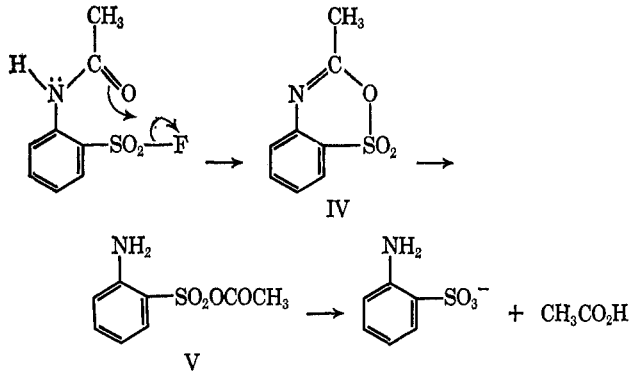
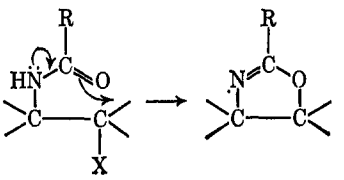
There is no nmr evidence for the existence of the intermediates IV and V, but both of them should be



very reactive under the hydrolysis conditions. This mechanism assumes that there is no intramolecular hydrogen bonding to the leaving fluoride ion which should be solvated by solvent water, and the hydrogen on the nitrogen atom is a far way from the fluoride atom in the transition state.

In this mechanism it is assumed that water molecules will solvate the departing fluoride ion and remove the amide proton. This mechanism is very similar to that proposed by Baker and his coworkers for the irreversible sulfonylation of a nucleophilic group of an enzyme by a sulfonyl fluoride.[7,8]

Amido groups provide powerful anchimeric assistance to ionization at saturated carbon,[29] and in this system the intermediate oxazoline can be isolated. In addition



intramolecular acylation of the conjugate base of an amide occurs very readily[30] by a reaction which is somewhat similar to that proposed here.

Acknowledgment.—We thank Professor B. R. Baker for helpful discussions and Mr. D. Hachey for technical assistance.

(29) S. Winstein and R. Boschan, *J. Amer. Chem. Soc.*, **72**, 4669 (1950).
(30) S. A. Bernhard, A. Berger, J. H. Carter, E. Katchalski, M. Sela, and Y. Shalitui, *ibid.*, **84**, 2421, (1962); J. A. Shafer and H. Morawetz, *J. Org. Chem.*, **28**, 1899 (1963); M. T. Behme and E. H. Cordes, *ibid.*, **29**, 1255 (1964).

Rearrangements of Sulfones to Sulfinic Acids *via* Carbanion Intermediates[1]

WILLIAM E. TRUCE AND WILLIAM W. BRAND

Department of Chemistry, Purdue University, Lafayette, Indiana 47907

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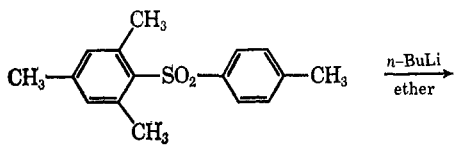
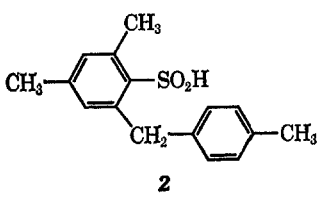
Mesityl 1-naphthyl sulfone was shown to rearrange to 2-(1′-naphthylmethyl)-4,6-dimethylbenzenesulfinic acid by treatment with *n*-butyllithium in ether, or to the 2′-naphthylmethyl isomer with potassium *t*-butoxide in dimethyl sulfoxide. In contrast, mesityl *p*-tolyl sulfone, mesityl *m*-tolyl sulfone, and mesityl *o*-tolyl sulfone were shown to rearrange to the corresponding 2-(4′-methylbenzyl)-, 2-(3′-methylbenzyl)-, and 2-(2′-methylbenzyl)-4,6-dimethylbenzenesulfinic acids, respectively, with either *n*-butyllithium in ether or potassium *t*-butoxide in dimethyl sulfoxide. Mesityl *m*-tolyl sulfone, on treatment with *n*-butyllithium in ether at 0° for a short time followed by quenching with CO_2 and subsequent decarboxylation, gave 1,5,7-trimethyl-4a,9a-dihydrothioxanthene 10,10-dioxide (**8**), the product of attack *ortho* rather than *para* to the tolyl methyl. Mesityl *o*-tolyl sulfone gave, in the same reaction, or by rapid quenching with water, 2,4,9a-trimethyl-4a,9a-dihydrothioxanthene 10,10-dioxide (**12**), resulting from ionization of the tolyl methyl. When **8** was treated with either base–solvent system, it rearranged to the same acid product as did its sulfone precursor. Sodium ethoxide in hot ethanol, however, caused **8** to rearrange to 2-(2′-methylbenzyl)-4,6-dimethylbenzenesulfinic acid. These results are discussed in terms of the proton-donating ability of the solvent, the aromatic character of the rings, and relative acid–base strengths.

Aryl sulfones containing an *o*-methyl group have been shown to rearrange to *o*-benzylbenzenesulfinic acids when treated with *n*-butyllithium in ether,[2] or with potassium *t*-butoxide in dimethyl sulfoxide (DMSO).[3] In the conversion of mesityl *p*-tolyl sulfone (**1**) to 2-(4′-methylbenzyl)-4,6-dimethylbenzenesulfinic acid (**2**),



1



2

the rearrangement was shown to proceed *via* displacement at the carbon bearing the sulfonyl group (*i.e.*, with retained orientation on the part of the migrating group).[3] The reaction was also shown to proceed with various substituents other than methyl in the migrating benzene ring.[4]

