Rearrangement of Mesityl Naphthyl Sulfones *via* a Novel Nucleophilic Addition–β Elimination Sequence[1]

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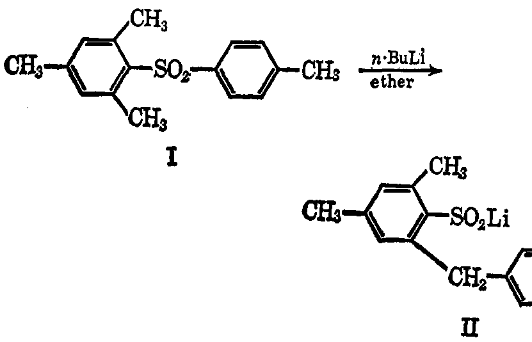
Abstract: Treatment of mesityl 1-naphthyl sulfone and mesityl 2-naphthyl sulfone with potassium *t*-butoxide in dimethyl sulfoxide induces rearrangement to 2-(2′-naphthylmethyl)-4,6-dimethylbenzenesulfinic acid (X) and 2-(1′-naphthylmethyl)-4,6-dimethylbenzenesulfinic acid (IV), respectively. However, mesityl *p*-tolyl sulfone rearranges to 3,4′,5-trimethyldiphenylmethane-2-sulfinic acid (II). Hence, different mechanisms for rearrangement are operative in the sulfones where phenyl and where naphthyl are the migrating groups. Direct nucleophilic displacement accounts for the retention of the *para* orientation in the migration of the *p*-tolyl moiety. An intramolecular carbanion addition–β elimination sequence is proposed for rearrangement of the naphthyl sulfones. The attempt to obtain a similar *inter*molecular nucleophilic addition–β elimination reaction with phenyl naphthyl sulfones was unsuccessful.

When treated with *n*-butyllithium in ether, *o*-methyldiphenyl sulfones have been shown to rearrange to *o*-benzylbenzenesulfinic acids.[4a–c] This rearrangement has been extended to substituted phenyl mesityl sulfones[5] and methylnaphthyl phenyl sulfones,[6] demonstrating an increasing utility for synthesis.

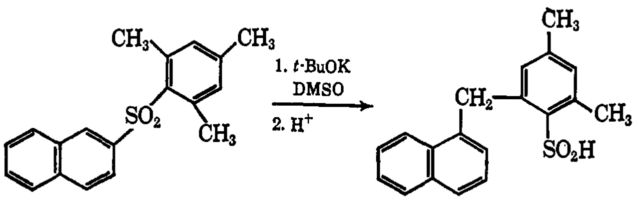


I

II

In these earlier studies, phenyl and substituted phenyl were the only groups shown to migrate. It was therefore of interest to determine whether aromatic systems other than phenyl could serve as migrating groups.

Mesityl 1-naphthyl and mesityl 2-naphthyl sulfones were prepared by Friedel–Crafts condensations of the appropriate naphthalenesulfonyl chlorides and mesitylene in the presence of aluminum chloride. These sulfones were treated with potassium *t*-butoxide in dimethyl sulfoxide and with *n*-butyllithium in ether. The techniques used in the rearrangement studies and the methods used to obtain derivatives of the sulfinic acids are described in the Experimental Section. Mesityl 2-naphthyl sulfone (III), when treated with potassium *t*-butoxide in dimethyl sulfoxide, was found to rearrange to 2-(1′-naphthylmethyl)-4,6-dimethylbenzenesulfinic acid (IV). Likewise mesityl 1-naphthyl sulfone, when treated with potassium *t*-butoxide in dimethyl sulfoxide or *n*-butyllithium in ether, was found to rearrange to 2-(2′-naphthylmethyl)-4,6-dimethylbenzenesulfinic acid. The rearrangement of the 1-naphthyl sulfone when induced by *n*-butyllithium produced only a 42% yield of sulfinic acid, while potassium *t*-butoxide in dimethyl sulfoxide gave an 84% yield of rearranged acid. Similarly the rearrangement of the 2-naphthyl sulfone gave a 5% yield of acid with *n*-butyllithium but an 84% yield with potassium *t*-butoxide. However, when mesityl *p*-tolyl sulfone (I) was treated with potassium *t*-butoxide in dimethyl sulfoxide and with *n*-butyllithium in ether, the yields of the corresponding 2-benzyl-4,6-dimethylbenzenesulfinic acid (II) were 74 and 88%, respectively. The distinct advantage of the potassium *t*-butoxide–dimethyl sulfoxide system for inducing rearrangement of the naphthyl sulfones is attributed to the enhanced nucleophilicity of the intermediate carbanions V and VI in the dipolar aprotic solvent DMSO.[7]



