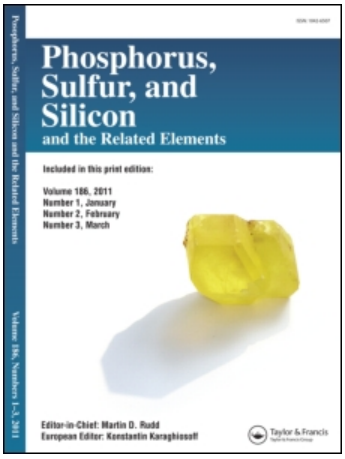

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REACTION OF DIMETHYL SULFITE WITH PHENYLLITHIUM. FORMATION OF BIPHENYL AND DIPHENYL SULFIDE VIA SULFURANE

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Dimethyl sulfite reacted with an excess of phenyllithium yielding biphenyl and diphenyl sulfide in good yield. Other dialkyl sulfites also reacted giving identical yields of biphenyl and diphenyl sulfide irrespective of the structure of the aryl groups, indicating that dialkyl sulfites can be used for the reaction with aryllithiums in place of diaryl sulfoxides. The mechanism of the reaction of diaryl sulfoxides with aryllithium is discussed on the basis of the isomer distribution of bitolyls, the effect of additives, and the ratio of the benzyne and sulfonium salt pathways. Sulfurane **1** is formed in an initial stage of the reaction of diaryl sulfoxide with aryllithium followed by its competitive collapse by way of benzyne and sulfonium salt pathways.

INTRODUCTION

In the course of a study of the reaction of dialkyl sulfite and alkylchlorosulfinate,[1] it seemed interesting to investigate the reaction of dialkyl sulfites with alkyllithiums. Although the reaction of alkyl and aryl sulfites with Grignard reagents has been reported to be an efficient synthetic approach to sulfoxides,[2] no attempt has made to employ organolithium compounds which are more reactive than the Grignard reagents.

In this paper, we report the reaction of dialkyl sulfites with aryllithiums. The most striking characteristic of the reaction is the avoidance of diaryl sulfoxides intermediates. By changing the structure of the aryllithiums, the mechanism can be discussed in terms of the reaction of diaryl sulfoxides with aryllithiums. A reaction pathway through a sulfurane intermediate **1** followed by its collapse to benzyne and the reaction products is proposed.

The reaction of triarylsulfonium salts with aryllithiums yielding biaryls and arylsulfides has been extensively studied. It was originally presumed by Wittig and Fritz[3] that this reaction involved the initial formation of an unstable pentacoordinate sulfur intermediate (sulfurane) which rapidly collapsed to biaryl and diaryl sulfide. However, there is much argument about the idea of the intervention of such a pentacoordinate species.[4] For example, in nucleophilic substitution on the sulfur atom it becomes of interest to inquire whether these reactions involve a simple S_N2 displacement or an intervention of a pentacoordinate intermediate.[5] The substantive mechanistic work was that of Harrington *et al.*[6] who used isotopic tracers to establish the intermediacy of tetraphenylsulfurane in a reaction settling more or less conclusively the controversy of the 1970–1972 papers cited in Refs. 4 and 5. In the

field of inorganic sulfur chemistry, however, several stable pentacoordinate compounds are known, e.g., SF_4, SCl_4, SCl_2F_2, and several others. Recently, diaryldialkoxysulfuranes were isolated and potential synthetic routes have been developed by using the sulfuranes as reagents.[7] All of these isolable compounds possess highly electronegative groups on the sulfur. The sulfuranes possessing only carbon ligands on the sulfur are thought to be possible intermediates in the reaction of triarylsulfonium salts with aryllithium. Trost[8] suggested the existence of a sulfurane intermediate in the reaction of tri-*p*-tolylsulfonium tetrafluoroborate with *p*-tolyllithium in tetrahydrofuran at $-78°C$ to give *p*,*p*′-bitolyl and di-*p*-tolyl sulfides in quantitative yield. Andersen *et al.*[9] obtained similar results by treating a slurry of tri-*p*-tolylsulfonium bromide with *p*-tolyllithium in ether. Thus, while the reactions of the sulfonium salts with aryllithiums have been studied in considerable detail, the reaction of diaryl sulfoxides with aryllithiums has scarcely been studied in contrast with the reactions of sulfonium salts.