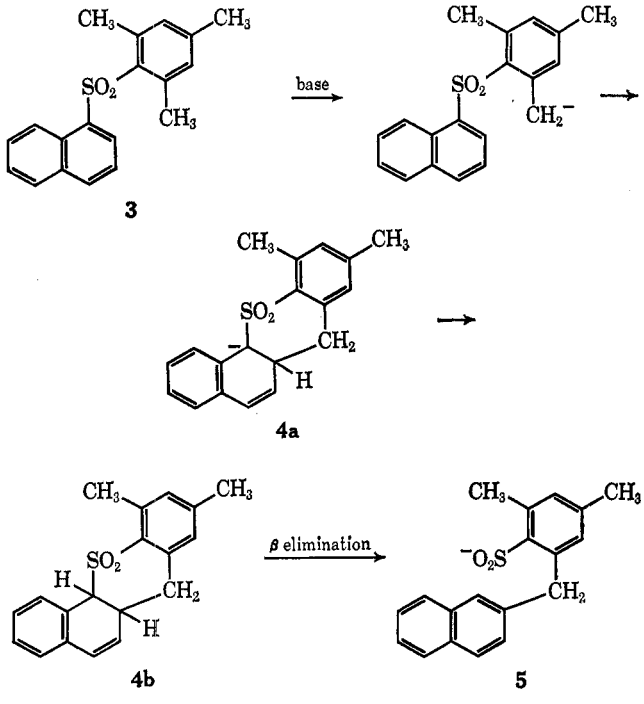
Drozd and coworkers have shown that, if mesityl *p*-tolyl sulfone is treated with *n*-butyllithium for a short time, followed by rapid quenching, a 4a,9a-dihydrothioxanthene 10,10-dioxide can be isolated from the reaction mixture.[5] Similar results were obtained with other diphenyl sulfones.[6,7] These products must result

(1) Paper VII in the series on rearrangements of aryl sulfones.
(2) W. E. Truce, W. J. Ray, Jr., O. L. Norman, and D. B. Eickemeyer, *J. Amer. Chem. Soc.*, **80**, 3625 (1958).
(3) W. E. Truce, C. R. Robbins, and E. M. Kreider, *ibid.*, **88**, 4027 (1966).
(4) W. E. Truce and M. M. Guy, *J. Org. Chem.*, **26**, 4331 (1961).
(5) V. N. Drozd and T. Yu. Frid, *Zh. Org. Khim.*, **3**, 373 (1967).
(6) V. N. Drozd, *Dokl. Akad. Nauk SSSR*, **169**, 107 (1966).
(7) V. N. Drozd, L. I. Zefirova, and U. A. Ustynyuk, *Zh. Org. Khim.*, **4**, 1794 (1968).

from intramolecular Michael addition of the initially formed benzylic carbanion to the 1,2 bond of the other benzene ring.

Results

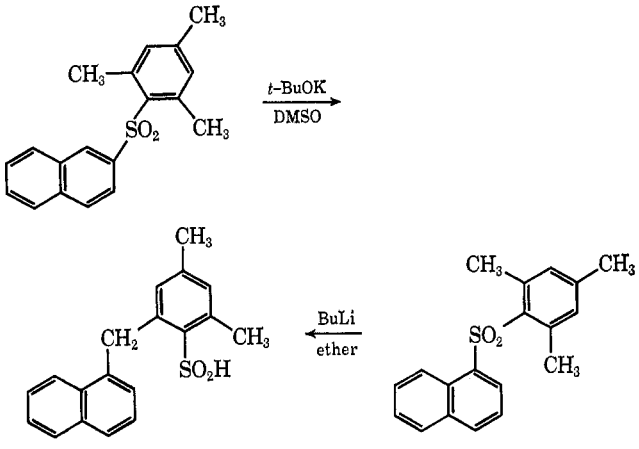
Mesityl Naphthyl Sulfones.—Previously it was shown[3] that treatment of mesityl naphthyl sulfones with potassium *t*-butoxide in DMSO resulted in rearrangement with a change in orientation on the part of the migrating naphthyl.[8] Mesityl 1-naphthyl sulfone (**3**) was rearranged under these conditions to 2-(2′-naphthylmethyl)-4,6-dimethylbenzenesulfinic acid (**5**). Similarly, mesityl 2-naphthyl sulfone rearranged to give the product with naphthyl substituted in the 1 position. The rearrangement was suggested to involve a Michael addition of the benzylic carbanion to the 1,2 bond of naphthalene, followed by a β elimination. Drozd and



3 **4a** **4b** **5**

coworkers,[9] and we,[10] independently, have been able to isolate the intermediate compound **4b** thus giving credence to this mechanism.

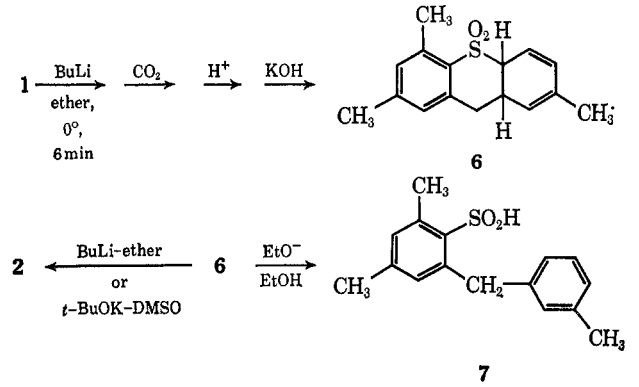
Mesityl 1-naphthyl sulfone, when treated with *n*-butyllithium in ether, gave a 42% yield of a sulfinic acid product, which was derivatized with 2-hydroxy-3,5-dichlorobenzyl chloride. This was found to be different from the derivative from the *t*-butoxide–DMSO-induced rearrangement product from mesityl 1-naphthyl sulfone, but identical (ir, melting point, and mixture melting point) with the derivative from the *t*-butoxide–DMSO-induced rearrangement product from mesityl 2-naphthyl sulfone. This product was previously shown[3] to be 2-(1′-naphthylmethyl)-4,6-dimethylbenzenesulfinic acid. Mesityl 1-naphthyl sulfone, therefore, will rearrange *via* direct displacement or addition–β elimination, depending on the base–solvent system used.



Mesityl 2-naphthyl sulfone rearranges with *n*-butyllithium in ether to the extent of only 5%. The product, sulfinic acid, was therefore not available in sufficient quantities for structure identification. Presumably this reaction also proceeds *via* direct displacement (to the extent that it occurs).

