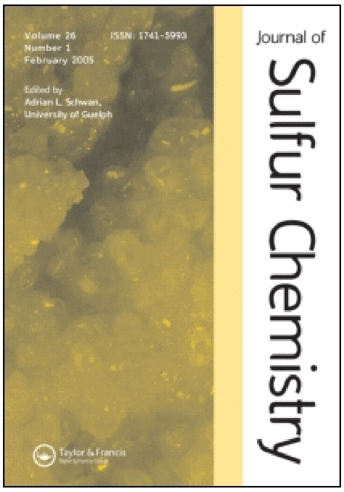

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The Chemistry of Metalated Arenesulfonyl Systems

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THE CHEMISTRY OF METALATED ARENESULFONYL SYSTEMS

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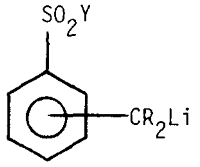
Benzylic metalation is readily accomplished on appropriate diaryl sulfones, *t*-alkyl aryl sulfones and phenyl arenesulfonates and N-methylarenesulfonanilides. The resulting metalated sulfones undergo rearrangement to isomeric sulfinic acid salts, wherein an aryl or *t*-alkyl unit has moved from the sulfur atom to the benzylic carbanionoid center. The metalated arenesulfonates and sulfonanilides undergo coupling-condensation to form bibenzylic-type products. These rearrangements and coupling-condensations are interesting in their own right, and also offer considerable potential in synthetic work, inasmuch as they involve new carbon-carbon bond formations between a benzylic carbon and an aryl group or *t*-alkyl group or another benzylic carbon moiety, respectively.

INTRODUCTION

This review will deal with the chemistry of arenesulfonyl systems which have been metalated at a benzylic position of an attached alkyl substituent, *cf.* **1**. Initially, *Y* will consist of aryl groups, then extend to alkyl units, and finally phenoxy and anilino structures. Also initially, the benzylic carbanionoid grouping will have an *ortho*-orientation, but later extended to a *para*-arrangement. Metalation is usually accomplished with organometallics, such as *n*-butyllithium; but other bases, *e.g.*, lithium diisopropylamide and potassium *t*-butoxide, can also be effective. The resulting sulfonyl carbanionoid systems undergo a number of interesting rearrangements and coupling-condensation reactions which will be described below.



1

DIARYL SULFONES

The metalation of arenesulfonyl systems was first observed[1] over thirty years ago when it was noted that diphenyl sulfone (**2**) is metalated at an *ortho*-position by *n*-butyllithium.

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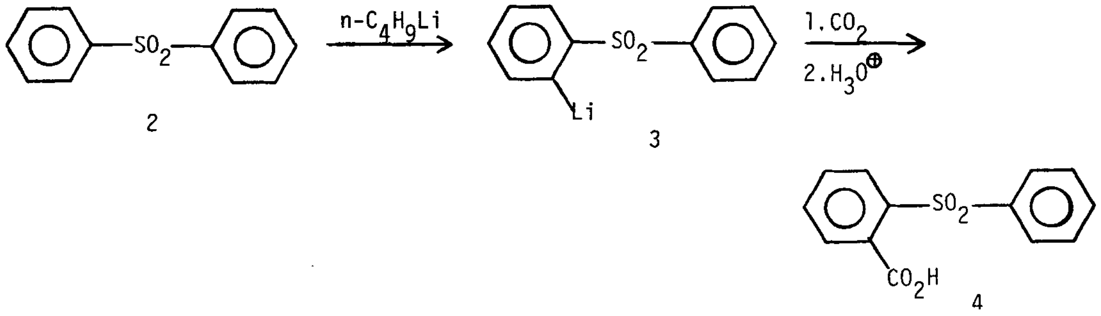
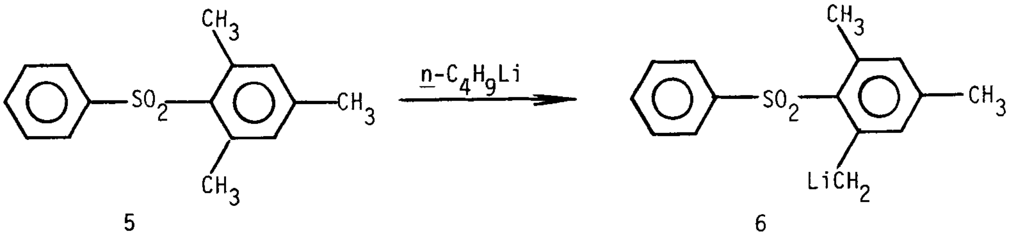
Formation of metalated sulfone **3** was confirmed by carbonation followed by acidification yielding carboxylic acid **4**.

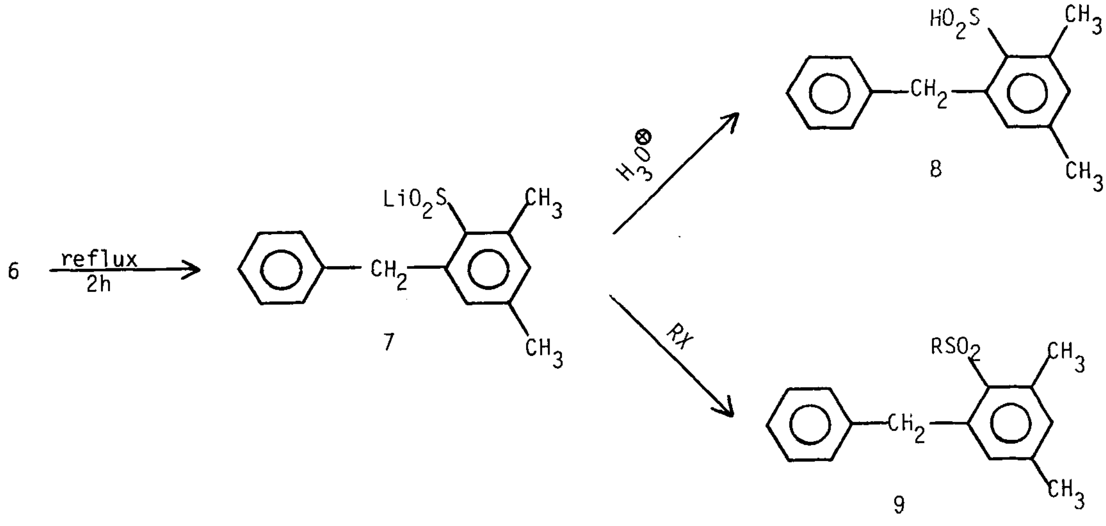


This procedure was later extended[2] to mesityl phenyl sulfone (**5**) with the interesting result that metalation occurred not at an open position, but at an *ortho*-methyl group to



yield **6**. This species could be trapped by ordinary electrophiles such as carbon dioxide or methyl iodide.

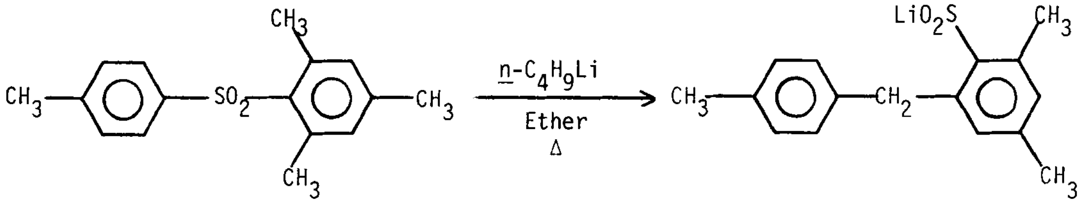
Upon refluxing an ether solution of **6** for two hours a novel rearrangement was observed. The product of this rearrangement was sulfinate salt **7** which could be isolated as such or, after acidification, as the acid **8** or as a sulfone derivative **9**. These transformations are illustrated in Scheme 1. Like results were obtained for numerous diaryl sulfones possessing an *ortho*-methyl or *ortho*-ethyl group.[3,4]



Scheme 1

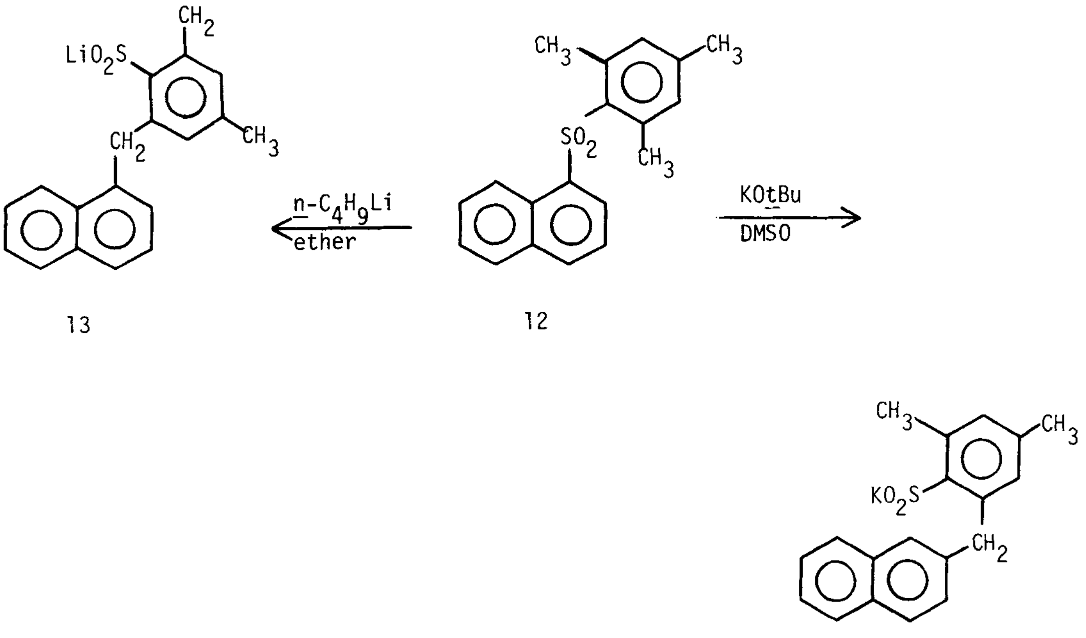
This process is analogous to the Smiles[3] rearrangement with the following two important differences: (1) whereas the nucleophilic center to which the aryl group migrates in the classical Smiles rearrangement is a heteroatom, usually oxygen, nitrogen or sulfur, in the Truce-Smiles modification it is a carbanionoid unit; (2) the Smiles rearrangement requires an activating substituent such as *ortho*- or *para*-nitro in the migrating aryl unit, possibly implicating a Meisenheimer complex intermediate.[5] Such activation is not needed and perhaps would not be tolerated in a metalated diaryl sulfone.

The orientation of the migrating aryl group both before and after this rearrangement is of importance. Note that with mesityl *p*-tolyl sulfone (**10**),[6] the migrating group, *p*-tolyl, retains its *para*-orientation in product **11**.



