triarylsulfonium ion (eq 7) which then reacts further, while the other may (eq 6) involve the formation of a novel tricoordinate S(II) species. Although such a structure may seem unusual, it should be remembered that formally this would be an intermediate present in nucleophilic substitution at dicoordinate S(II) or upon the addition of two electrons in the reduction of sulfoxides to a sulfide. Sekera, Rumpf, and coworkers[20] have written structures similar to **8** as possible intermediates in the reaction of alkyl sulfoxides with organomagnesium halides. While **8** and analogous species may be formulated as transition states rather than as intermediates, our evidence suggests that **7** and similar sulfuranes in which three ligands are carbon and one ligand is oxygen or nitrogen may have sufficiently long lifetimes so that they can react with other substances in the reaction mixture.

Experimental Section

General. *p*-Tolyllithium (**2**) was prepared from *n*-butyllithium and *p*-bromotoluene in hexane-benzene solutions at 60° in nitrogen-flushed, serum-capped centrifuge tubes and washed with benzene seven times, after which it was dissolved in diethyl ether.[21] The ethereal solutions were standardized by titration with benzoic acid according to the procedure of Eppley and Dixon.[22] Gas-liquid chromatographic analyses were carried out using a 20 ft × 0.25 in. column packed with Apiezon L on Chromosorb W (80/100) and a thermal conductivity detector. Biphenyl was the internal standard used to obtain quantitative results.[23]

Reaction of Tolyl Sulfoxide (1) with *p*-Tolyllithium (2).—An ethereal solution of **2** (5.0 ml, 1.44 mmol) was added by syringe to **1** (0.0630 g, 0.274 mmol) dissolved in ether (*ca.* 20 ml) contained in a nitrogen-flushed, serum-capped 200-ml flask. After being stirred magnetically for 20 min, the mixture was hydrolyzed with 5% hydrochloric acid. The organic layer was dried over magnesium sulfate and the ether was removed by distillation through a 25-cm Vigreux column. The residue, analyzed by glc, contained *p*-tolyl sulfide (**3**, 0.0388 g, 0.181 mmol, 66%), *p,p'*-bitolyl (**4**, 0.0157 g, 0.0861 mmol, 31%), and *m,p'*-bitolyl (**5**, 0.0128 g, 0.0702 mmol, 26%). Lower boiling products such as toluene were neglected. Compounds **3–5** were identified by retention-time comparisons and by ir comparisons with authentic samples. Sulfide **3** was oxidized to the sulfone, mp 159–160° (lit.[24] mp 159°). Bitolyl (**4**), after recrystallization from methanol, did not depress the melting point of an authentic sample (lit.[25] mp 119–120°). An authentic sample of **4** was available commercially. Bitolyl **5** was synthesized from 3-methylcyclohexanone and *p*-tolylmagnesium bromide according to the method of Ito and Hey.[26] Sulfide **3** was obtained by the acid-catalyzed, iodide ion reduction of commercially available **1**.[27]

Reaction of Tri-*p*-tolylsulfonium Bromide with 2. An ethereal solution of **2** (8.6 ml, 2.47 mmol) was added to a suspension of tri-*p*-tolylsulfonium bromide (0.154 g, 0.400 mmol) in *ca.* 20 ml of ether as described above. Analysis of the hydrolyzed reaction mixture gave **3** (0.0744 g, 0.347 mmol, 87%), **4** (0.0521 g, 0.286 mmol, 72%), and **5** (0.0037 g, 0.0203 mmol, 5%).

Reaction of *N*-*p*-Toluenesulfonyl-*S*,*S*-di-*p*-tolylsulfimide (10) with 2. An ethereal solution of **2** (14.7 ml, 6.7 mmol) was added to a suspension of **10** (0.382 g, 1.0 mmol) in ether as described above except that the mixture was stirred overnight. Analysis of the hydrolyzed reaction mixture gave **3** (0.153 g, 0.716 mmol, 72%), **4** (0.120 g, 0.656 mmol, 66%) and **5** (0.0022 g, 0.0121 mmol, 1.2%). *p*-Toluenesulfonamide (0.111 g, 65%), mp 135–136.5° (lit.[28] mp 138.5–139.0°), was obtained from the ether layer by extraction with aqueous sodium hydroxide. A second reaction gave **3** (83%), **4** (67%), **5** (2.0%), and *p*-toluenesulfonamide (58%).

Reaction of Methoxydi-*p*-tolylsulfonium Fluorosulfonate with 2. Methyl fluorosulfonate (0.258 g, 2.2 mmol) was added to **1** (0.460 g, 2.0 mmol) in 20 ml of methylene chloride. The solution was stirred for 8 hr, after which 30 ml of ether was added. The solvents were decanted from the resulting oil. Additional ether (10 ml) was used to wash the oil. Ether (30 ml) and **2** (12 ml, 6 mmol) were added and the mixture was stirred for 16 hr. After the usual work-up, the mixture was shown to contain **3** (0.94 g, 0.44 mmol, 22%), **4** (0.057 g, 0.31 mmol, 16%), and **5** (0.00059 g, 0.0032 mmol, 0.16%) as well as a large amount of **1**.

Reaction of Methyl *p*-Toluenesulfinate (12) with 2. An ethereal solution of **2** (0.86 ml, 3.85 mmol) was added to **12** (0.103 g, 0.60 mmol) in ether (30 ml). After 2 hr, the reaction mixture was worked up as above to give **3** (99.2 mg, 46 mmol, 77%), **4** (41.0 mg, 22.5 mmol, 37%), and **5** (34.6 mg, 19.0 mmol, 32%). Repetition of the reaction gave **3** (69%), **4** (44%), and **5** (25%).