Diaryl sulfoxides are known to react with arylmagnesium halides to yield triarylsulfonium salts,[10] and possibly for this reason the analogous route to triarylsulfonium salts from sulfoxides was of less interest. However, Andersen[9,11] reported evidence for the intermediacy of benzyne in reactions of diaryl sulfoxides with aryllithiums. These apparently contradictory results suggested the need for a more detailed study. Our approach to the study of the reaction of diaryl sulfoxides with aryllithium actually starts with the dialkyl sulfites.

RESULTS

The addition of dimethyl sulfite to five molar equivalents of phenyllithium in anhydrous diethyl ether yields both biphenyl and diphenyl sulfide in high yields as listed in Table I and both products are obtained in identical yields irrespective of the structure of the sulfite. Thus, we employed dimethyl sulfite as the dialkyl sulfite in most of this study. When the ratio of phenyllithium to dimethyl sulfite is small, diphenyl sulfoxide is also isolated in a high yield together with biphenyl and diphenyl sulfide. For example, the addition of an ethereal dimethyl sulfite solution to twice the molar equivalents of phenyllithium under reflux yields diphenyl sulfoxide (66%), biphenyl (9%), and diphenyl sulfide (12%) after 2 hr. These results imply that the reaction of dialkyl sulfites with phenyllithium proceeds by the same reaction pathway irrespective of the structure of dialkyl sulfites,

$$\mathrm{ROS(O)OR} + \mathrm{C_6H_5Li} \longrightarrow \mathrm{ROS(O)C_6H_5} \xrightarrow[\text{(fast step)}]{+\ \mathrm{C_6H_5Li}}$$

$$\mathrm{C_6H_5S(O)C_6H_5} \xrightarrow{+\ \mathrm{C_6H_5Li}} \mathrm{C_6H_5\text{-}C_6H_5} + \mathrm{C_6H_5SC_6H_5}$$

An alkyl benzenesulfinate is assumed to be an intermediate and the reaction of sulfinates with organolithium compounds or with the Grignard reagents is known to be a valuable synthetic method for optically active sulfoxides.[12] When an ethereal

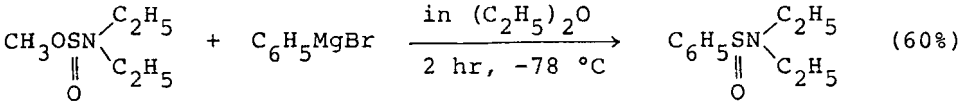
TABLE I

Reaction of alkyl- and arylsulfites with excess phenyllithium in reflux ether

Sulfite or Sulfoxide	Reaction Condition	Products (mol %)	
		C_6H_5—C_6H_5	$C_6H_5SC_6H_5$
$(CH_3O)_2SO$	in reflux ether, 2 hr	75	98
$(C_2H_5O)_2SO$	"	73	quant.
$(n\text{-}C_3H_7O)_2SO$	"	79	quant.
$(C_6H_5O)_2SO$	"	74	quant.
$(C_6H_5)_2SO$	"	quant.	quant.
$(C_6H_5)_2SO$[a]	in ether at room temp, 15 min.	40	75

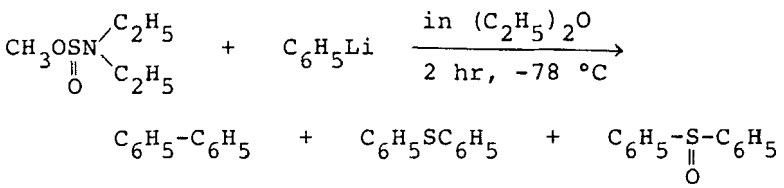
[a] Cited from reference 10.

dimethyl sulfite solution was refluxed for 2 hr with an equimolar amount of phenyllithium, the diphenyl sulfoxide was obtained in a 37% yield, but half of the original dimethyl sulfite was recovered and the expected methyl benzenesulfinate was not isolated. This suggests that the second step proceeds rapidly as compared with the rate of the first step. It is actually known that the rate of base-catalyzed hydrolysis of methyl *p*-toluenesulfinate[13] is about twenty times faster than that of methyl methanesulfinate.[14] Similar results were also derived from the reaction of dimethyl sulfite with an equimolar amount of the less reactive phenylmagnesium bromide even at −78°C. To confirm the existence of the sulfinate intermediate, the reaction of *S*-methoxysulfinyldiethylamine with an equimolar amount of phenylmagnesium bromide for 2 hr was shown to give *N*,*N*-diethylbenzenesulfinamide in a 60% yield,



(60%)

On the other hand, the reaction with an excess of the more reactive phenyllithium yielded both biphenyl (94%) and diphenyl sulfide (94%) while diphenyl sulfoxide was also formed but in a low yield (2%),



Therefore, although methyl benzensulfinate could not be isolated, it is most likely an intermediate in the reaction of dimethyl sulfinate with phenyllithium, and the sulfinate may react rapidly with excess phenyllithium.