10 11

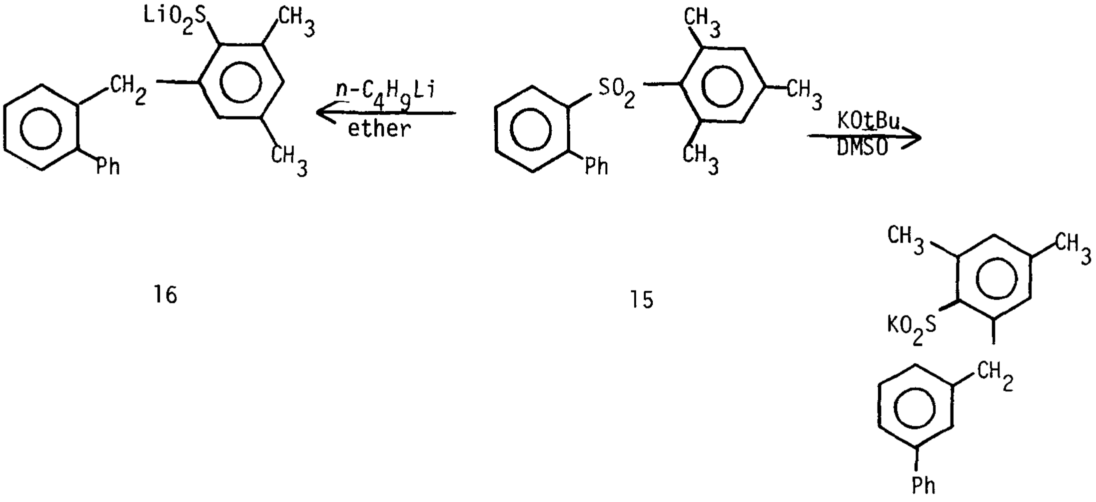
However, an interesting example of an alternate mode of rearrangement is provided by α-naphthyl mesityl sulfone (**12**).[6,7] In this case rearrangement can be effected by either *n*-butyllithium in ether or potassium *t*-butoxide in DMSO. The former reagent gives the "normal" rearrangement product (**13**), but with the latter base/solvent system,[7] the product is the isomeric sulfinate **14**, wherein the migrating unit has undergone a change of orientation to *β*-naphthyl.



13 12

14

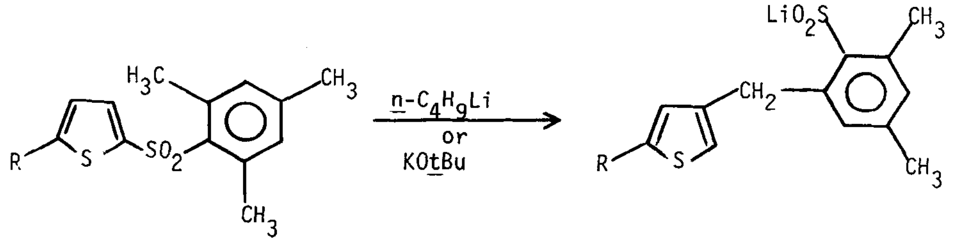
Other aryl systems have also been observed to rearrange with a change in orientation. These include 2-biphenylyl (**15**)[8] which reacts in analogy to **12** to give the "normal" Truce-Smiles product (**16**) with *n*-butyllithium in ether and the product (**17**) having altered orientation (3-biphenylyl) with potassium *t*-butoxide in DMSO, and the thienyl systems (**18**),[9] which yield the product of altered orientation (**19**) with both *n*-butyllithium and potassium *t*-butoxide. In **18a** it was observed that two equivalents of *n*-butyllithium were necessary as the first equivalent was consumed to form **18c**.



16

15

17



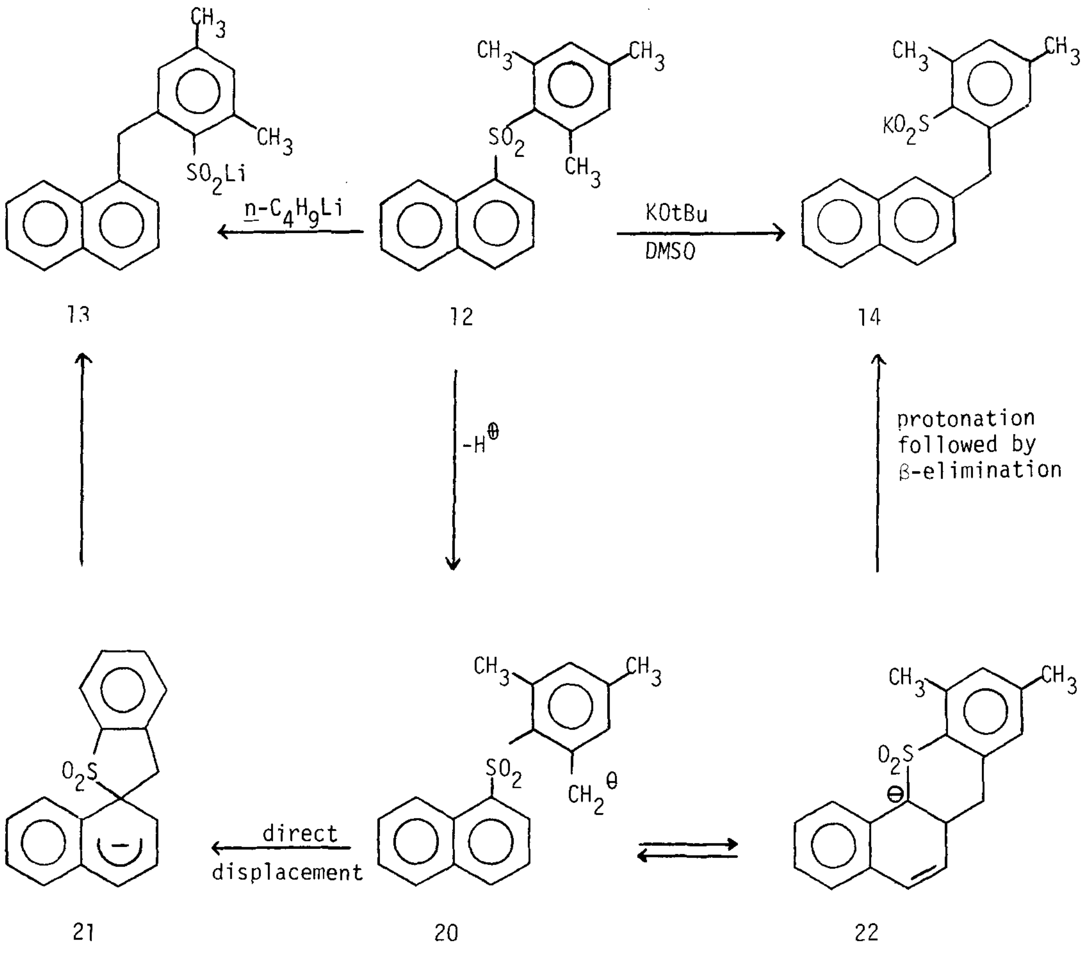
18

a: R=H
b: R=CH_3
c: R=Li

19

a: R=H
b: R=CH_3
c: R=Li

These results can be rationalized by invoking two competing pathways (Scheme 2). The "normal" Truce-Smiles rearrangement may involve internal nucleophilic attack by the carbanionoid unit in **20** at the *ipso*-position of the migrating aryl group to give a Meisenheimer type intermediate (**21**), or transition state of similar structure, followed by expulsion of sulfinate (however, mechanisms involving electron transfers and/or radical

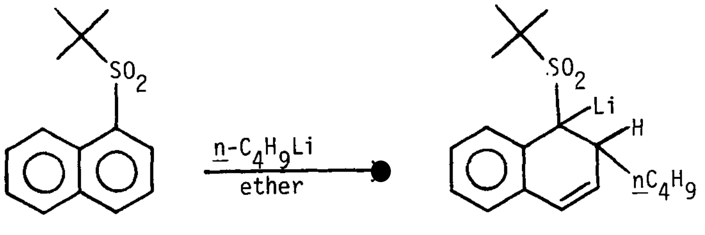


Scheme 2

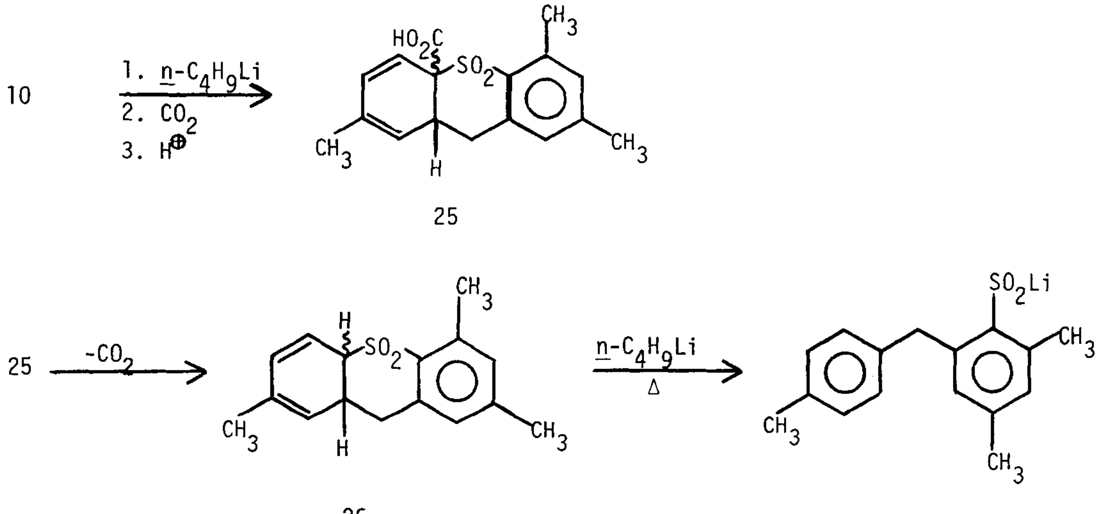
intermediates cannot be excluded from consideration). Henceforth, rearrangement with retained orientation for the migrating aryl group will be referred to as "direct displacement". On the other hand, rearrangement with a change in orientation involves an "addition-elimination sequence". Initial reaction leads to an internal Michael type adduct (**22**) followed by an E2-type elimination to yield a product (**14**) wherein the migrating aryl grouping has an altered orientation.

Of the diaryl sulfones studied, rearrangement *via* the direct displacement route is most common. In fact all save thienyl and 5-methylthienyl sulfones (*cf.* **18**) rearrange *via* this route under the influence of *n*-butyllithium in ethereal solvent. Additionally, although α- and β-naphthyl and 2-biphenylyl systems have been observed to give rearrangement *via* direct displacement with *n*-butyllithium, use of potassium *t*-butoxide in DMSO gives rearrangement *via* the addition-elimination route. Such observations may reflect the greater tendency of these aromatic systems to undergo reactions of addition, as evidenced[10] by the addition of *n*-butyllithium to α-naphthyl *t*-butyl sulfone (**23**) to give adduct **24**.

Considerable evidence exists for the equilibria presented in Scheme 2. For instance, it is possible[6,11] to trap the internal Michael adducts with either carbon dioxide or protic acids. Consequently, when the metalated intermediate derived from mesityl *p*-tolyl sulfone (**10**) was carbonated and the resulting mixture acidified, carboxylic acid **25** was formed. In the presence of aqueous base, **25** was readily decarboxylated to give dihydrothioxanthene 10,10-dioxide **26** which, upon treatment with *n*-butyllithium in ether, gave **11** (Scheme 3). Apparently metalation *alpha* to the sulfone group is followed by unzipping to metalated **10** which undergoes "direct displacement".