III

IV

The products from the rearrangement of the naphthyl sulfones indicate that nucleophilic displacement has occurred at the ring carbon β to the point of attachment of the sulfone, rather than directly at the ring carbon bearing the sulfone group, as was observed in the phenyl sulfone series. The following mechanism is consistent with the facts observed in this novel rearrangement.

The sulfinic acids formed in these reactions were characterized by infrared spectra, decomposition points, and by sulfone formation with 2-hydroxy-3,5-dichlorobenzyl chloride.[8] The sulfone derivatives were characterized by microanalyses, molecular weights, and infrared spectra.

The structure of sulfinic acid IV from rearrangement of mesityl 2-naphthyl sulfone (III) was proved by

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(1) Paper VI in the series on Rearrangements of Aryl Sulfones. Presented in part at the 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1964.

(2) Taken in part from the Ph.D. Thesis of C. R. Robbins, Purdue University, 1964.

(3) National Science Foundation Cooperative Graduate Fellow, 1963–1964, 1965–1967.

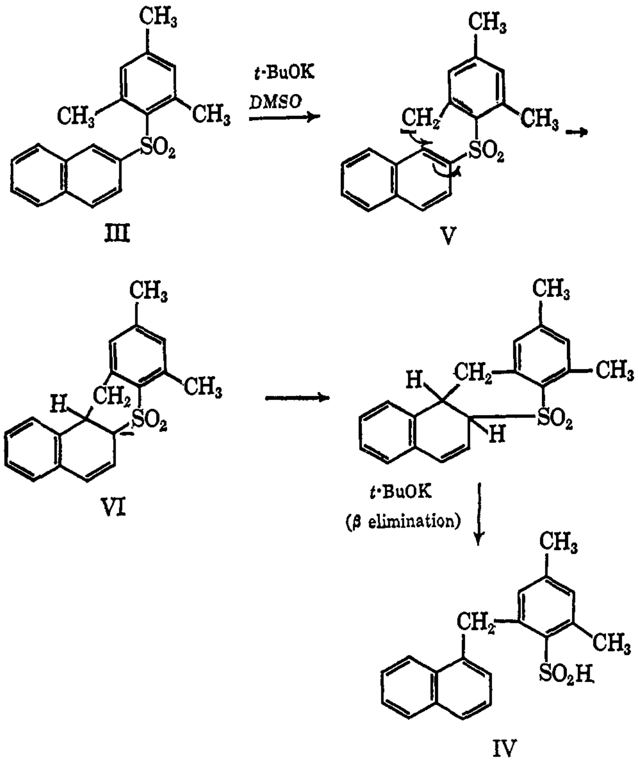
(4) (a) W. E. Truce, W. J. Ray, Jr., O. L. Norman, and D. B. Eickemeyer, *J. Am. Chem. Soc.*, **80**, 3625 (1958); (b) W. E. Truce and W. J. Ray, Jr., *ibid.*, **81**, 481 (1959); (c) *ibid.*, **81**, 484 (1959).

(5) W. E. Truce and M. M. Guy, *J. Org. Chem.*, **26**, 4331 (1961).