Mesityl *o*-, *m*-, and *p*-Tolyl Sulfones.—The three isomeric mesityl tolyl sulfones were prepared and rearranged under Truce–Smiles conditions to determine whether at least a small amount of a common product could be seen in the nmr of the crude sulfinic acid products arising from some addition–β elimination in the rearrangement of one or more of these sulfones with either base–solvent system. The product acids were found by nmr to be isomerically pure, however, and different from each other. Our earlier results[3] that mesityl *p*-tolyl sulfone gives the same product with either *n*-butyllithium in ether or potassium *t*-butoxide in DMSO were confirmed. It therefore appears that with the mesityl tolyl sulfones no addition–β elimination occurs under Truce–Smiles conditions.

Drozd[5,7] has isolated the cyclized product 2,5,7-trimethyl-4a,9a-dihydrothioxanthene 10,10-dioxide (**6**) from mesityl *p*-tolyl sulfone by treating the sulfone with *n*-butyllithium at 0° for a few minutes and by subsequent pouring onto CO_2, followed by decarboxylation with 10% KOH solution. This product could be caused to rearrange to **2** by treatment with *n*-butyllithium in ether or to 2-(3′-methylbenzyl)-4,6-dimethylbenzenesulfinic acid (**7**) by treatment with sodium ethoxide in ethanol. We have also found that treatment of **6** with potassium *t*-butoxide in DMSO leads to the same product, **2**, as treatment with *n*-butyllithium in ether.



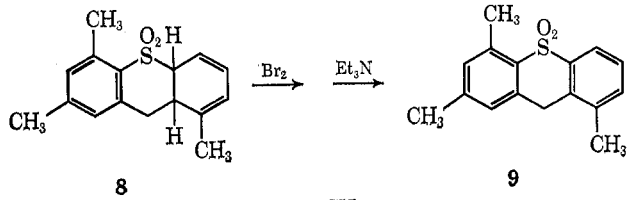
(8) Our earlier report[3] that the naphthalene compounds give the same rearrangement product with either potassium *t*-butoxide in DMSO, or with *n*-butyllithium in ether was in error. The structure proof in that paper was carried out only on the products from rearrangement with potassium *t*-butoxide in DMSO.

(9) V. N. Drozd and Kh. A. Pak, *Zh. Org. Khim.*, **3**, 2079 (1967).

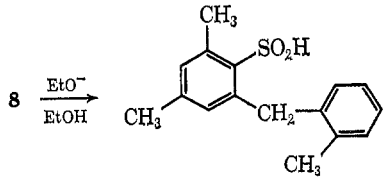
(10) E. M. Kreider, Ph.D. Thesis, Purdue University, Aug 1967.

Mesityl *m*-tolyl sulfone, when treated with *n*-butyllithium in ether, gave an 83% yield of an unstable sulfinic acid which was shown, through derivatization with 2-hydroxy-3,5-dichlorobenzyl chloride, to be identical with the acid **7**, produced from the ethoxide-induced rearrangement of **6**. In analogy to the *p*-tolyl system, mesityl *m*-tolyl sulfone was rearranged by potassium *t*-butoxide in DMSO in 82% yield to the same product, **7**, as with *n*-butyllithium in ether. The lithium salt of **7** could be isolated by filtering the butyllithium reaction mixture before hydrolysis with water. When this salt was desulfurized by treatment with aqueous $HgCl_2$ followed by removal of mercury with hot HCl in aqueous ethanol, and the resulting hydrocarbon was compared with authentic samples of 3,3′,5- and 3,4′,5-trimethyldiphenylmethanes prepared earlier by known methods,[3] the hydrocarbon was found to be identical with the 3,3′,5 isomer, but different from the 3,4′,5 isomer (ir, nmr, $n^{27}D$, and boiling point), thus indicating rearrangement with retained *meta* orientation.

The product 1,5,7-trimethyl-4a,9a-dihydrothioxanthene 10,10-dioxide (**8**) could be isolated by treatment of mesityl *m*-tolyl sulfone with *n*-butyllithium at 0° for a short time followed by carboxylation–decarboxylation. The product in which the benzyl carbanion added to the *ortho* rather than the *para* position relative to the tolyl methyl group was isolated exclusively. The structure of this product was confirmed by bromination and dehydrohalogenation to give a thioxanthene 10,10-dioxide, **9**, which was different from both the 2,4,6- and 2,4,7-trimethyl derivatives. The 2,4,6 isomer showed the hydrogen on the carbon adjacent to the carbon carrying the SO_2 (on C_5) to be a singlet in the nmr;[11] the 2,4,7 isomer showed the hydrogen on C_5 to be a doublet with J = 8.6 Hz;[11] **9**, however, had a triplet, J = 4.5 Hz, for the C_5 hydrogen. The structure of this compound was therefore assumed to be 1,5,7-trimethylthioxanthene 10,10-dioxide. This compound was also alternately synthesized from 2-(2′-methylbenzyl)-4,6-dimethylbenzenesulfinic acid *via* a chlorination and Friedel–Crafts reaction (see below). While this work was in progress, Drozd[7] independently reported the isolation of **8** and its aromatization to **9**.



8 **9**



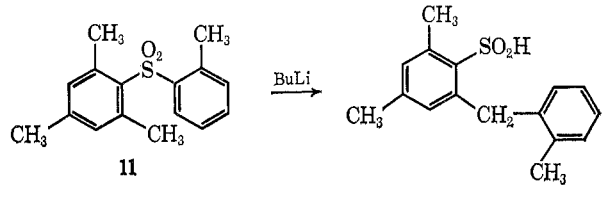
10

Further proof of the structure of the dihydro compound, **8**, was obtained when it was treated with an excess of sodium ethoxide in ethanol giving a 48% yield of a sulfinic acid. This acid was different from the *n*-butyllithium-induced rearrangement product from either *p*- or *m*-tolyl mesityl sulfone and was assumed, by analogy to the ethoxide-induced rearrangement of **6**, to be the isomeric 2-(2′-methylbenzyl)-4,6-dimethylbenzenesulfinic acid (**10**). However, treatment of **8** with either potassium *t*-butoxide in DMSO or *n*-butyllithium in ether caused rearrangement to the same product, **7**, as was obtained by treating mesityl *m*-tolyl sulfone under the same conditions.

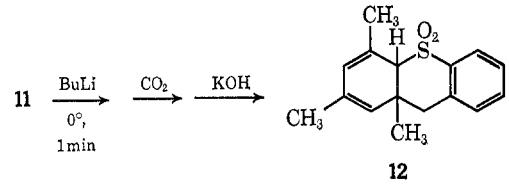
When either mesityl *p*-tolyl or mesityl *m*-tolyl sulfone was treated with an excess of sodium ethoxide in ethanol under the same conditions as were used with **6** and **8**, no acidic product resulted, and only starting sulfone could be recovered.