The second step in our reaction scheme consists of the formation of diphenyl sulfoxide. To confirm the intermediacy of the sulfoxide, the reaction of dimethyl

TABLE II

Compositions of the products formed from the reaction of dimethyl sulfite with isomeric tolyllithium in ether

Tolyl-lithium	Reaction Condition	Products							
		Bitolyls					Total Yield[c]	Ditolyl sulfide[d]	Ditolyl sulfoxide
		p,p'-	*m,p'*-	*m,m'*-	*o,m'*-	*o,o'*-			
p-	in reflux ether, 2 hr	64	36				quant.	quant.	
p-[a]	"	66	34				quant.	quant.	
p-	−78°C, 2 hr	58	42				67	73	27
p-[a]	"	60	40				90	95	trace
m-	in reflux ether, 2 hr		15	76	9		quant.	quant.	
m-	−78°C, 2 hr		17	67	16		46	47	53
o-[b]	in reflux ether, 2 hr				34	66	7	8	

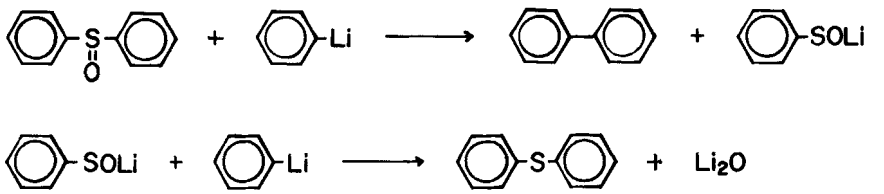
[a] Di-*p*-tolylsulfoxide was employed instead of dimethyl sulfite.
[b] The by-product, 2-methyl-2'-(2-methylphenylmethyl)diphenyl sulfide, was obtained in a 70% yield.
[c] Based on the starting dimethyl sulfite.
[d] Di-*p*-, di-*m*-, and di-*o*-tolyl sulfides were formed from the corresponding tolyllithium.

sulfite with *p*-tolyllithium was compared with that of di-*p*-tolyl sulfoxide with *p*-tolyllithium. The addition of an ethereal solution of dimethyl sulfoxide to six or seven molar equivalents of *p*-tolyllithium yielded *m,p'*-bitolyl (36%), *p,p'*-bitolyl (64%), and di-*p*-tolyl sulfide (quant.). The same products were also obtained in identical yields from the latter reaction [*m,p'*-bitolyl (34%), *p,p'*-bitolyl (66%), and di-*p*-tolyl sulfide (quant.)]. These results imply that the reaction of dimethyl sulfite with *p*-tolyllithium proceeds via the formation of di-*p*-tolyl sulfoxide. This would be a reasonable conclusion from the fact that sulfoxides have been synthesized by the reaction of dialkyl sulfites with the Grignard reagent.[2]

The products obtained in the reaction of dimethyl sulfite with isomeric tolyllithiums are listed in Table II. With *o*-tolyllithium, bitolyls and di-*o*-tolyl sulfide have been obtained in a low yield together with a 70% yield of 2-methyl-2'-(2-methylphenylmethyl)diphenyl sulfide. On the other hand, with *p*-tolyllithium, *m,p'*-bitolyl is obtained in smaller yield (36%) than *p,p'*-bitolyl (64%), suggesting that the benzyne mechanism competes with other mechanisms since if the reaction proceeded simply by way of a benzyne mechanism, both *p,p'*-bitolyl and *m,p'*-bitolyl should be formed with the identical yield from an intermediate 4-methylbenzyne. With *m*-tolyllithium both *m,p'*- and *o,m'*-bitolyl are obtained together with *m,m'*-bitolyl. Furthermore, the distribution of products changed with the preparative of the reaction in support of the existence of competition reactions.