23 24

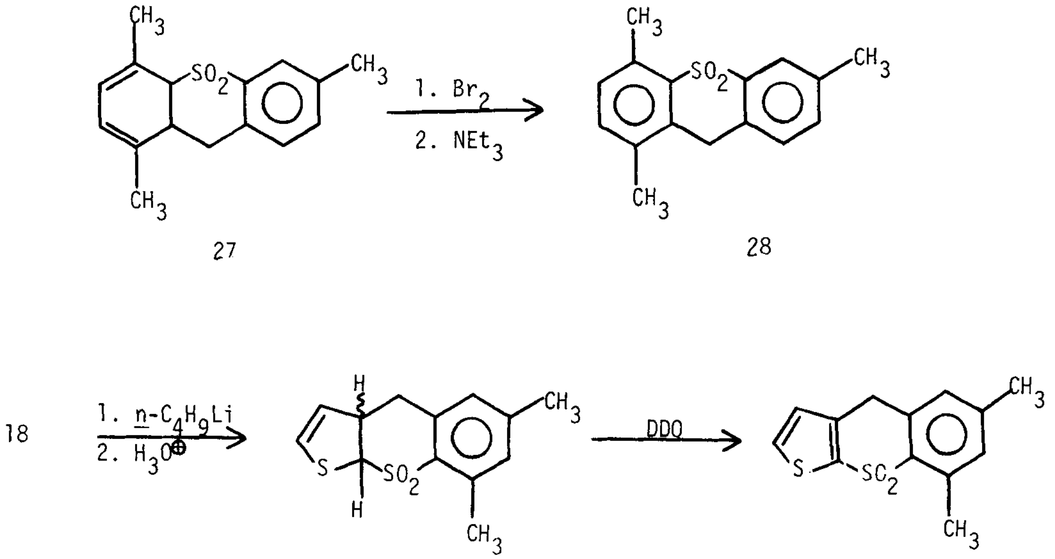


10 25 26 11

Scheme 3

It is possible to effect other transformations on compounds analogous to **26**. The dihydrothioxanthene 10,10-dioxides synthesized by the sequence described above (Scheme 3) and therefore the starting diaryl sulfones, are readily converted to the corresponding thioxanthene 10,10-dioxides. For example **27** was converted to **28** by bromination followed by dehydrobromination and **29**, derived from **18a**, was dehydrogenated[9] with DDQ to give **30** (Scheme 4).

The product sulfinic acids can also be transformed to thioxanthene 10,10-dioxides. An example[9] involves a method used to verify the orientation of the migrating grouping in

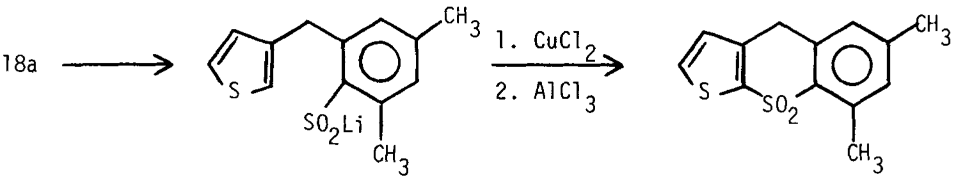


27 28

29 30

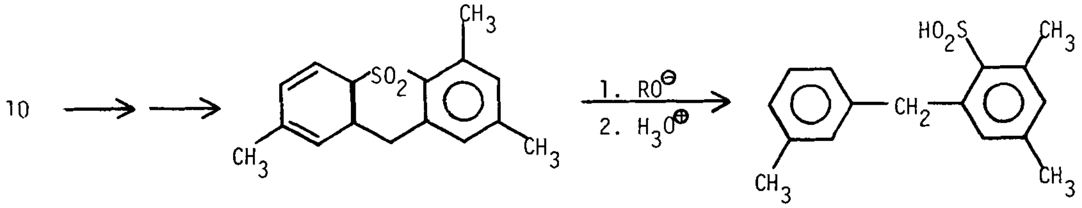
Scheme 4

the rearrangement of **18**. The rearrangement product **19a** was converted to the sulfonyl chloride followed by treatment with $AlCl_3$ to give **30**.



19a 30

Dihydrothioxanthene 10,10-dioxides undergo internal β-elimination in the presence of alkoxide bases to give sulfinic acids which are formally the products of rearrangement proceeding *via* the addition-elimination sequence already described. Accordingly, **10** can be converted[12] to **32** *via* intermediate product **31**.

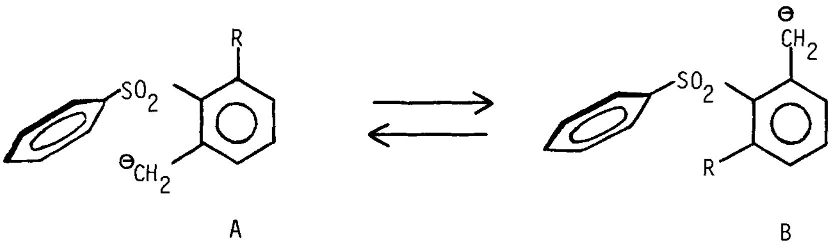


31 32

It is apparent from the above that a diaryl sulfone, metalated at an *ortho*-methyl group, is capable of undergoing several transformations. It can react to yield a sulfinic acid *via* *ipso*-substitution ("direct displacement"), *i.e.*, a classical Truce-Smiles rearrangement. It can also be converted to a dihydrothioxanthene 10,10-dioxide of a known substitution pattern and from there to a thioxanthene 10,10-dioxide or to the product of an addition-elimination pathway for Truce-Smiles type rearrangement.

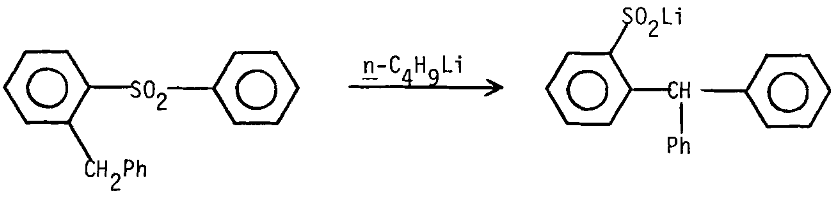
The factors affecting orientation and reactivity in the Truce-Smiles rearrangement have been studied. The rate of rearrangement has been measured[13,14] for a variety of metalated sulfones. The reaction was found to be first order in metalated sulfones where the rate of initial metalation was very high. Sulfones with a methyl group at the 6-position of the ring containing the α-lithioalkyl unit were also found to react approximately one order of magnitude more rapidly than those with an open 6-position.

The accelerating effect of a 6-methyl substituent is also known[14] for the Smiles rearrangement. One interpretation of this effect is that the metalated sulfone exists in a conformational equilibrium as depicted in Scheme 5. Presumably displacement occurs via conformer A. Factors favoring this form over conformer B should accelerate the rate of rearrangement. Accordingly, when R is hydrogen, conformer B becomes favored for steric reasons and reaction occurs more slowly.



Scheme 5

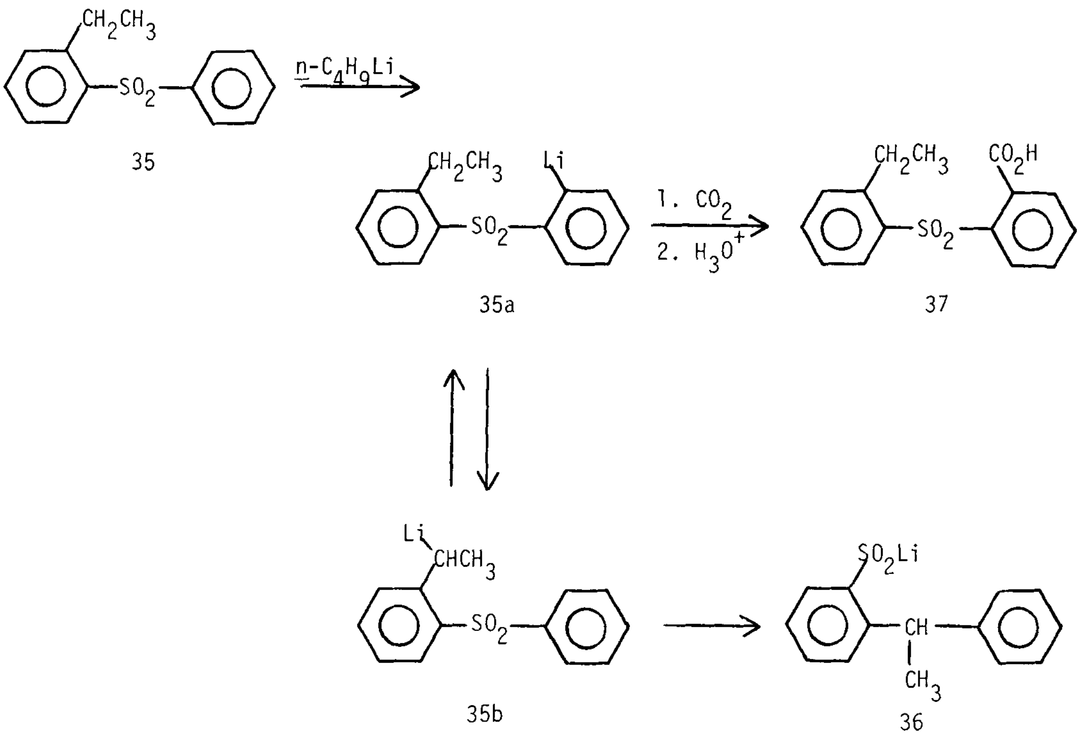
The rate of "direct displacement" type rearrangement shows[4] an additional dependence upon the proportion of cyclic (internal Michael adduct) *vs.* non-cyclic carbanion. Thus, for aryl mesityl sulfones, the rate is roughly proportional to the amount of non-cyclic carbanion in equilibrium with the cyclic form. Metalated sulfones, which exist almost entirely in the cyclic form, such as with α-naphthyl mesityl sulfone (**12**), rearrange slowly[7,15] if at all, under direct displacement conditions (*n*-butyllithium/ ether). Conversely, *o*-benzyldiphenyl sulfone (**33**), for which a cyclic species is not observed, readily rearranges[16] to sulfinic acid salt **34**.



33

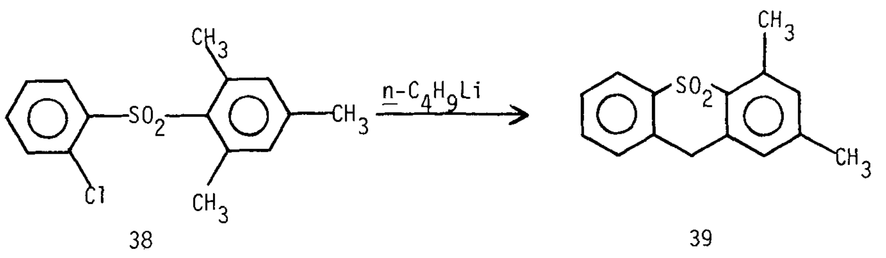
34

Factors which lower the acidity of the *ortho*-benzylic hydrogens relative to the ring hydrogens, such as replacement of methyl with higher alkyl groupings,[17,18] the presence of electron-withdrawing groups[19] on the ring, *etc.*, may affect the rate of rearrangement by allowing competing metalation of the aromatic ring. For instance, *o*-ethyldiphenyl sulfone (**35**) rearranges[17] very slowly to **36**. The isolation of acid **37** after carbonation and acidification of the reaction mixture shortly after metalation confirmed the existence of an equilibrium between carbanions **35a** and **35b** (Scheme 6).