Treatment of mesityl *o*-tolyl sulfone (**11**) with *n*-butyllithium in ether gave a 71% yield of a fairly stable sulfinic acid. This acid was identical with **10** produced from the ethoxide-induced rearrangement of **8**. The same product, **10**, was obtained in 96% yield when **11** was treated with potassium *t*-butoxide in DMSO. The sulfinic acid **10** was treated with Cl_2 followed by cyclization with $AlCl_3$ to give a product which was identical with **9**, thus confirming its structure as 2-(2′-methylbenzyl)-4,6-dimethylbenzenesulfinic acid. Therefore, all three of the isomeric mesityl tolyl sulfones rearrange under the Truce–Smiles conditions with retention of orientation.

When a solution of mesityl *o*-tolyl sulfone was treated with *n*-butyllithium at 0° for a short time followed by either protonation or carboxylation–decarboxylation, 2,4,9a-trimethyl-4a,9a-dihydrothioxanthene 10,10-dioxide (**12**) was the product rather than the expected



11 **10**



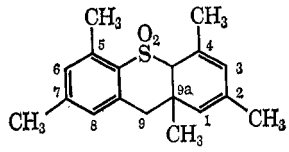
12

2,4,5- or 2,4,8a-trimethyl isomers. Only a 4% yield of **12** could be obtained from the carboxylation procedure along with 19% of the recovered starting material and 77% of the rearranged sulfinic acid, **10**. However, when the cold reaction mixture was poured directly into water, and the organic layer was dried and evaporated, 49.4% of a white solid was obtained which nmr indicated to be approximately 40% **12** and 60% starting material, thus giving a *ca.* 20% yield of **12**. None of the other two possible products was detected in the nmr.

The structure of the product was determined by analogy to the nmr of the cyclized product from dimesityl sulfone.[12] This compound has the methyl groups at C_5 and C_7 as typical aryl methyls (δ 2.29 and 2.63), the C_4 methyl at δ 2.10, the C_2 methyl at δ 1.63, and the C_{9a} methyl at δ 1.20. **12** has its methyl peaks

(11) V. N. Drozd and L. I. Zefirova, *Zh. Org. Khim.*, **4**, 165 (1968).

(12) V. N. Drozd and V. I. Scheichenko, *ibid.*, **3**, 554 (1967).



at δ 1.20, 1.55, and 2.10 in analogy to the methyls at C_{9a}, C_2, and C_4; no peaks appear in the δ 2.2–2.9 region which is the normal region for aromatic methyls. This eliminates the other two possible isomers, as well as strongly implicating the 2,4,9a-trimethyl isomer.

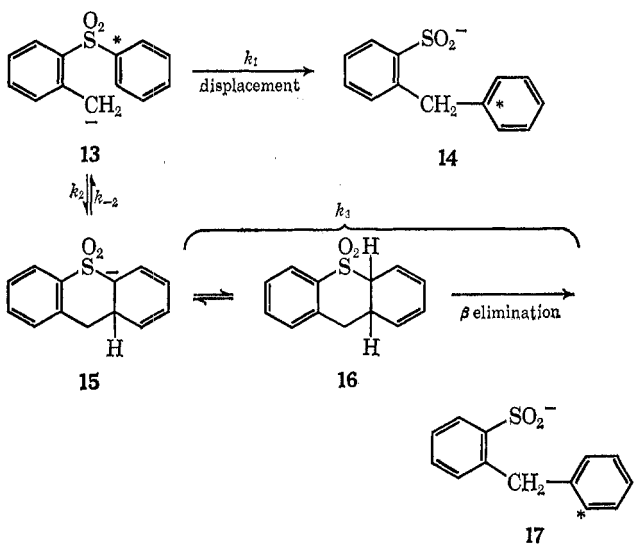
When mesityl *o*-tolyl sulfone was allowed to react with *n*-butyllithium in ether for 4.5 hr followed by pouring onto CO_2 and subsequent decarboxylation, no product precipitated, thus indicating that **12** is formed reversibly and can go on under the reaction conditions to give rearranged sulfinic acid **10**.

The fact that the only cyclization product which is isolable from the *o*-tolyl sulfone results from ionization of the tolyl methyl group, followed by addition across the α,β bond of the mesityl ring, rather than ionization of a mesityl methyl, followed by addition across the tolyl α,β bond, would seem to indicate that the cyclizations are, indeed, only side equilibria in these reactions and not intermediate steps as was suggested.[13] If these were actually intermediates, the *o*-, *m*-, and *p*-tolyl compounds which give analogous rearrangements would be expected to give analogous intermediates. Such is not the case.

Conclusions

Rearrangements of *o*-methylaryl sulfones to sulfinic acids *via* carbanion intermediates can occur by at least two mechanisms, as summarized in Scheme I, *i.e.*, (1) a direct displacement by the benzylic center on the sulfone-bearing carbon, and (2) a Michael addition–β-elimination sequence. Which pathway is followed is determined by the nature of the sulfone and the base–solvent system.

SCHEME I



In both systems, ionization (metalation) to a benzylic carbanion, **13**, is the first step. Apparently, in ether an equilibrium is set up with **15**. No proton source is available, however; so rearrangement to a sulfinic acid can only occur *via* the direct displacement reaction, regardless of the nature of the migrating ring. In DMSO, however, the solvent can act as a proton source, and the picture is more complex. Again, an equilibration between **13** and **15** is established. Which path operates, then, in DMSO is a function of the relative magnitudes of the rates k_1, and k_3, and the equilibrium constant $K = k_2/k_{-2}$. The rate constants k_1 and k_3 should not vary greatly from phenyl to naphthyl. K, however, will be greatly changed. In the equilibration between **13** and **15**, the aromaticity of phenyl or naphthyl is lost. The loss of resonance energy from one ring of the naphthyl system should be considerably less than the stabilization energy loss from a phenyl ring. This difference in energy required for the cyclization should cause the equilibrium constants, K, to differ by perhaps a factor of 10^3–10^6. This could easily be enough difference to cause a change from seeing exclusively one product (**14**) when phenyl migrates, to seeing exclusively the other product (**17**) when naphthyl migrates.