DISCUSSION

Although it has been reported that the reactions of Grignard compounds with aliphatic and aromatic sulfites as well as thionyl chloride yields symmetrical sulfoxides and that the alkyl or aryl groups introduced in the sulfoxides originate from the Grignard reagent,[2] there is no information about the reaction of organic sulfites



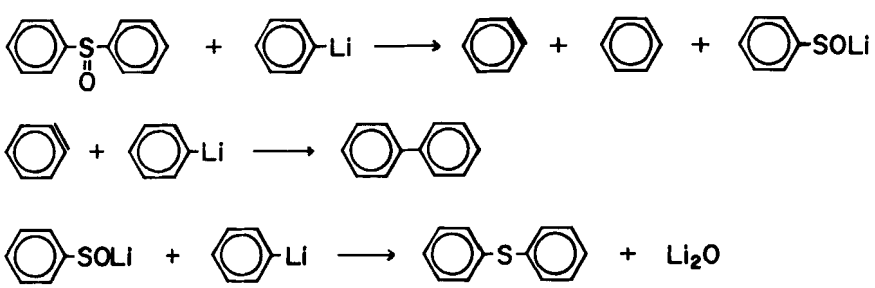
SCHEME 1

with organolithium which is more reactive than Grignard reagent. We obtained biaryl and diaryl sulfides in good yield from the reaction of dialkyl sulfites with excess aryllithium. Several reactions have revealed the existence of intermediate alkyl arylsulfinates in our reactions, followed by reaction with excess aryllithium yielding diaryl sulfoxide.

Let us consider the reaction of diphenyl sulfoxide with phenyllithium yielding biphenyl and diphenyl sulfide. There are several possible routes but, as described above, a simple benzyne route could not explain our product distributions. Aromatic nucleophilic substitution of phenyllithium upon diphenyl sulfoxide is the simplest route among those conceivable. As shown in Scheme 1, diphenyl sulfide is produced from phenylsulfenate salt which forms in an amount equivalent to biphenyl. Thus, if Scheme 1 is operative, the yield of diphenyl sulfide should be less than that of biphenyl. The formation of benzyne (Scheme 2) is also a conceivable route. The possibility of both schemes, especially Scheme 2, has been examined in the following three experiments.

(1) *n*-Butyllithium, which is a stronger nucleophile and more reactive toward benzyne than phenyllithium,[15] has been used in place of phenyllithium in anticipation of obtaining *n*-butylbenzyne. *n*-Butylbenzyne was obtained but, contrary to our expectations, the yield was no more than 3%. (With regard to other products, see Experimental.) The result may arise from ligand exchange equilibrium being faster[16] and may indicate that the use of alkyllithiums might not be feasible for the study of the reaction with diaryl sulfoxides.

(2) Reaction of diphenyl sulfoxide with phenyllithium has been done varying the molar ratio of phenyllithium to diphenyl sulfoxide. As depicted in Figure 1, diphenyl sulfide always exceeds biphenyl in yield, indicating that Scheme 1 can be ruled out. Figure 1 also suggests that Scheme 2 would be also ruled out by taking into



SCHEME 2

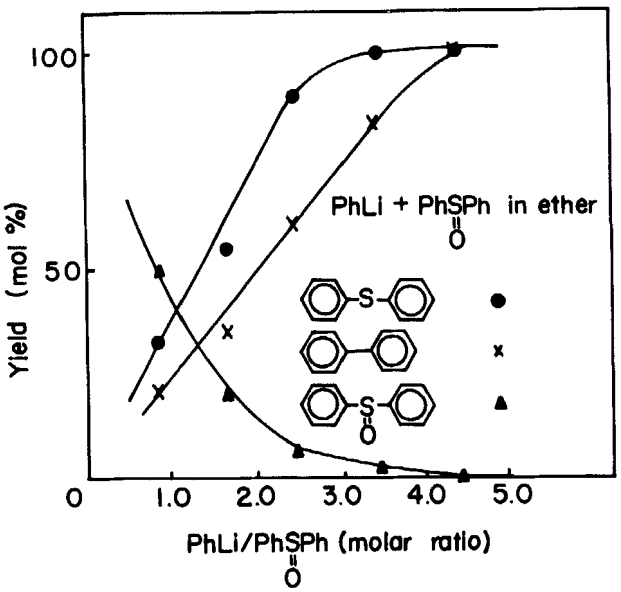


FIGURE 1 Relationship between yield of products from the reaction of diphenyl sulfoxide with phenyllithium and the feed ratio.