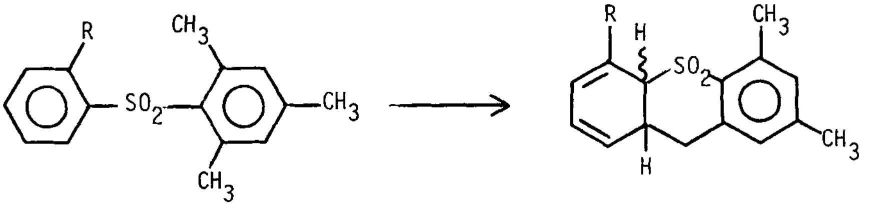


Scheme 6

In addition to allowing competing ring metalation, electronegative groups which can act as leaving groups have been observed to divert the reaction from the normal Truce-Smiles route to a simple internal nucleophilic aromatic substitution at the position occupied by that substituent. An example is *o*-chlorophenyl mesityl sulfone (**38**)[20] which, when metalated, reacts cleanly to yield thioxanthene 10,10-dioxide **39**.



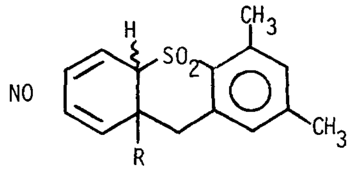
Alkyl substitution on the migrating ring shows an influence on the nature of the cyclic species formed by metalation and subsequent internal Michael addition. Substituents at the *para*-position of the migrating ring offer no complications as only a single cyclic species is possible (*cf.* compound **10**). Two modes of addition are available, however, to sulfones in which the migrating ring contains an *ortho*- or *meta*-substituent. Nevertheless, only a single product is normally observed. For example, a sulfone bearing an *ortho*-alkyl substituent, such as **40**,[12,21] usually yields only **41** as product. The alternate product, **42**, is not observed.



40

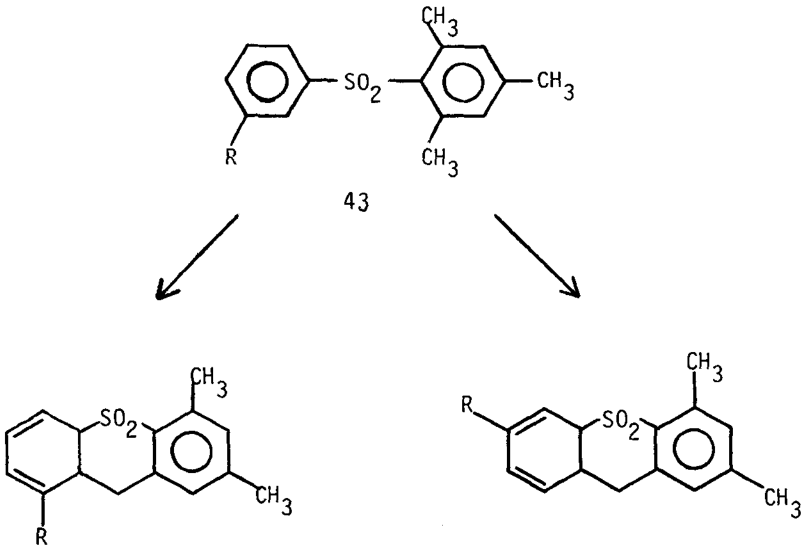
R=Et, i-Pr, t-Bu

41



42

Meta-substituents also exhibit significant selectivity. In **43**, internal Michael addition can occur to yield either **44** or **45**, but in the systems studied,[4] **44** was the only observed product, except where R is *t*-butyl.



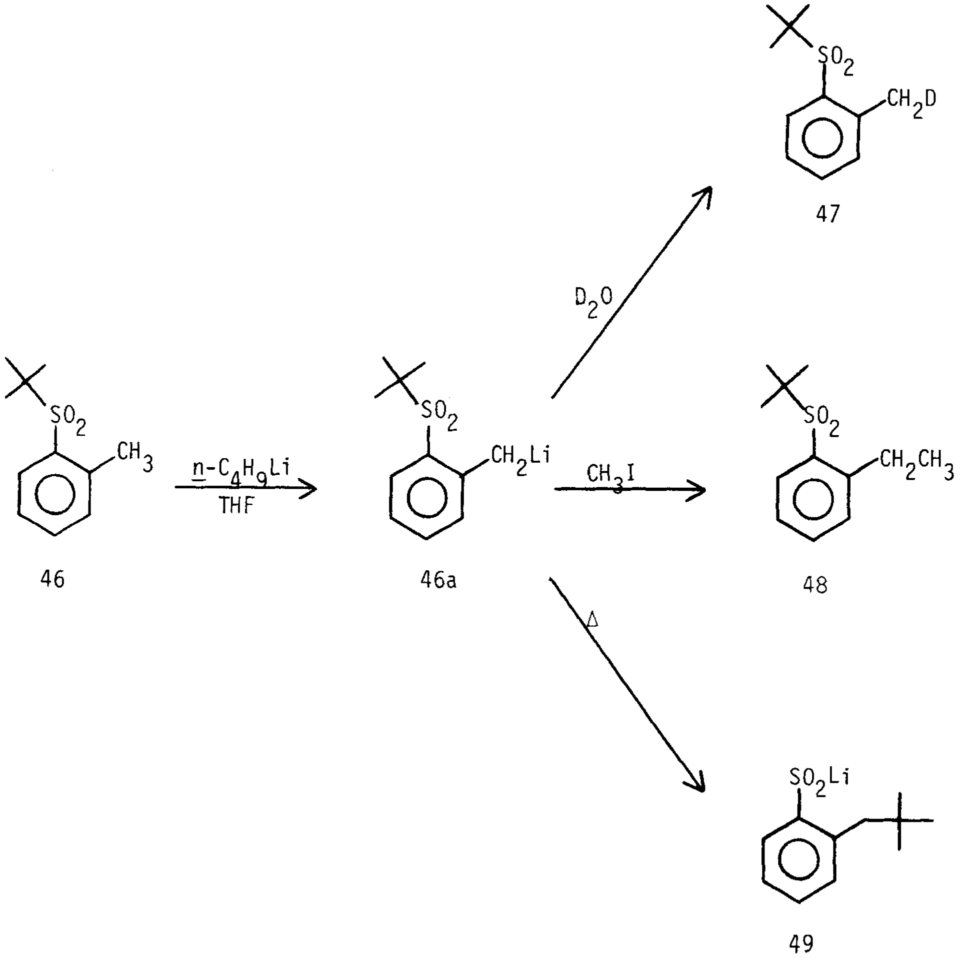
43

44

45

ARYL ALKYL SULFONES

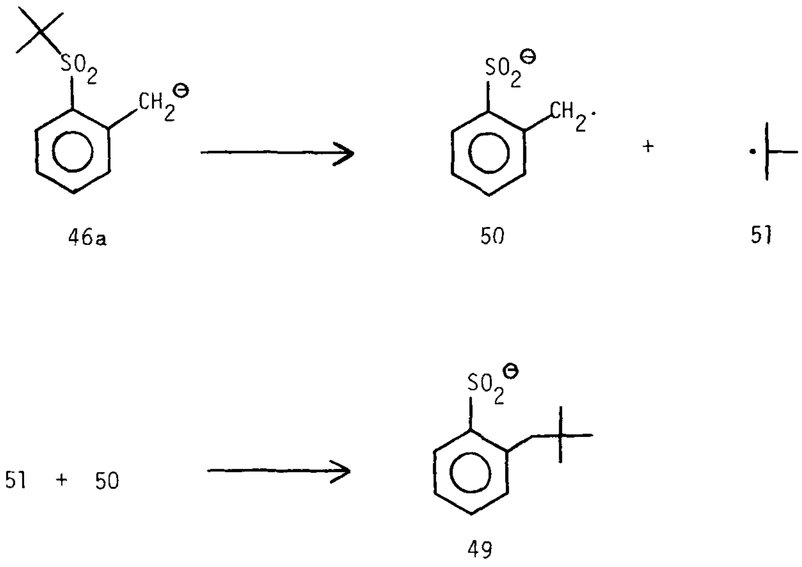
Recently,[22] *t*-alkyl as a migrating unit in a formally Truce-Smiles fashion was encountered with *o*-tolyl *t*-butyl sulfone (**46**). When (**46**) was treated with *n*-butyllithium in THF solution, facile metalation to yield **46a** was observed. At room temperature and below the metalated sulfone is stable and its presence can be verified[23] by quenching with D_2O or methyl iodide to give **47** and **48**, respectively (Scheme 7). However, upon refluxing the solution for several hours, reaction occurs to yield a compound identified as the lithium salt of *o*-neopentylbenzenesulfinic acid (**49**). Several other aryl *t*-alkyl sulfones gave similar results.[23,24]



Scheme 7

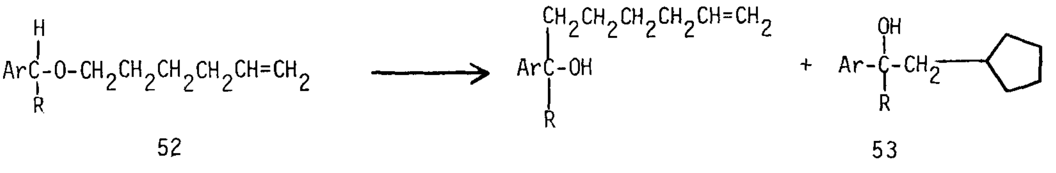
One of the mechanistic pathways under consideration for this process involves a concerted (pericyclic) reaction analogous to that first postulated for the Truce-Smiles rearrangement of diaryl sulfones. Orbital symmetry considerations[25] require that such a process occur suprafacially with inversion of configuration at the migrating center or antarafacially with retention of configuration. With *t*-butyl as migrating group the steric requirement of either transition state would appear to severely limit this possibility.

A pathway involving the intermediacy of free radicals would appear more likely. One such mechanism is illustrated in Scheme 8. In this route, the initial step involves fragmentation of the metalated sulfone **46a** to the two radical species, *t*-butyl (**51**) and the benzylic radical-sulfinate species **50**. This fragmentation is followed by simple recombination to give the observed product (**49**). (A more critical evaluation of this radical pair mechanism awaits determination of any solvent cage effect, the state of aggregation of the metalated sulfonyl compounds, etc.).