Treatment of the cyclized species **16** with various bases is simply a matter of acid and base strengths. With the very strong bases, *n*-butyllithium–ether or potassium *t*-butoxide–DMSO, the kinetically most acidic hydrogen, that α to the sulfonyl, is abstracted, leading once again to the equilibrating anions **15** and **13**, to which the above arguments apply. The weaker base, ethoxide in ethanol, is too weak to form a carbanion; therefore, a concerted β elimination is the only pathway available leading to product **17**.

Experimental Section[14]

General Procedure for the *n*-Butyllithium-Induced Rearrangement of Sulfones.—The rearrangements were carried out in a three-neck, round-bottom flask equipped with a mechanical stirrer, gas inlet, pressure-equalizing dropping funnel, and a drying tube. The apparatus was flame dried and cooled by passing nitrogen through. The sulfone was dissolved in ether[15] and stirred in a nitrogen atmosphere, and an equivalent amount of commercial *n*-butyllithium in pentane (Foote Mineral Co., *ca.* 1.3 *M*) was added dropwise. The initially deep-red reaction mixture was stirred at room temperature for 4–6 hr in a nitrogen atmosphere. It was then poured into water and the layers were separated. Starting material was recovered by drying and evaporating the ether layer. The aqueous layer was acidified to pH 1 with concentrated HCl and extracted with ether. The ether extracts were combined and extracted with 0.5 *N* aqueous NaOH. The resulting basic solution was acidified to pH 1 and extracted with ether. The ether was dried ($MgSO_4$) decolorized, and evaporated giving the sulfinic acid products.

General Procedure for the Potassium *t*-Butoxide–Dimethyl Sulfoxide Induced Rearrangement of Sulfones.—The same dry apparatus was used as for the *n*-butyllithium-induced rearrangements. The potassium *t*-butoxide was dissolved in DMSO (previously dried over CaH_2), and to this well-stirred solution was added dropwise a solution of the sulfone in DMSO. The reaction mixture was stirred at room temperature for 6–18 hr, poured into water, and worked up in the same way as the *n*-butyllithium reactions except that ether extracts were washed several times with water to remove DMSO.

General Procedure for the Preparation of 2-Hydroxy-3,5-dichlorobenzyl Derivatives of Sulfinic Acids.[3]—The sulfinic acid was dissolved in a minimum amount of methanol, and the solu-

(13) V. N. Drozd and L. A. Nikonova, *Zh. Org. Khim.*, **4**, 1060 (1968).

(14) Microanalyses were determined by Dr. C. S. Yeh. Melting points and boiling points are uncorrected. Nmr spectra were taken on a Varian A-60 spectrometer using TMS as an internal standard.

(15) Mallinckrodt anhydrous ether was used after further drying over sodium.

tion was neutralized to a phenolphthalein end point with 1 *N* methanolic NaOH. An equimolar amount of 2-hydroxy-3,5-dichlorobenzyl chloride[16] in a minimum of methanol was added to the sulfinate solution. After standing overnight the crystalline sulfone was filtered and recrystallized from ethanol or ethyl acetate.

Rearrangement of Mesityl 1-Naphthyl Sulfone with *n*-Butyllithium in Ether.—The sulfone (1.55 g, 0.005 mol), on treatment with a 10% excess of *n*-butyllithium in hexane, rearranged to a sulfinic acid in 44% yield (0.68 g, yellow semisolid). The 2-hydroxy-3,5-dichlorobenzyl derivative was prepared: mp 203–207° [lit.[3] mp 207–209° for 2-(1′-naphthylmethyl)-4,6-dimethylbenzenesulfinic acid, 175.5–177° for 2′-naphthylmethyl compound], mmp [with derivative from 2-(1′-naphthylmethyl)-4,6-dimethylbenzenesulfinic acid] 204–207°. The ir spectra of the 1′ and the 2′ derivatives were virtually identical except for the region 12–13 μ, in which the 1′-naphthyl compound showed peaks at 12.47, 12.57, and 12.72 μ, while the 2′-naphthyl compound showed peaks at 12.20 and 12.90 μ. The derivative prepared above had an ir identical with that of the 1′-naphthyl, but different from that of the 2′-naphthyl compound.

***m*-Toluenesulfonyl Chloride.**—The method of Zincke and Frohneberg was used.[17] *m*-Thiocresol (Aldrich, 59 g, 0.476 mol) was dissolved in 285 ml of glacial acetic acid, and chlorine was bubbled into the stirred solution for 4.5 hr. The solution initially darkened and then changed to a light yellow during the course of the reaction. After the reaction was complete, the solvent was evaporated at 50° under reduced pressure, and the residue was diluted with ether and washed with water. The ether solution was then washed with a $NaHCO_3$ solution until the wash was basic and then again with water and saturated NaCl. The resulting ether solution was dried over $MgSO_4$ and decolorized, and the ether was evaporated. The residue was vacuum distilled giving 83.78 g (92.5%) of a slightly yellow liquid: bp 88–90° (0.4 mm); ir (neat) 7.23 and 8.50 μ.

***o*-Toluenesulfonyl Chloride.**—The same procedure was used as that for the preparation of *m*-toluenesulfonyl chloride. When 116.55 g (0.94 mol) of *o*-thiocresol (Consol) in 500 ml of glacial acetic acid was used, and chlorine was passed into the solution for 4.5 hr, a 70% yield (124.7 g) of the sulfonyl chloride was obtained: bp 88–92° (1.5 mm); ir (neat) 7.25 and 8.42 μ.

Mesityl *m*-Tolyl Sulfone.—In a 1-l. three-neck flask were mixed 140.94 g (0.74 mol) of *m*-toluenesulfonyl chloride, 96 g (0.80 mol) of mesitylene, and 400 ml of carbon disulfide. To this well-stirred solution was slowly added 107 g (0.80 mol) of $AlCl_3$. The reaction was stirred at reflux for 20 hr. The solvent was then evaporated, the residue poured into 400 ml of ice-cold 3 *N* HCl, and the flask rinsed with HCl and ether. The aqueous acidic mixture was boiled for 1.5 hr to remove excess mesitylene and ether, cooled, and filtered, and the precipitate was washed with water. On recrystallization from 95% ethanol, 151.40 g (75%) of mesityl *m*-tolyl sulfone was obtained. After two more recrystallizations from ethanol an analytical sample was obtained: mp 101–103°; ir (Nujol mull) 7.60 and 8.68 μ; nmr ($CDCl_3$) δ 2.26 (s, 3 H), 2.35 (s, 3 H), 2.58 (s, 6 H), 6.93 (s, 2 H), and 7.2–7.7 (m, 4 H).