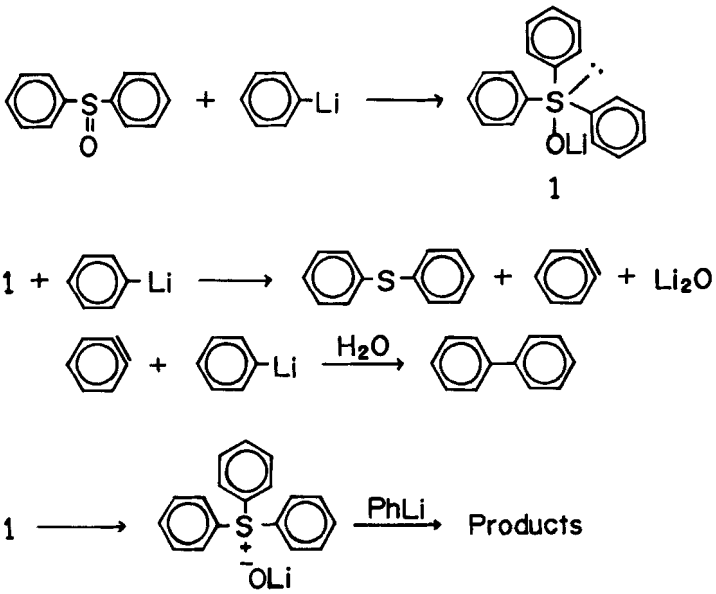
consideration the considerably large activation energy difference between diphenyl sulfide formation and biphenyl formation, since the former reaction involves elimination of the oxyanion ($^{-}$OLi) and the latter is an addition reaction.

(3) From both (1) and (2), a key question is whether or not the lithium salt of phenylsulfenate is a precursor. The sulfenate salts are generally unisolable, other than those of peculiar structures,[17] and the ambident nucleophilicity of sulfenate anions has been studied.[18,19] Thus, the reaction of phenyl benzenethiolsulfinate was initiated with *n*-butylmagnesium bromide,[20] and then phenyllithium was added dropwise into the reaction mixture

$$C_6H_5SOMgBr + C_6H_5Li \longrightarrow \underset{\text{(quant.)}}{\text{n-Bu-SC}_6H_5} + \underset{\text{(trace)}}{\text{n-Bu-SOC}_6H_5}$$

n-Butyl phenyl sulfide was formed quantitatively but diphenyl sulfide could not be detected, clearly indicating that phenylsulfenate salt is not a precursor of diphenyl sulfide. Thus, the routes shown in Schemes 1 and 2 can be ruled out.

Reaction routes through a sulfurane intermediate are conceivably possible as proposed by Trost *et al.*[21,22] for the reaction of tri-*p*-tolylsulfoniumtetraphenylboride with *p*-tolyllithium yielding *p*,*p*′-bitolyl and di-*p*-tolyl sulfide. Andersen *et al.*[23] studied the reactions of *p*,*p*′-ditolyl sulfoxide and tri-*p*-tolylsulfonium bromide with *p*-tolyllithium in ether at room temperature in which initial formation of sulfurane was presumed. Providing that the sulfurane route can be applied to our reactions, it would be represented as Scheme 3 in which sulfurane **1** forms in an initial reaction stage from the reaction of diphenyl sulfoxide with phenyllithium, followed by a competitive collapse process. An orthoproton in **1** is abstracted by phenyllithium yielding both diphenyl sulfide and benzyne; the latter then reacts with excess



SCHEME 3

phenyllithium giving biphenyl. The other collapse process of **1** involves dissociation into sulfonium ion and oxyanion ($^{-}$OLi), and the resulting sulfonium ion reacts with excess phenyllithium to give biphenyl and diphenyl sulfide. Scheme 3 is more likely for diphenyl sulfide formation than biphenyl formation coinciding with the experimental results. To confirm the sulfurane mechanism, effects of additives on the ratio of biphenyl to diphenyl sulfide were examined. Reaction of benzyne with a stronger base than aryllithium should change the ratio. The lithium salt of piperidine satisfies such a condition and has less nucleophilicity toward benzyne than aryllithium.[15,24] Actually, addition of lithium piperidide into the reaction of dimethyl sulfite with *p*-tolyllithium resulted in an increase of *m,p'*-bitolyl by reason of increased 4-methylbenzyne formation (see Table III). Addition of acetic anhydride, on the other hand, brought about an increase of *p,p'*-bitolyl. Acetic anhydride is widely used as

TABLE III

Effects of the additives on the compositions of bitolyls formed from the reaction of dimethyl sulfite with *p*-tolyllithium in ether