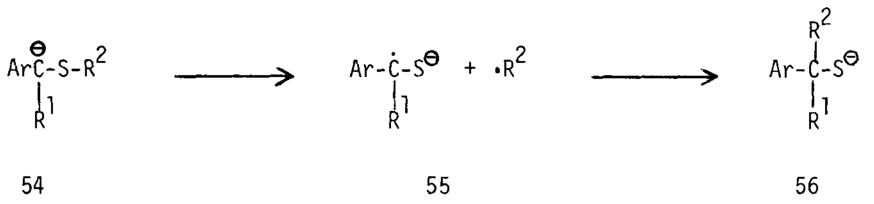


Scheme 8

It is noted that this process shows considerable similarity to the Wittig rearrangement,[26] which is believed[27,28] to proceed by similar routes. Evidence in favor of such an interpretation includes the observation that the migratory aptitudes parallel the order of radical stability, 3° > 2° > 1°. Furthermore when 5-hexenyl ether **52** was subjected to Wittig rearrangement, in addition to the normal product, a substantial quantity of **53** was isolated. This further supports the intermediacy of free radicals since the 5-hexenyl radical is known[29] to undergo ring closure to give cyclopentylmethyl. Another related system is depicted in Scheme 9 for the rearrangement of metalated benzyl alkyl sulfides.[28] The metalated sulfide (**54**) is thought to fragment to an alkyl radical and the radical

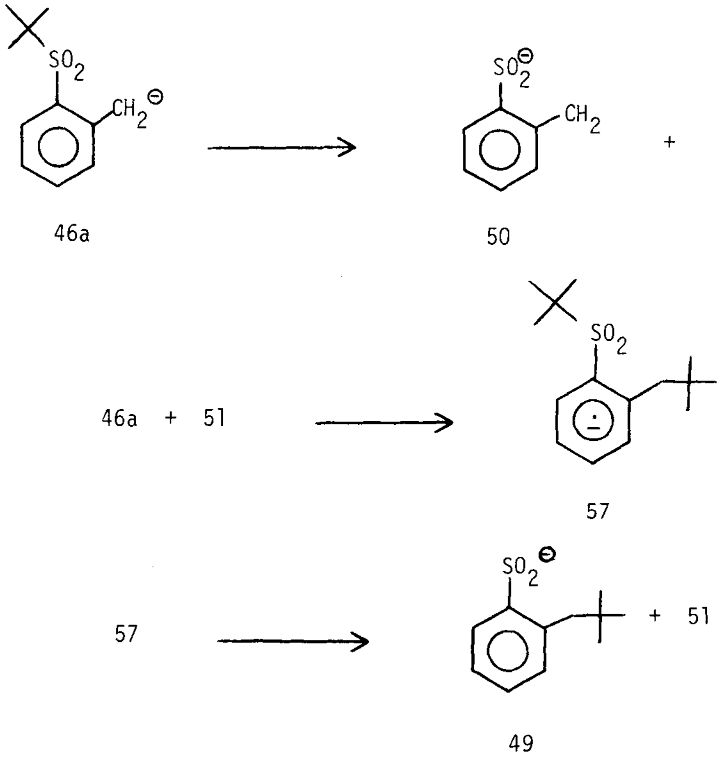


thiolate ion **55**. Subsequent recombination at the benzylic site of **55** leads to the production of **56**.



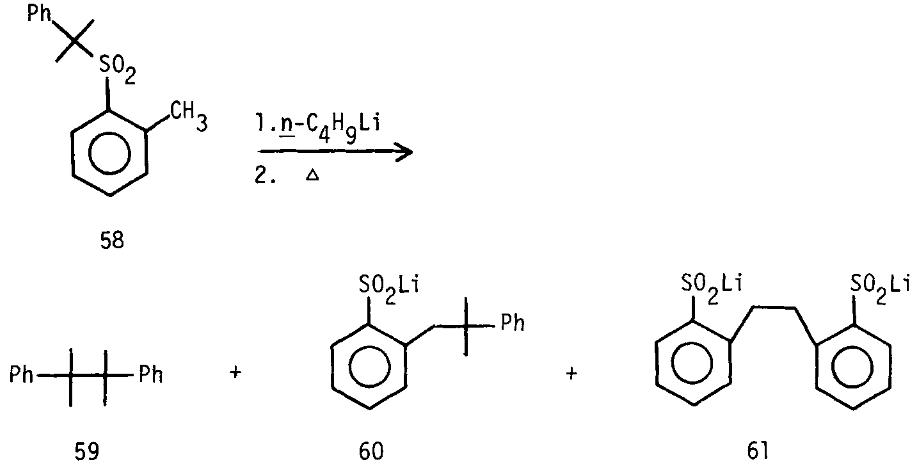
Scheme 9

Besides the simple fragmentation-recombination sequence given in Scheme 8, another route can be envisioned (Scheme 10) which involves a radical chain process. In this mechanism, generation of **51** is followed by this species attacking the benzylic position of a molecule of metalated sulfone **46a** to give rise to radical anion **57**, which fragments to give product **49** in addition to regenerating **51**. Similar radical chain processes have been shown[30,31] to operate in other systems including nucleophilic substitution at benzylic[30] as well as aryl[31] carbons.



Scheme 10

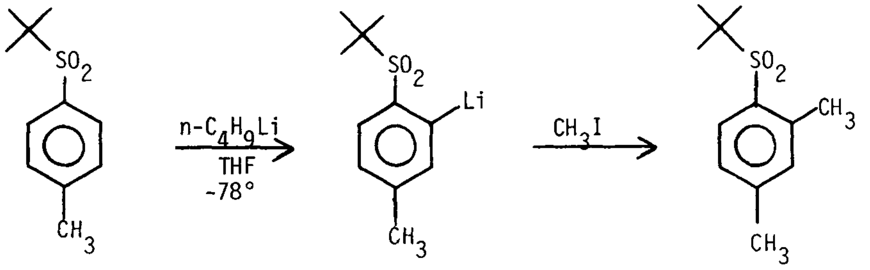
Although a definitive answer is not yet available, the data in general appear to support radical intermediates. For example, it was found[23] that *o*-tolyl cumyl sulfone (**58**) can be metalated by *n*-butyllithium and, upon refluxing a solution of the metalated sulfone for



Scheme 11

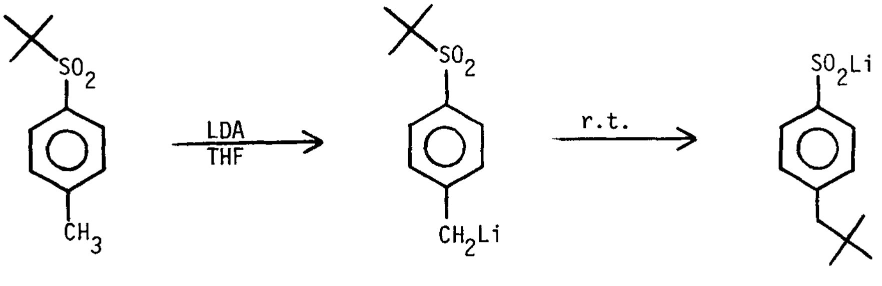
several hours, bicumyl (**59**) is obtained along with **60** and **61** (Scheme 11). Note that **60** and **61** are isolated as the corresponding hydrocarbons after desulfurization.

Further useful data became available when these studies were extended to *p*-tolyl *t*-butyl sulfone (**62**). An attempt[23] to metalate **62** with *n*-butyllithium in THF, resulted in metalation, not at the *para*-methyl group, but instead at an open *ortho*-position (**63**) as confirmed by quenching the reaction mixture with methyl iodide to obtain sulfone **64**.



62 63 64

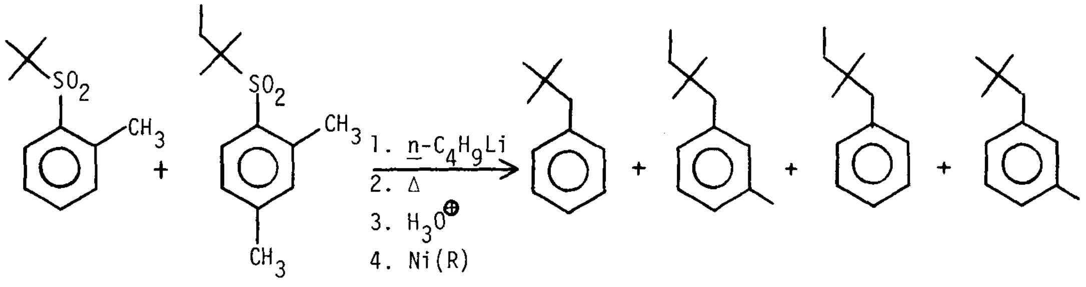
Based on earlier observations[32] that lithium diisopropylamide (LDA) metalates at the *p*-methyl group of tosylate esters, benzylic metalation of **62** was effected[22] with LDA in THF. The resulting metalated sulfone **62a** was found to rearrange (to **65**) even more



62 62a 65

readily[24] than metalated *o*-tolyl *t*-butyl sulfone **46a**. Rearrangement is over half complete in five minutes at room temperature and at least 85% complete in 30 minutes. This facile rearrangement is a strong argument against a concerted (cyclic) process which, while unlikely in the *o*-tolyl case, is impossible for the corresponding *p*-tolyl systems.

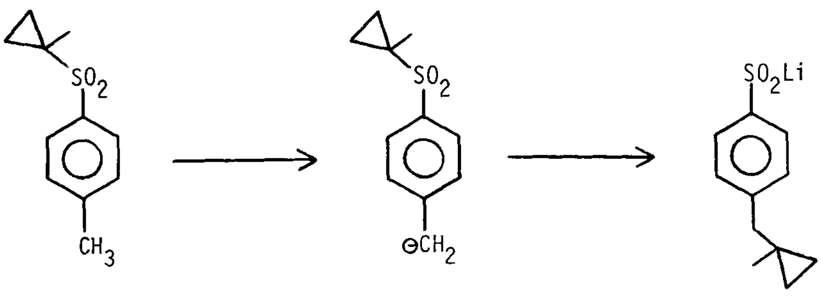
Other evidence consistent with the intermediacy of free radicals involves a crossover study undertaken[23] on **46** and 2,4-xylyl *t*-amyl sulfone (**66**). These sulfones (**46** and **66**) were mixed in equimolar amounts and subjected to the normal rearrangement conditions. The resulting mixture of sulfinic acids was not separated, but was desulfurized over Raney nickel and the resulting hydrocarbon mixture was separated by GLC. An approximately statistical mixture of four hydrocarbons (**67–70**) was found. Hydrocarbons **67** and **68** are, of course, the products expected of the normal rearrangement of **46** and **66**, respectively. However, **69** and **70** require an intermolecular transfer of alkyl groups between molecules.