Anal. Calcd for $C_{16}H_{18}SO_2$: C, 70.04; H, 6.61; S, 11.69; mol wt, 274.4. Found: C, 70.23; H, 6.62; S, 11.70; mol wt, 274.6.

Mesityl *o*-Tolyl Sulfone.—The same procedure was used as that for the preparation of mesityl *m*-tolyl sulfone. When 124.7 g (0.654 mol) of *o*-toluenesulfonyl chloride and 80 g (0.667 mol) of mesitylene in 350 ml of CS_2 were treated with 93.2 g (0.70 mol) of $AlCl_3$, 131.88 g (73.6%) of mesityl *o*-tolyl sulfone was obtained after one recrystallization from ethanol. Decolorization with Darco followed by several more recrystallizations gave an analytical sample: mp 133–135°; ir (Nujol mull) 7.65 and 8.65 μ; nmr ($CDCl_3$) δ 2.27 and 2.30 (two unresolved singlets, 6 H), 2.47 (s, 6 H), 6.92 (s, 2 H), and 7.0–8.1 (m, 4 H).

Anal. Calcd for $C_{16}H_{18}SO_2$: C, 70.04; H, 6.61; S, 11.69; mol wt, 274.4. Found: C, 70.25; H, 6.52; S, 11.53; mol wt, 280.5.

Rearrangement of Mesityl *p*-Tolyl Sulfone with Potassium *t*-Butoxide in DMSO.—Mesityl *p*-tolyl sulfone (2.82, g 0.01 mol) in 60 ml of DMSO was treated with 1.5 g (0.014 mol) of potassium *t*-butoxide in 75 ml of DMSO for 6.5 hr. Pouring of the deep green reaction mixture into ice–water followed by work-up gave 0.91 g (32%) of recovered mesityl *p*-tolyl sulfone plus 1.53 g (54.3%) of sulfinic acid product as a white solid. The 2-hydroxy-3,5-dichlorobenzyl derivative was prepared and shown by ir, melting point, and mixture melting point to be identical with that obtained from the *n*-butyllithium-induced rearrangement of mesityl *p*-tolyl sulfone.

Treatment of 6 with Potassium *t*-Butoxide in DMSO.—The cyclized product **6** (1.41 g, 0.005 mol), prepared by the method of Drozd,[5] was rearranged by the same procedure as that used for the rearrangement of mesityl *p*-tolyl sulfone. Treatment with 0.75 g (0.007 mol) of potassium *t*-butoxide in 75 ml of DMSO for 7.5 hr gave 0.90 g (63.8%) of crude acidic product as an off-white solid. The 2-hydroxy-3,5-dichlorobenzyl derivative had mp 140–141.5° (EtOH). Mixture melting point with the derivative from authentic 2-(4′-methylbenzyl)-4,6-dimethylbenzenesulfinic acid showed no depression.

Rearrangement of Mesityl *m*-Tolyl Sulfone with *n*-Butyllithium.[7]—When the *meta* sulfone (2.08 g, 0.0076 mol) in 40 ml of ether was treated with 5.9 ml (0.0076 mol) of *n*-butyllithium in pentane diluted with 7.7 ml of ether, the initially deep red solution changed to a bright orange within *ca.* 2 min and slowly faded. After 4 hr at room temperature the turbid reaction mixture was almost colorless. On pouring into water and working up, the reaction gave 1.72 g (83.7%) of the unstable sulfinic acid **7**: ir (neat) 3.1–3.7, 3.9 (broad), 9.2 (broad), and 9.5 μ; nmr ($CDCl_3$, impure compound with very poor integration) δ 2.17 and 2.20 (two unresolved singlets), 2.63 (s), 4.26 (s), 6.6–7.2 (m), and 7.87 (broad singlet).

The 2-hydroxy-3,5-dichlorobenzyl derivative was prepared in 72.6% yield: mp 198.5–200.5° (EtOH); ir (Nujol mull) 2.97, 7.60, 7.75, 8.50, and 8.70 μ; nmr ($CDCl_3$) δ 2.25 (s, 6 H), 2.56 (s, 3 H), 3.6 (very broad peak, *ca.* 1 H), 4.27 (s, 2 H), 4.45 (s, 2 H), 6.8–7.2 (m, 7 H), and 7.44 (d, J = 2 cps, 1 H).

Anal. Calcd for $C_{23}H_{22}Cl_2SO_3$: C, 61.45; H, 4.94; Cl, 15.38; S, 7.12; mol wt, 449. Found: C, 61.25; H, 4.92; Cl, 15.66; S, 7.35; mol wt, 447.

Desulfination of the Sulfinic Acid, 7.—The lithium salt (3.68 g, 0.0131 mol) of the sulfinic acid was dissolved in 40 ml of boiling water, and 3.6 g (0.0132 mol) of $HgCl_2$ in 12 ml of hot water was added. The cloudy mixture was stirred and boiled for 20 min after which it was cooled, and the water was decanted off. The residue was washed with water and then stirred with 20 ml of ethanol and 20 ml of concentrated HCl with boiling for 1.5 hr. After cooling, acetone was added to the reaction mixture to precipitate inorganic products which were filtered off. The filtrate was evaporated on a hot plate giving a dark oil and tar which was distilled giving *ca.* 1 ml of clear liquid, bp 113–118° (0.5 mm), $n^{27}D$ 1.5614 [lit.[3] bp 114–120° (0.17 mm), $n^{27}D$ 1.5689]. The ir matched perfectly an authentic sample of 3,3′,5-trimethyldiphenylmethane, but was different from the ir of 3,4′,5-trimethyldiphenylmethane.[3] The nmr was identical with the published spectrum:[3] nmr ($CDCl_3$) δ 2.27 and 2.31 (two unresolved singlets, 6 H), 3.87 (s, 2 H), 6.84 (s, 3 H), and 7.0–7.2 (m, 4 H).