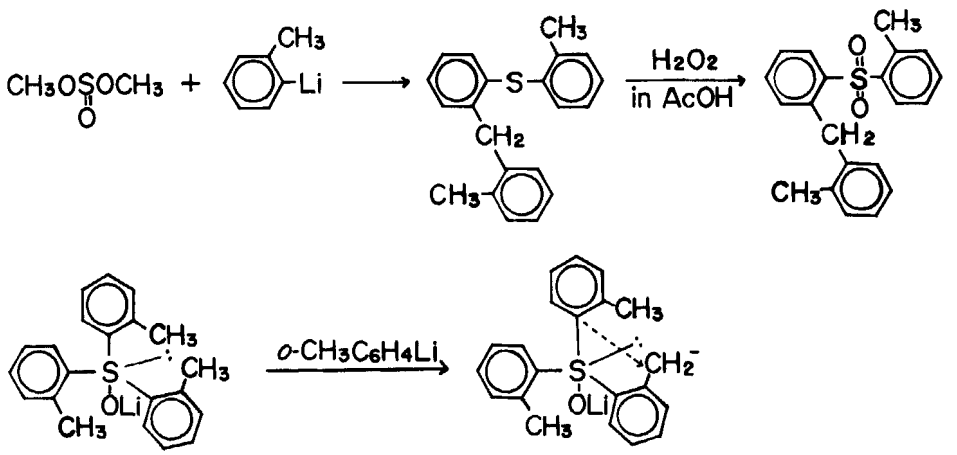
Additive	Reaction Condition	Products				
		Bitolyls		Total Yield	Di-*p*-tolyl sulfide	Di-*p*-tolyl sulfoxide
		m,p'-	*p,p'*-			
None	in reflux ether, 2 hr	36	64	quant.	quant.	
None	−78°C, 2 hr	42	58	67	73	27
lithium Piperidido	in reflux ether, 2 hr	48	52	73	76	7
Acetic Anhydride	"	25	75	43	79	trace
"	−78°C, 2 hr	33	67	18	25	56

reducing agent for sulfoxide,[25] and acetoxydimethylsulfonium salt is formed in an initial stage of reaction of sulfoxide with acetic anhydride.[26] Addition of acetic anhydride into a reaction system consisting of sulfoxide and aryllithium would also favor conversion of the oxyanion to acetoxy which is a better leaving group than oxyanion. Thus, formation of sulfonium salt would become more favored compared with the case without acetic anhydride, leading to enhanced formation of *p,p'*-bitolyl.

Further consideration of the sulfurane route was approached by changing the structure of the sulfuranes. *N*-*p*-Tolyl-di-*p*-tolylsulfilimine was used in place of dimethyl sulfite to react with *p*-tolyllithium. The sulfurane bearing a better leaving group, *p*-toluenesulfoneamide, was expected to give an increased yield of *p,p'*-bitolyl. The overall yield was not high by reason of insolubility of the sulfilimine in ether, but, coinciding with our expectations from Scheme 3, *p,p'*-bitolyl formed in a 38% yield while *m,p'*-bitolyl was formed in 2% yield.

As described, 2-methyl-2'-(2-methylphenylmethyl)diphenyl sulfide is obtained in a 70% yield from the reaction of dimethyl sulfite with *o*-tolyllithium (see Table II). This product can also be explained by assuming the initial formation of sulfurane as shown in Scheme 4. Proton abstraction from the methyl group, rather than from ring ortho protons with excess *o*-tolyllithium leads to formation of intermediate carbanion, followed by a Smiles rearrangement of carbanion yielding the sulfide.[27] Thus, all of the experimental results obtained with the reactions of dialkyl sulfites with aryllithium could be explained by Scheme 3 in which the initial formation of sulfurane is assumed, and then the sulfurane collapses by a competition reaction.

It is interesting to estimate the ratio of benzyne pathway to sulfonium salt intermediate pathway for formation of bitolyls by taking into consideration the selectivity for nucleophilic attack of aryllithium on methyl-substituted benzyne. The selectivity has been explained on the basis of either kinetic or thermodynamic control,[28] and product orientation can be estimated to the methyl-substituted benzyne. That is, it is known that aryllithium attacks with the same possibility from



SCHEME 4

TABLE IV

Ratio of benzyne pathway to sulfonium salt pathway in the reaction of dimethyl sulfite with tolyllithium

Tolyllithium	Reaction Condition	Benzyne Pathway / Sulfonium Salt Pathway
p-	in reflux ether	1.1–1.3
p-	−78°C	2.0–2.6
m-	in reflux ether	0.9
m-	−78°C	2.7
o-	in reflux ether	0.3

both sides of 3-methylbenzyne and that the meta position is favored by a factor of two over the ortho position.[29] Thus, we can calculate each proportion of benzyne pathway by the bitolyl compositions formed. In the calculations of proportions, the sulfonium salt pathway is assumed to give only one isomer, e.g., with *p*-tolyllithium solely *p,p'*-bitolyl is formed. This assumption may be reasonable since the reaction of tri-*p*-tolylsulfonium salt with *p*-tolyllithium yielded *p,p'*-bitolyl and no meta-isomers were detected.[8]

The ratios were estimated for the reaction of dimethyl sulfite with tolyllithiums as listed in Table IV. The benzyne pathway becomes more favored than the sulfonium salt pathway on lowering the reaction temperature, indicating that dissociation of oxyanion from the sulfurane requires more activation energy than ortho proton elimination from sulfurane.