46 66 67 68 69 70

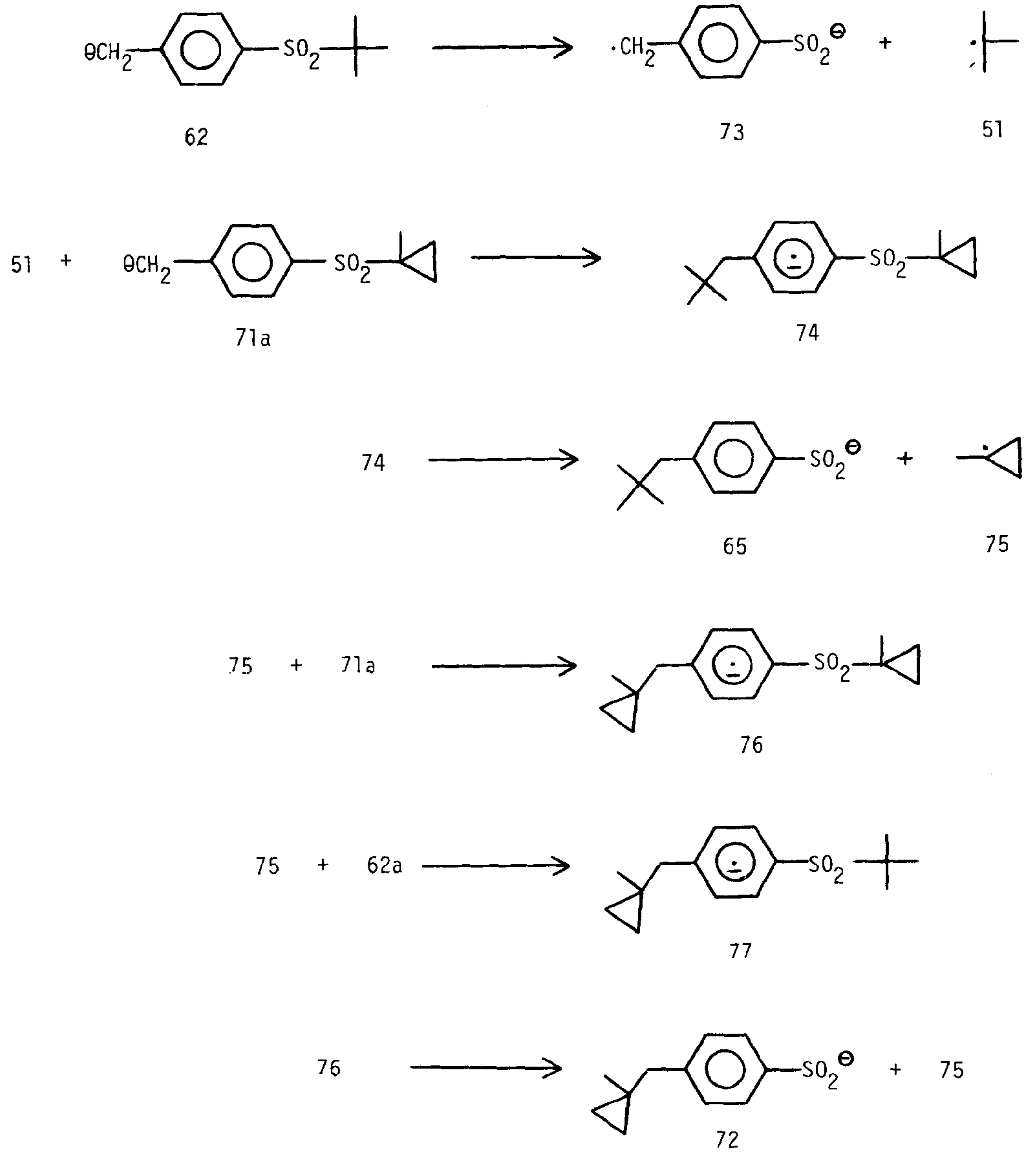
It therefore appears reasonable to invoke a mechanism involving radical intermediates in the rearrangement of aryl alkyl sulfones, although the details of the actual pathway are not yet clear. Attempts to distinguish between the fragmentation-recombination route (Scheme 8) and the radical chain process have not been conclusive, but some recent data exist to support a chain process (Scheme 10).

In the course of investigations on the rearrangement of *p*-tolyl *t*-alkyl sulfones, it was observed[24] that metalated 1-methylcyclo-propyl *p*-tolyl sulfone (**71a**) rearranged readily to **72** upon refluxing in THF, but failed to react at room temperature. Such a result is consistent with the reported difficulties[33,34] in the generation of cyclopropyl free radicals.



71 71a 72

The result that **71a** does not rearrange at room temperature provides a basis for an experiment to distinguish between the non-chain and chain processes (Schemes 8 and 10, respectively). If indeed a chain mechanism (Scheme 10) is operative, difficulty in generating the alkyl free radical would probably inhibit the reaction. If, however, an external source of free radicals were available, such as **62a**, some of these radicals should attack **71a** to give the corresponding radical anion (**74**), which could fragment to product **65** and 1-methyl-cyclopropyl radical (**75**) which is then available to carry on the chain

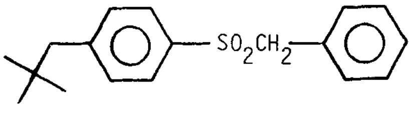


Scheme 12

(Scheme 12). Once **75** is available it could attack either **71a**, as shown in Scheme 12, to give **76**, or it could attack **62a**, which would yield radical anion **77**. Either radical anion **76** or **77** would be expected to fragment to the corresponding sulfinate (**72**) plus a new alkyl radical (**51** or **75**).

On the other hand, at room temperature a simple fragmentation-recombination route (Scheme 8) should fail to produce **72** regardless of the presence of **62a**. Thus a mixture of **62** and **71**, when metalated would be expected to yield only rearrangement product **65**; but, upon workup, **71** should be recovered unchanged.

When approximately equimolar quantities of **62** and **71** were metalated by LDA in THF at 0 °C and then stirred at room temperature for several hours, quenched with H_2O and the water-soluble portion of the product mixture alkylated with benzyl chloride,[24] NMR spectroscopy clearly showed the presence of the benzyl sulfone derivative of both products **78** and **79**. Furthermore, a substantial quantity of **62** in addition to **71** remained unchanged, which is not observed when **62** reacts alone. This observation that **62** apparently promotes the formation of **72** from **71a** can be interpreted in terms of a chain process similar to Scheme 10.



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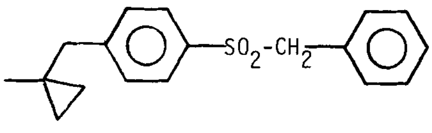
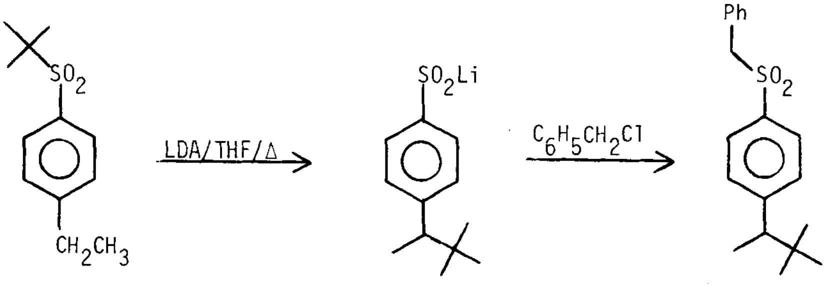


79

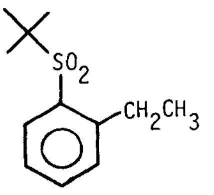
The mechanism for rearrangement of *o*-tolyl sulfones (*cf.* **46**) is less clear. A crossover experiment similar to that shown above was attempted[24] with **46** and **62**, but only **62** was seen to rearrange. This could be interpreted as indicating that metalated *o*-alkylphenyl *t*-alkyl sulfones rearrange by a non-chain process; but, the possible intervention of steric factors complicates the interpretation of this result.

Other experiments have also dealt with the metalation of *ortho*-and *para*-alkyl groupings other than methyl. For *p*-ethylphenyl *t*-butyl sulfone (**80**),[24] metalation by LDA in THF was sluggish, but did occur on heating to give **81** as the only observed product, isolated as the corresponding benzyl sulfone (**82**). Metalation of *o*-ethylphenyl



80 81 82

(**83**) and *o*-isopropylphenyl (**84**) *t*-butyl sulfones[23] with *n*-butyllithium resulted mainly in metalation at the open *ortho*-position followed by loss of *t*-butylsulfinate on heating to yield what were believed to be benzyne intermediates, which in the case of **84** could be trapped with 2,5-dimethylfuran to form **85** in low yield.



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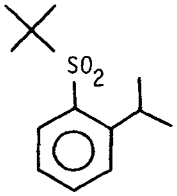

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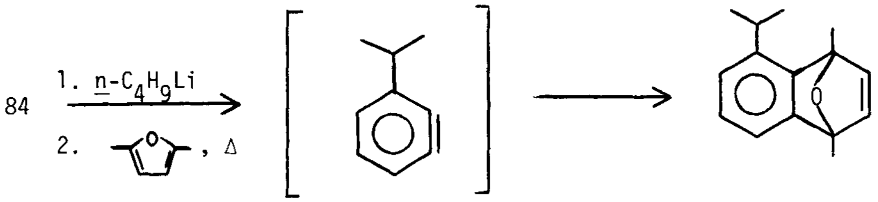
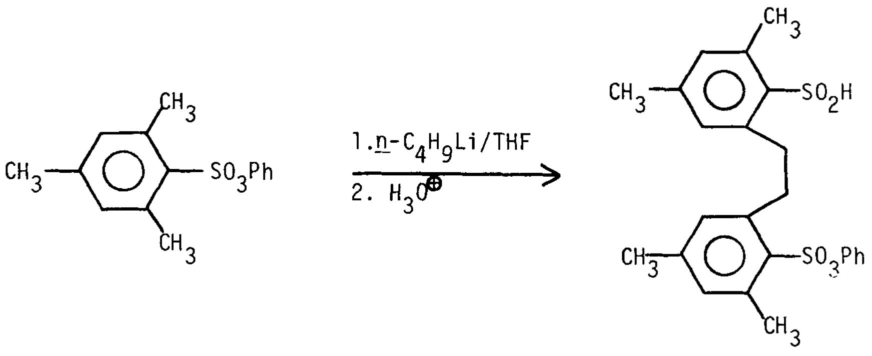


85

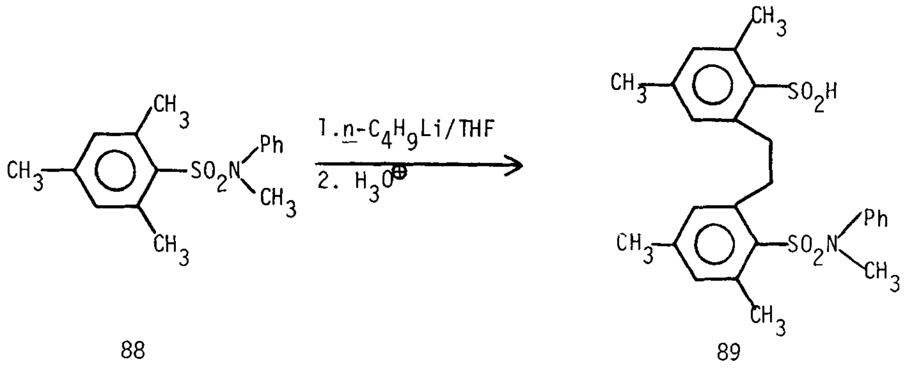
Although currently available results do not offer a full understanding of mechanism(s), the scope of the Truce-Smiles rearrangements has been greatly expanded. Not only can such rearrangements be utilized to form new C—C bonds between benzylic units and aryl groups, but, also between benzylic units and alkyl groupings (initially tertiary alkyl; however, recent work[24] has extended the migrating group to isopropyl and cyclohexyl).