Reaction of Mesityl Sulfoxide (13) with Mesityllithium. Mesityl sulfoxide (3.00 g, 0.0105 mol) suspended in ether (100 ml) was added to mesityllithium prepared from mesityl bromide (10.45 g, 0.053 mol) and excess lithium dispersion in *ca.* 70 ml of ether. The bright orange mixture was stirred for 2 hr, hydrolyzed, and then extracted with chloroform, and the dried organic layers were concentrated to an oil (9 g) which was chromatographed on alumina. The cobalt test for sulfonium salts was negative on both this oil and the aqueous layer.[29] Tlc of the oil showed bimesityl and mesityl sulfide to be absent. The column chromatography gave an initial fraction (5.5 g), shown to be primarily mesitylene by glc. A second fraction gave a white, crystalline, solid **14a,** mp 160–161° (acetone) [0.064 g, 1.7 mmol, 16%; mol wt by osometry in toluene, 390 (calcd, 388)].

Anal. Calcd for $C_{27}H_{32}S$: C, 83,51; H, 8.25; S, 8.25. Found: C, 83.50; H, 8.42; S, 7.98.

The remaining materials obtained from the chromatograph were not identified.

Oxidation of 14a. Compound **14a** (165 mg, 0.425 mmol) was dissolved in 15 ml of acetic acid–chloroform (2:1) and 30% hydrogen peroxide (180 mg, 1.6 mmol) in acetic acid solution (2.8 ml) added in 0.1–0.2-ml portions at room temperature. The reaction mixture was diluted with water and extracted with chloroform. The combined chloroform layers were washed with aqueous sodium carbonate and sodium bicarbonate, dried ($MgSO_4$), and concentrated to give an oil, which crystallized upon standing. Recrystallization gave 112 mg (0.28 mmol, 65%), mp 149–150° (aqueous EtOH). This product (67 mg) was further purified by preparative tlc (silica gel, methylene chloride) to give, after recrystallization, 27 mg of **14b,** mp 167–168° (MeOH).

Anal. Calcd for $C_{27}H_{32}OS$: C, 80.15; H, 7.97. Found: C, 80.21; H, 7.98.

Reaction of Triphenylsulfonium Bromide with Lithium Oxide. A slurry of triphenylsulfonium bromide (119 mg, 0.348 mmol) and lithium oxide (292 mg, 9.7 mmol) in ether was stirred continuously. After 2 days at room temperature, tlc (silica–chloroform) indicated the possible presence of phenyl sulfide. After 9 days, the mixture was hydrolyzed with dilute sulfuric acid and ether extracted. The dried ($MgSO_4$) ether extracts were concentrated to give an oil (51 mg) which was almost totally aliphatic (nmr), although a small aromatic peak (<2%) indicative of phenyl sulfide was present. Glc (5% SP–100 on 80/100 ABS, 6 ft × 2 mm, fid) gave a peak with the same retention time as phenyl sulfide. Chloroform extraction of the water layer, which was shown by the cobalt and bismuth spot tests[27] to contain a sulfonium salt, after the addition of sodium bromide (5 g) gave crude triphenylsulfonium bromide (171 mg).

Registry No.—**1,** 1774-35-2; **2,** 2417-95-0; **10,** 50546-27-5; **12,** 672-78-6; **13,** 3972-22-3; **14a,** 50273-63-7; **14b,** 50458-30-5; tri-*p*-tolylsulfonium bromide, 50273-64-8; methoxydi-*p*-tolylsulfonium fluorosulfonate, 50273-65-9; mesityllithium, 5806-59-7; triphenylsulfonium bromide, 50273-67-1; lithium oxide, 12057-24-8.

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The Mechanism of Hydride Reduction of 1-Alkyn-3-ols

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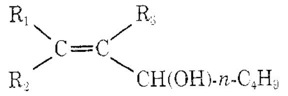
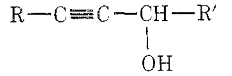
Hydride reduction of 1-alkyn-3-ols (3) is shown to proceed *via* site-specific hydride transfer to C-2. A mechanism is proposed which rationalizes the observed reciprocal relationship between solvent basicity and the extent of cis reduction for these systems.

In connection with another problem in this laboratory, it was necessary to synthesize the isotopically labeled allylic alcohols **1a** and **1b**. One convenient route to allylcarbinolic substrates of this type which has been of considerable synthetic use in the past is the lithium aluminum hydride reduction of propargylic alcohols.[2] Mechanistic observations reported on this and related reductions however, suggest that the detailed course of this reaction might be quite structure dependent, thus detracting from its general utility for isotopic labeling.



1a, $R_1 = R_2 = H; R_3 = D$
b, $R_1 = R_2 = D; R_3 = H$
c, $R_1 = R_3 = H; R_2 = D$
d, $R_2 = R_3 = H; R_1 = D$



$$R{-}C{\equiv}C{-}\underset{\displaystyle OH}{\underset{|}{CH}}{-}R'$$

3a, $R = H; R' = n\text{-}C_4H_9$
b, $R = D; R' = n\text{-}C_4H_9$
c, $R = H; R' = CH_3$
d, $R = D; R' = CH_3$

Early work[3-5] in this area indicated that the reduction proceeded *via* specific hydride transfer from the aluminum bound to oxygen to the adjacent carbon of the acetylenic linkage, leading after hydrolysis to the olefin resulting from exclusive trans reduction (Scheme I). Corey and coworkers have since demonstrated that for certain substrates (principally 2-alkyn-1-ols) the hydride transfer was not site specific.[6] More recently it was observed that the LiAlH$_4$ reduction of phenyl-substituted propargyl alcohols of type 2 proceeded *via* specific hydride attack[7,8] as