EXPERIMENTAL

General. Aryllithiums were prepared according to the method of Trost *et al.*[22] The preparations of dialkyl and diaryl sulfites were described elsewhere.[1b] Reaction products were identified by comparison of their IR spectra and the retention times with those of authentic samples. Yields of the products estimated on the basis of starting sulfite or sulfoxide were determined by means of GLC in which diphenylmethane was used as an internal standard.

Reaction of Dialkyl Sulfites with Phenyllithium. An ethereal solution of dialkyl sulfite (10 mmol) was added dropwise to phenyllithium (50 mmol) in anhydrous diethyl ether (*ca.* 50 ml) contained in a nitrogen-flushed flask. After being stirred magnetically for 2 hr at the appropriate temperature, the reaction mixture was hydrolyzed with dilute aqueous hydrochloric acid, and then diphenylmethane was added. Diethyl ether was evaporated at reduced pressure from the reaction mixture after drying over anhydrous sodium sulfate. The residue was analyzed by GLC. An authentic pure sample of biphenyl was available commercially. Diphenyl sulfide and diphenyl sulfoxide were prepared by the conventional methods.

Reaction of N-Methoxysulfinyl Diethylamine with Phenyllithium and with Phenylmagnesium Bromide. *N*-Methoxysulfinyldiethylamine was prepared according to the method of Zinner:[30] bp 74–76°C/10 mm (lit.[30] 73–74°C/10 mm). Anal. Calcd for $C_5H_{13}NO_2S$: C, 39.73; H, 8.61. Found C, 39.92; H, 8.32.

The reaction with phenyllithium was done essentially in the same manner as described in the reaction of dialkyl sulfites with phenyllithium. To the ethereal solution of phenylmagnesium bromide was added an equimolar amount of *N*-methoxysulfinyldiethylamine dissolved in diethyl ether at −78°C. After reaction had continued for 2 hr, an excess chloroform was added to the reaction mixture which was then treated with aqueous hydrochloric acid, and finally separated and dried by anhydrous sodium sulfate. Solvent was removed by evaporation and crude *N,N*-diethylbenzenesulfinamide was isolated by distillation under reduced pressure to afford a 60% yield: bp 118–130°C/3 mm (crude). During distillation,

some decomposition was noticed. The crude product was finally purified by preparative TLC; IR 1052, 1085 cm^{-1} (S=O); NMR δ 1.1 (t, 6 H, $-N(CH_2CH_3)_2$), 3.15 (q, 4 H, $-N(CH_2CH_3)_2$), 7.3–7.8 ppm (m, 5 H, arom.). Anal. Calcd for $C_{10}H_{15}NO_2S$: C, 60.86; H, 7.68; N, 7.10. Found C, 61.07; H, 8.27; N, 6.97.

Reaction of Dimethyl sulfite with Tolyllithiums. Dimethyl sulfite (3.0 mmol) in diethyl ether (*ca.* 40 ml) was added dropwise over about 15 min with stirring to an ethereal solution of a tolyllithium (21 mmol). The reaction mixture was treated in a similar way to that with phenyllithium. Duplicate experiments were performed for the reaction of dimethyl sulfite with *p*-tolyllithium in order to determine the exact distribution of products. Bitolyl products distribution could be determined within an experimental error of 2–3%. We were unable to separate bitolyls into *p,p'*-bitolyl and *m,p'*-bitolyl under ordinary GLC conditions with a 2 m column of 25% SE 30 on Chromosorb P. Therefore, GLC equipped with a 6 m column packed with Apiezon L on Chromosorb W and with a flame ionization detector was used. The relative retention times of various bitolyls are as follows; *o,o'*-bitolyl, 0.87; diphenylmethane (standard), 1.00; *o,m'*-bitolyl, 1.15; *m,m'*-bitolyl, 1.75; *m,p'*-bitolyl, 1.85; *p,p'*-bitolyl, 2.03. Each authentic sample of ditolyl sulfoxides was prepared from the reaction of dimethyl sulfite with the corresponding tolylmagnesium bromides. Symmetrical bitolyls such as *p,p'*-, *m,m'*-, and *o,o'*-bitolyls were obtained via an Ullman reaction from the corresponding iodotoluenes. Asymmetric bitolyls were synthesized from the reaction of methylcyclohexanone with the tolylmagnesium bromides according to the method of Ito and Hey.[31] Ditolyl sulfides were obtained with the iodine ion reduction of the corresponding sulfoxides.[32] When the reaction of dimethyl sulfite with *o*-tolyllithium was performed, the dried organic layer was concentrated to a yellowish viscous oil (70% yield) which was chromatographed on silica gel after the GLC analysis. This material which was finally purified by preparative TLC was assigned the structure 2-methyl-2'-(2-methylphenylmethyl)diphenyl sulfide on the basis of IR and NMR spectra and the elementary analysis: IR 740 cm^{-1} (ortho derivative); NMR δ 2.13 (s, 3 H, $-CH_3$), 2.31 (s, 3 H, $-CH_3$), 4.05 (s, 2 H, $-CH_2-$), 6.80–7.20 (m, 18 H, arom.). Anal. Calcd for $C_{21}H_{23}S$: C, 82.84; H, 6.63. Found C, 82.77; H, 6.68.