Rearrangement of Mesityl *m*-Tolyl Sulfone with Potassium *t*-Butoxide in DMSO.—Mesityl *m*-tolyl sulfone (2.82 g, 0.01 mol) in 60 ml of DMSO was treated with 1.5 g (0.014 mol) of potassium *t*-butoxide in 75 ml of DMSO for 6 hr. Work-up gave 0.34 g (12.1%) of recovered mesityl *m*-tolyl sulfone plus 2.31 g (82%) of acidic product as a clear tar. The 2-hydroxy-3,5-dichlorobenzyl derivative was prepared in 62% yield: mp 200–202.5°; mmp (with derivative from *n*-butyllithium-induced rearrangement of mesityl *m*-tolyl sulfone) 201–203°; ir identical with *n*-butyllithium product.

1,5,7-Trimethyl-4a,9a-dihydrothioxanthene 10,10-Dioxide (8).[7]—Mesityl *m*-tolyl sulfone (2.7 g, 0.01 mol) was dissolved in 60 ml of ether, and 7.7 ml (0.01 mol) of *n*-butyllithium in pentane was added as rapidly as possible. After 1 min the deep-red reaction mixture was carefully poured onto crushed CO_2, and the pasty mixture was allowed to warm to room temperature. H_2SO_4 (10%) was then added and the two clear layers were separated. The organic layer was extracted with 10% KOH and the resulting basic solution was allowed to stand 16 hr while the product precipitated. The product was then filtered off and washed with water giving 0.75 g (27.8%) of **8** as a white solid: mp 176–180° (MeOH) (lit.[7] mp 179.5–180.5°); ir (Nujol mull) 6.03, 6.22, 6.35, 7.73, 8.68, and 8.80 μ; nmr ($CDCl_3$) δ 1.83 (s with fine splitting, 3 H), 2.25 (s, 3 H), 2.65 (s, 3 H), 2.9–4.2 (very broad multiplet, 4 H), 5.7–6.2 (m, 3 H), and 6.92 (s, 2 H).

(16) C. A. Buehler, *et al.*, *J. Org. Chem.*, **6**, 902 (1941).
(17) T. Zincke and W. Frohneberg, *Ber.*, **43**, 840 (1910).

1,5,7-Trimethylthioxanthene 10,10-Dioxide (9) from 8.[7]—**8** (1.37 g, 0.005 mol) was dissolved in 20 ml of $CHCl_3$, and 0.76 g (0.00475 mol) of bromine in 20 ml of $CHCl_3$ was added. The reaction mixture was stirred for 30 min after which the solvent was evaporated. The residue was heated at reflux with 20 ml of triethylamine for 6.25 hr. After evaporation of the solvent, the residue was stirred with benzene, filtered, and washed with benzene. The filtrate was dried ($MgSO_4$) and evaporated giving 1.2 g (88.3%) of a yellow solid which, after recrystallization from methanol, cyclohexane, and methanol again, gave a white solid: mp 167.5–169.5° (lit.[7] mp 167–167.5°); nmr ($CDCl_3$) δ 2.27 (s, 3 H), 2.35 (s, 3 H), 2.74 (s, 3 H), 4.07 (s, 2 H), 6.9–7.4 (m, 4 H), and 7.90 (t, J = 4.5 cps, 1 H).

Reaction of 8 with Potassium *t*-Butoxide in DMSO.—The same procedure was used as for the rearrangement of the mesityl tolyl sulfones. A 5.5-hr reaction time gave 9% of recovered starting material plus 75% of sulfinic acid product as an oil. The 2-hydroxy-3,5-dichlorobenzyl derivative had mp 197–201.5°; mmp [with derivative from authentic 2-(3′-methylbenzyl)-4,6-dimethylbenzenesulfinic acid] 198–202°; ir of derivatives identical.

Reaction of 8 with *n*-Butyllithium in Ether.—The same procedure was used as for the rearrangment of the mesityl tolyl sulfones. When 0.005 mol of **8** was treated with 0.005 mol of *n*-butyllithium in 40 ml of ether, a quantitative yield of crude acid was obtained. The 2-hydroxy-3,5-dichlorobenzyl derivative had mp 198–201°, mmp 198–201°.

Preparation of 10 from 8 with Sodium Ethoxide in Ethanol.—Soldium ethoxide was prepared by dissolving 2 g (0.087 g-atom) of Na in 40 ml of EtOH. This solution was slowly added to a suspension of 1.58 g (0.0029 mol) of the sulfone **8** in 20 ml of EtOH in a nitrogen atmosphere. The reaction mixture became homogeneous on heating to reflux, and stirring was continued at reflux for 20 hr. The reaction mixture was then poured into 100 ml of water and worked up in the same way as in the *n*-butyllithium-induced rearrangements giving 0.76 g (48%) of an acidic product. The nmr of the sulfinic acid was different from that obtained by butyllithium-induced rearrangement of mesityl *p*-tolyl or *m*-tolyl sulfone: nmr ($CDCl_3$) δ 2.19 (s with very fine splitting, 6 H), 2.63 (s, 3 H), 4.34 (s, 2 H), 6.8–7.3 (m, 6 H), and 8.87 (s, 1 H).

The 2-hydroxy-3,5-dichlorobenzyl derivative was prepared in 37% yield and had mp 168–172°, which was also greatly different from the two isomeric sulfinic acid derivatives. It was therefore assumed, in analogy to the reaction of **6** with sodium ethoxide, that the sulfinic acid had the structure of 2-(2′-methylbenzyl)-4,6-dimethylbenzenesulfinic acid: derivative ir (Nujol mull) 2.89, 7.6, 7.75, and 8.7μ; nmr ($CDCl_3$) δ 2.24 (s, 6 H), 2.60 (s, 3 H), 4.17 (s, 2 H), 4.32 (s, 2 H), 5.86 (broad s, 1 H), and 6.7–7.3 (m, 8 H).