ARYL ARENESULFONATES AND ARENESULFONANILIDES

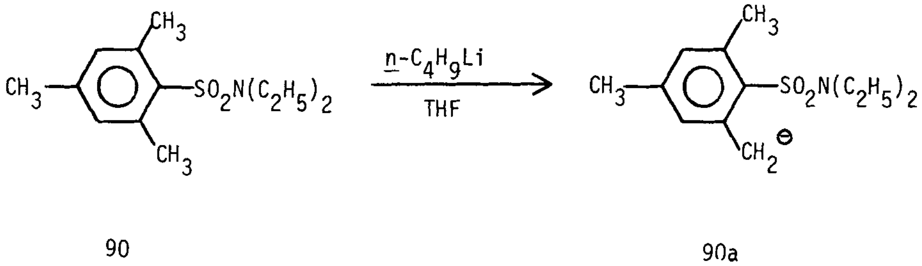
Another interesting[35,37] reaction displayed by metalated arenesulfonyl systems is a coupling condensation when the migrating aryl or alkyl unit of a sulfone is replaced by *N*-alkylanilino or phenoxy. For example, when sulfonate ester **86** was metalated at low temperature by *n*-butyllithium and allowed to stir for several hours followed by acidification, an unsymmetrical bibenzylic coupling product **87** resulted. Likewise sulfonamide **88** gave **89** as product.

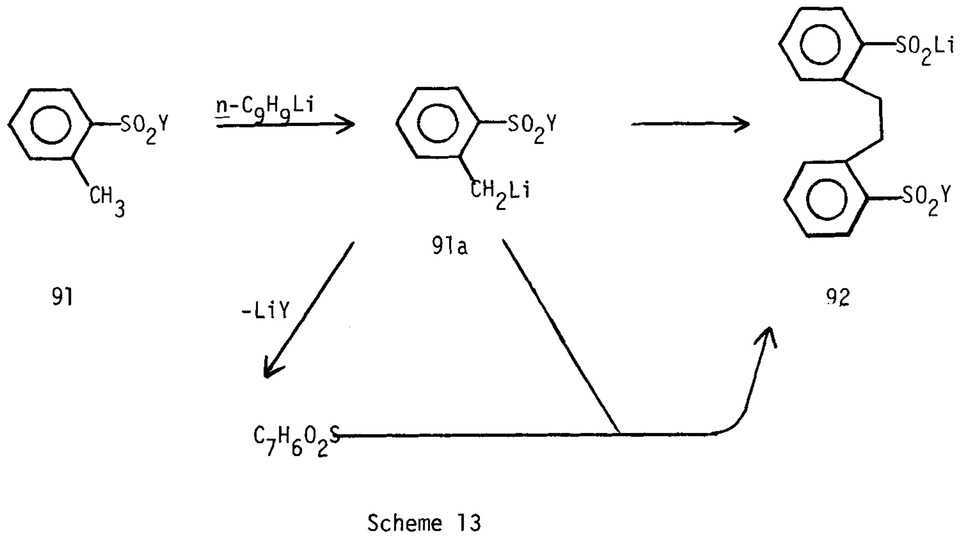


86 87



This coupling condensation was observed for several other similar compounds. The facility of this reaction is at least in part dependent on the nature of the "leaving group". For instance, while coupling condensation occurs readily for phenyl sulfonates and *N*-alkylsulfonanilides, *N*,*N*-dialkylarenesulfonamides failed to yield coupling condensation product. Thus although *N*,*N*-diethylmesitylene-sulfonamide **90** can be metalated at an *ortho*-methyl group, the resulting carbanionoid species **90a** is stable toward the normal reaction conditions (−72 °C to room temperature) and subsequent acidification yields only recovered starting material.

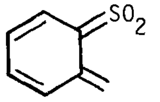




Scheme 13

Attempts to establish the mechanistic pathway of this reaction have been inconclusive. Several pathways were considered, including one where the initial product of metalation, **91a**, loses lithium anilide or lithium phenoxide (LiY, where Y = anilide or phenoxide) to form an intermediate $C_7H_6O_2S$, to which more of the metalated derivative might add to yield the final product **92** as shown in Scheme 13.

Assuming such an elimination-addition sequence to represent a viable mechanism, there were three reasonable prospects for the identity of $C_7H_6O_2S$, as depicted below:



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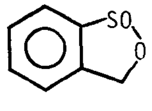

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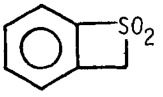
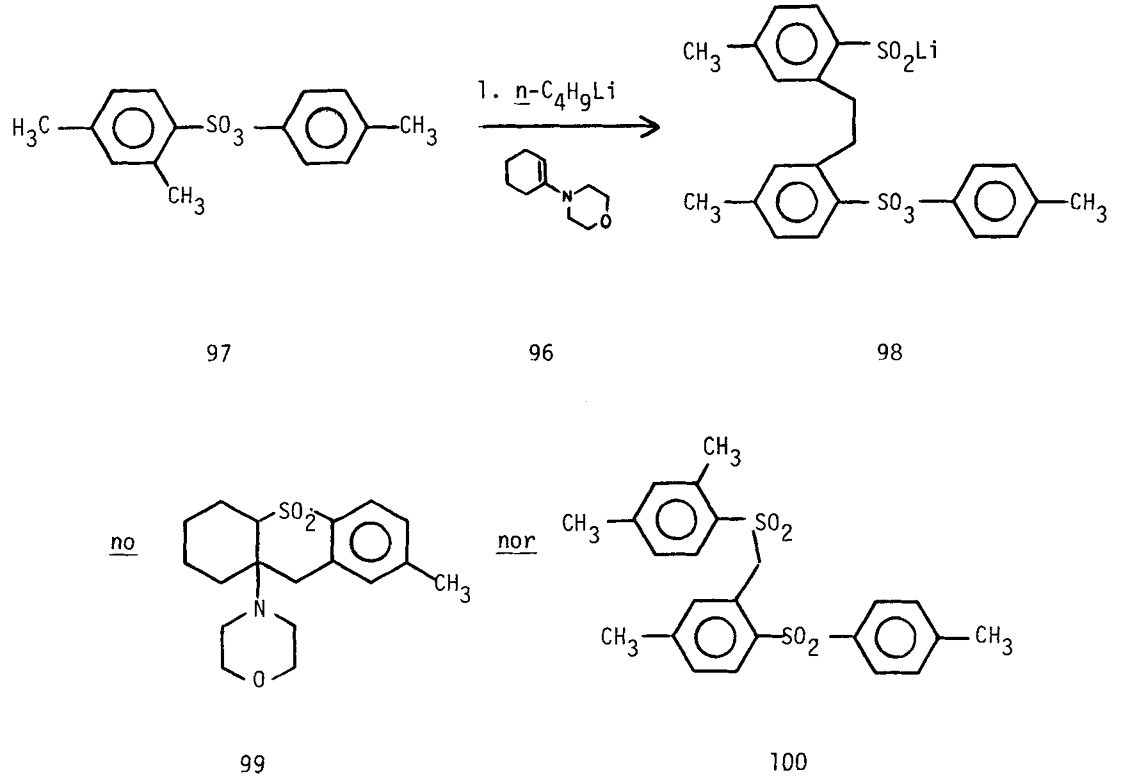


95

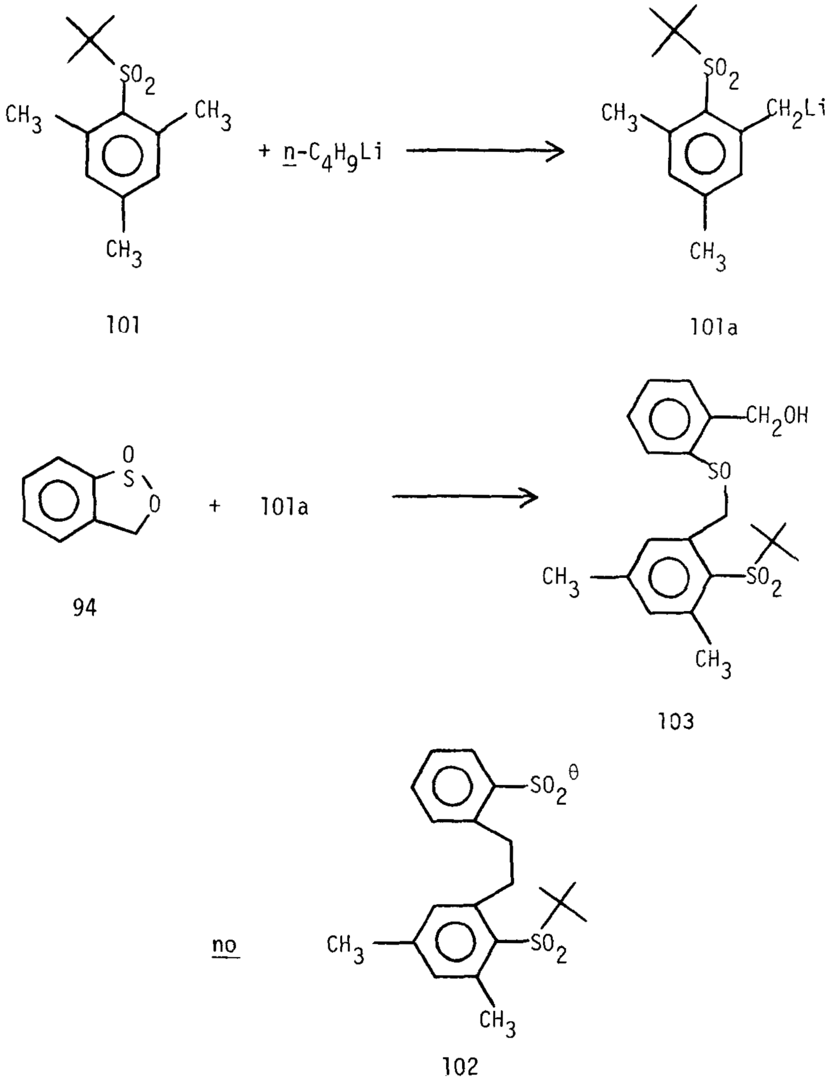
Structure **93** is a benzosulfene. Sulfene intermediates are known[36] and, while apparently enjoying only a fleeting existence, can be trapped by a variety of agents, notably enamines. In an attempt to ascertain whether a benzosulfene occurs as an intermediate in this coupling condensation, the enamine of morpholine and cyclohexanone (**96**) was added[35] to a solution of sulfonate **97** subsequent to metalation. The coupling condensation proceeded normally to give **98** and none of the sulfene adduct **99** was detected (Scheme 14). Furthermore (LDA) was an effective metalating agent for the



Scheme 14

coupling condensation reaction. In this case, a sulfene trap, diisopropylamine was generated in solution, but no *N*,*N*-diisopropylsulfonamides were detected. These results appear to rule out the intermediacy of **93**. Moreover the sulfur unit in sulfenes commonly exhibits electrophilic character.[36,38] It would therefore be reasonable to expect that were **93** actually formed, it would add a second molecule of metalated sulfonyl derivative **91a** at sulfur to give **100**. This mode of reaction has, however, not been observed.