The assignment for this compound was further confirmed by the oxidation with hydrogen peroxide in acetic acid. The corresponding sulfone formed, which crystallized upon standing, was purified by preparative TLC to give yellowish solid: mp 114°C. IR 1302 cm^{-1} ($-SO_2-$). Anal. Calcd for $C_{21}H_{23}O_2S$: C, 74.89; H, 5.94. Found C, 74.96; H, 5.93.

Reaction of N-Butyllithium with Diphenyl Sulfoxide. *n*-Butyllithium was prepared by the conventional method. The 2.5 equimolar ethereal solution of *n*-butyllithium was added to diphenyl sulfoxide in refluxing ether. After 2 hr, the reaction mixture was treated in a similar way to that with phenyllithium. The reaction affords the various products of which the seven compounds were identified by GLC; *n*-butylbenzene (3%), biphenyl (10%), *n*-butylphenyl sulfide (5%), diphenyl sulfide (22%), *n*-butyl sulfide (5%), *n*-butyl sulfoxide (9%), and *n*-butylphenyl sulfoxide (26%). Authentic samples of *n*-butylbenzene and *n*-butyl sulfide were synthesized by the conventional methods. *n*-Butyl sulfide was available commercially, and *n*-butylphenyl sulfoxide and *n*-butyl sulfoxide were synthesized by oxidation of the corresponding sulfides according to the method of Oae.[33]

Reaction of Phenylsulfenate Salt with Phenyllithium. Phenyl benzenethiolsulfinate was employed as a source of phenylsulfenate salt. Phenyl benzenethiolsulfinate was synthesized according to the procedure of Kice:[34] mp 71°C (lit.[34] 69.5–71°C). Anal. Calcd for $C_{12}H_{10}OS$: C, 61.54: H, 4.27. Found C, 61.19; H, 4.20.

To the reaction mixture, prepared from the reaction of phenyl benzenethiolsulfinate with *n*-butylmagnesium bromide in ether, was added an equimolar amount of phenyllithium at the ether refluxing temperature. After 2 hr the reaction mixture was treated with aqueous hydrochloric acid and dried over anhydrous magnesium sulfate. The concentrated reaction mixture was analyzed by GLC. A quantitative yield of *n*-butyl phenyl sulfide and a trace amount of *n*-butyl phenyl sulfoxide was obtained, but we could not detect diphenyl sulfide.

Reaction of N-Tosyl-p-tolylsulfilimine with p-Tolyllithium. *N-p*-Tosyl-*p*-tolylsulfilimine was synthesized as described for the reaction of dimethyl sulfite with tolyllithium:[35] mp 149–150°C. Anal. Calcd for $C_{21}H_{21}NO_2S$: C, 65.75; H, 5.52; N, 3.65. Found C, 64.78; H, 5.48; N, 3.32.

Reaction of Dimethyl Sulfite with p-Tolyllithium in the Presence of Additive. To the ethereal solution of *p*-tolyllithium was added dropwise a mixture of dimethyl sulfite and an additive such as acetic anhydride dissolved in ether. Relative reagent concentration of *p*-tolyllithium : dimethyl sulfite : additive was 8 : 1 : 1.5 molar ratio. The reaction mixture was treated in the same manner as described in the reaction of dimethyl sulfite with tolyllithium.

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