Rearrangement of Mesityl *o*-Tolyl Sulfone with *n*-Butyllithium.—When 2.7 g (0.01 mol) of mesityl *o*-tolyl sulfone in 90 ml of ether was treated with 7.7 ml of butyllithium in pentane (0.01 mol) diluted with 10 ml of ether, the initially deep-red reaction mixture slowly lightened to an orange. After 5.5 hr at room temperature followed by pouring into water and working up, 1.92 g (71%) of acidic product, **10**, was obtained as a white solid, which darkened only slightly on standing 6 weeks: mp 86–87° dec. The nmr and ir were identical with the spectra of the product produced from the ethoxide induced rearrangement of **8**.

The 2-hydroxy-3,5-dichlorobenzyl derivative was prepared in 66% yield: mp 169.5–171.5°; ir and nmr spectra identical with those from the derivative prepared from the ethoxide product. Mixture melting point showed no depression.

Anal. Calcd for $C_{23}H_{22}Cl_2SO_3$: C, 61.45; H, 4.94; Cl, 15.38; S, 7.12; mol wt, 449. Found: C, 61.38; H, 4.91; Cl, 15.65; S, 7.08; mol wt, 457.

Rearrangement of Mesityl *o*-Tolyl Sulfone with Potassium *t*-Butoxide in DMSO.—When 2.5 g (0.0089 mol) of mesityl *o*-tolyl sulfone in 60 ml of DMSO was treated with 1.5 g (0.014 mol) of *t*-BuOK in 75 ml of DMSO for 6 hr followed by work-up, 2.39 g (96%) of sulfinic acid product was obtained as a white solid. The 2-hydroxy-3,5-dichlorobenzyl derivative was prepared in 50% yield: mp 170–172°; mmp [with derivative from authentic 2-(2′-methylbenzyl)-4,6-dimethylbenzenesulfinic acid] 169–172°.

1,5,7-Trimethylthioxanthene 10,10-Dioxide (9) from 10.—**10** (41.33 g, 0.151 mol) was dissolved in 30% NaOH and neutralized with concentrated HCl until just basic to phenolphthalein (*ca.* 150-ml total volume). Cl_2 was then bubbled into the stirred solution for 4 hr, after which the turbid reaction mixture was extracted with benzene and ether, and the organic extract was dried, decolorized, and evaporated giving 38.04 g of a yellow tar. This tar was dissolved in 200 ml of CH_2Cl_2, and 20.10 g (0.151 mol) of $AlCl_3$ suspended in 250 ml of CH_2Cl_2 was slowly added. The reaction mixture was stirred for 16 hr at room temperature. It was then poured into an ice–concentrated HCl mixture, and the organic layer was separated and washed with 6 *N* HCl, water, and saturated NaCl, dried over $MgSO_4$, and evaporated giving 21.33 g of a thick red tar. The red tar was stirred with ethanol at room temperature, filtered, and washed with ethanol giving 1.14 g (2.76%) of a brown solid. Concentration of the filtrate followed by cooling in an ice bath led to several more crops of off-white crystals giving a total of 4.93 g (12%) of the product which was identical with the product from bromination–dehydrohalogenation of **8**.

Preparation of 2,4,9a-Trimethyl-4a,9a-dihydrothioxanthene 10,10-Dioxide (12). A. Protonation Work-Up.—Mesityl *o*-tolyl sulfone (6.8 g, 0.025 mol) in 250 of ether was cooled in an ice bath. To this well-stirred solution was rapidly added 19.1 ml (0.025 mol) of *n*-butyllithium in pentane, and the cold solution was stirred for 2.5 min. It was then rapidly poured into 200 ml of water and the layers were separated. The aqueous layer on work-up gave 2.43 g (35.8%) of sulfinic acid product, **10**. The organic layer was washed with saturated NaCl, dried over $MgSO_4$, and evaporated, giving 3.36 g (49.4%) of white solid which consisted of starting sulfone and product. Recrystallization from methanol gave very little separation. An nmr of the product mixture showed an approximate composition of 40% **12** to 60% starting sulfone, thus giving an actual yield of **12** of *ca.* 20%.

B. Carboxylation–Decarboxylation Work-Up.—A nonhomogenous mixture of 54 g (0.2 mol) of mesityl *o*-tolyl sulfone and 1900 ml of ether was rapidly stirred in an ice bath. To this was added as rapidly as possible 155 ml (1 equiv) of *n*-butyllithium in pentane. As soon as addition was complete, the deep-red reaction mixture was carefully poured onto 1 lb. of crushed CO_2. The slurry was stirred and allowed to warm to room temperature, after which 900 ml of 10% H_2SO_4 was added with stirring, and the layers were separated. The organic layer was then washed with water and extracted with a total of 1 l. of 10% KOH. Upon drying and evaporating the organic solution, 10.42 g (19.3%) of starting sulfone was recovered. The basic extract was left standing 6 days during which time the product precipitated giving, on filtration and washing with water, 2.18 g (4.04%) of a white crystalline solid: mp 157–158° (EtOH); ir (Nujol mull) 5.92, 7.72, and 8.95 μ; nmr ($CDCl_3$) δ 1.23 (s, 3 H), 1.55 (s, 3 H), 2.10 (s, 3 H), 2.90 and 3.27 (two incompletely resolved, distorted doublets, J = 14.5 cps, 2 H), 3.62 (s, 1 H), 4.84 (broad singlet, 1 H), 5.82 (broad singlet, 1 H), 7.1–7.6 (m, 3 H), and 7.7–8.0 (m, 1 H).

Anal. Calcd for $C_{16}H_{18}SO_2$: C, 70.04; H, 6.61; S, 11.69; mol wt, 274.4. Found: C, 70.19; H, 6.90; S, 11.83; mol wt, 271.6.

The basic filtrate was acidified with concentrated HCl and extracted with ether, the ether extracted with 0.5 *N* NaOH, and the resulting aqueous solution acidified and extracted with ether. The ether solution was dried, decolorized, and evaporated giving 41.33 g (76.6%) of impure sulfinic acid **10**.

Registry No.—*m*-Toluenesulfonyl chloride, 1899-93-0; *o*-toluenesulfonyl chloride, 133-59-5; mesityl *m*-tolyl sulfone, 21128-93-8; mesityl *o*-tolyl sulfone, 21991-14-0; **7**, 21991-15-1; **7** (2-hydroxy-3,5-dichlorobenzyl derivative), 24299-63-6; **8**, 24343-77-9; **9**, 21128-30-3; **10**, 21128-31-4; **12**, 21995-82-4.

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