A further possibility considered was the benzosultine **94**. Similar intermediates have been observed[39,40] in the reactions of sulfenes, presumably the result of electrocyclic ring closure. If **94** were an intermediate in the coupling-condensation, treatment with metalated sulfone **101a** would be expected to form bibenzylic product **102** (Scheme 15).

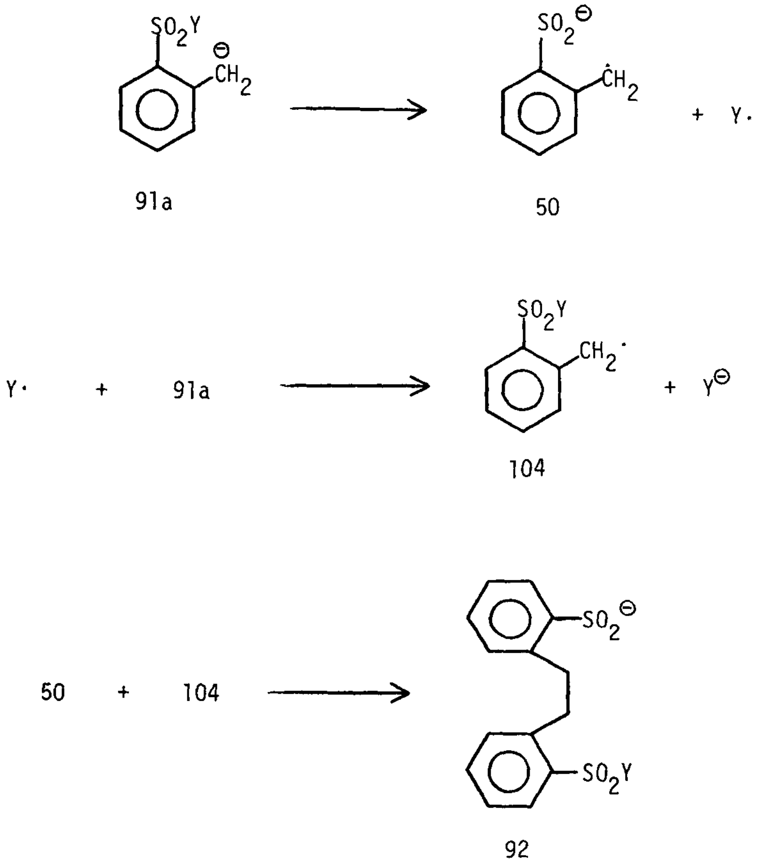


Scheme 15

However, this reaction proceeds[37] to give the product of attack at sulfur (**103**), consistent with the normal behavior of sulfinate esters towards organometallics wherein sulfoxides are formed.[41]

The third intermediate considered was benzothiete dioxide **95**.[39] This compound was prepared[37] and treated with **101a**. If **95** were a viable intermediate, its reaction with **101a** would be expected to give **102** as product. However, only transmetalation appeared to occur giving **101**; there was no evidence for the formation of **102**.

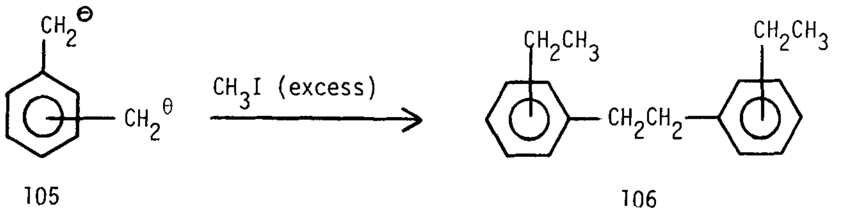
The above data do not support mechanisms that would involve as intermediates structures **93**–**95**. However, other plausible pathways can be envisioned, two of which involve radical intermediates and are analogous to the processes described (Schemes 8 and 10) for the Truce-Smiles rearrangement of aryl t-alkyl sulfones. One such pathway is illustrated in Scheme 16.



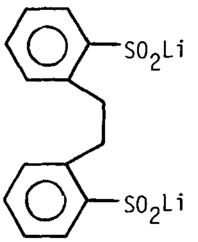
Scheme 16

This process is similar to the pathway described in Scheme 8. Initial reaction of **91a** is to form **50** and radical Y·. The latter species is then rapidly (perhaps even simultaneously with initial fragmentation) reduced to Y^- by a second molecule of **91a** leaving a benzylic radical species **104**. The intermediates, **50** and **104** thus generated combine to give **92**.

The pathway of Scheme 16 is similar to that suggested[42] for the coupling of xylyl dianions **105** in the presence of excess methyl iodide giving bibenzyls **106**, where reaction is believed to occur by initial electron transfer from **105** to methyl iodide to form a radical intermediate, followed by bibenzylic coupling and subsequent methylation.



A weakness of such a mechanism in the case of metalated sulfonyl systems is that symmetrical products such as **107** and **108** would be expected as part of the product



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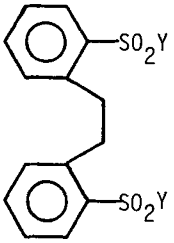


108

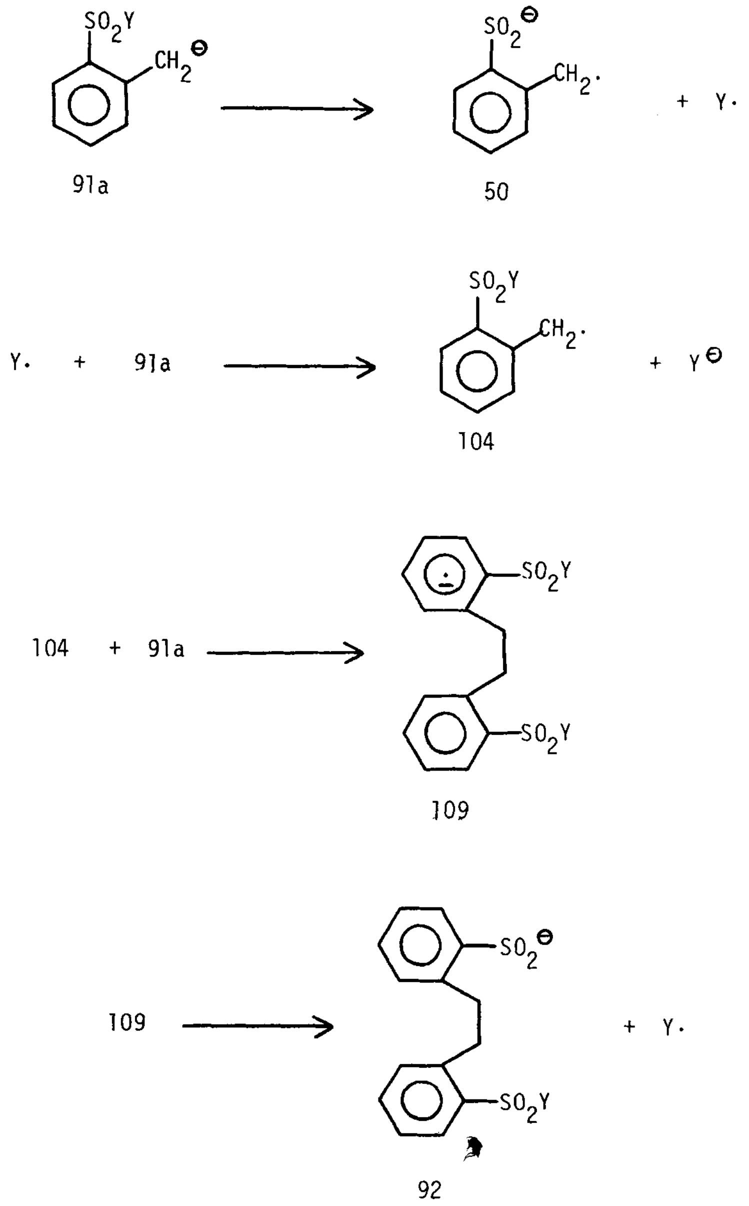
mixture. However, their absence may be rationalized by a radical chain mechanism (Scheme 17).

The process described in Scheme 17 is similar to the pathway described in Scheme 10. Once again, the initial step involves generation of a reactive radical intermediate plus a molecule of **50**. The radical (Y·) is then reduced as in Scheme 16 to give Y^- plus **104**. Addition of **104** to a second molecule of metalated sulfonyl derivative **91a** yields radical ion **109** which fragments to Y· plus a molecule of the observed bibenzylic coupling product **92**.

An analogous electron transfer-coupling sequence has been postulated for the reaction of *p*-nitrotoluene with strong bases, resulting in the formation of *p,p'*-dinitrobibenzyl.[43]

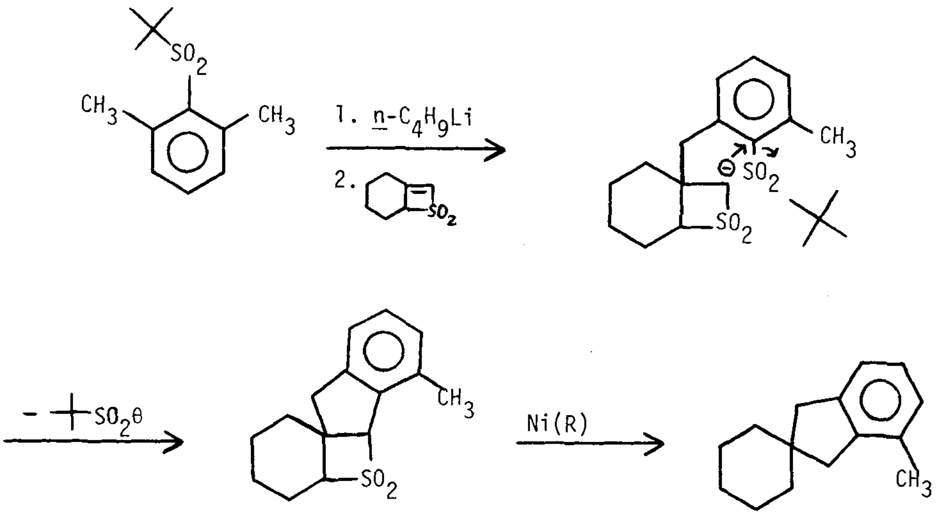
CONCLUSION

Metalated arenesulfonyl systems undergo interesting rearrangements and coupling condensations. Although further work is needed before the mechanistic aspects are clearly defined, the potential synthetic utility of Truce-Smiles rearrangements and related reactions is already apparent inasmuch as both the rearrangement itself as well as the related coupling condensations involve novel carbon-carbon bond-forming operations.



Scheme 17

One application[23,37] of related chemistry involves the novel synthesis of a 1′,3′-dihydrospiro[cyclohexane-1,2′-[2H]indene] (**110**) as depicted in Scheme 18. The basic carbon skeleton produced by this process is contained in a number of structures[44] which exhibit a range of biological properties. As shown, an interesting entry into this ring system is offered through utilization of some of the chemistry of metalated arenesulfonyl systems.



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Scheme 18

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