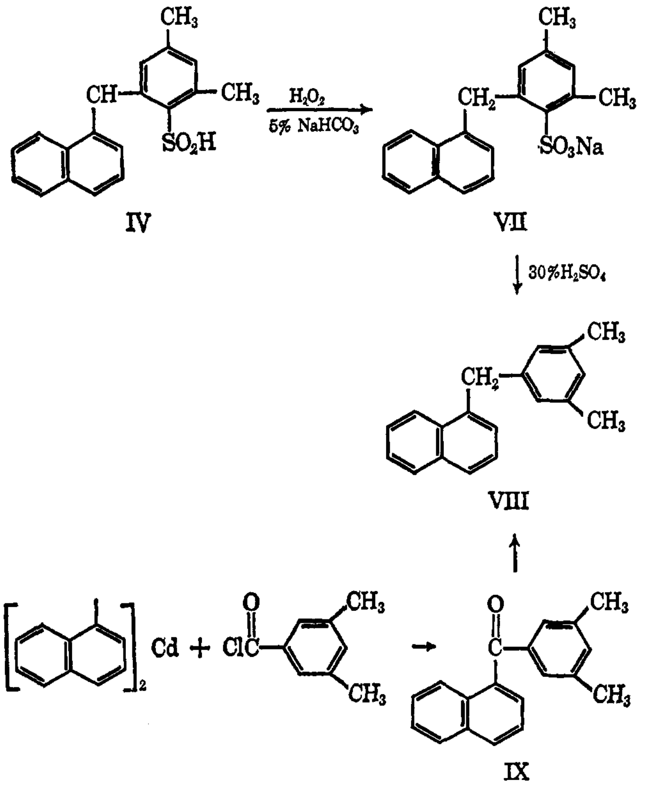
(6) W. E. Truce and D. C. Hampton, *ibid.*, **28**, 2276 (1963).

(7) A. J. Parker, *Quart. Rev.* (London), **16**, 163 (1962).

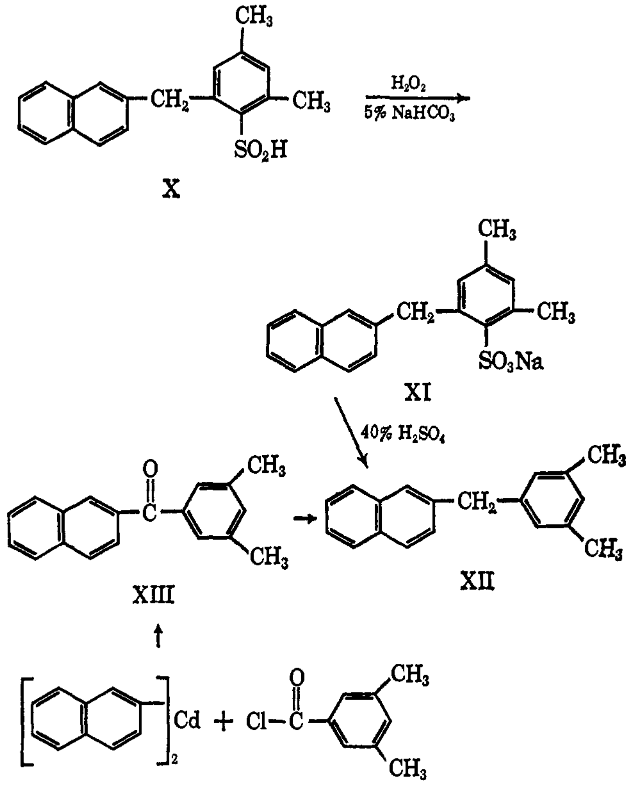
(8) M. T. Beachem, *et al.*, *J. Am. Chem. Soc.*, **81**, 5430 (1959).



oxidation to sulfonic acid VII and desulfonation to 1-naphthyl-3′,5′-dimethylphenylmethane (VIII), which was alternately synthesized by Wolff–Kishner reduction of 1-naphthyl 3,5-dimethylphenyl ketone (IX). This ketone was prepared by the reaction of di(1-naphthyl)-cadmium with 3,5-dimethylbenzoyl chloride, and also by acylation of naphthalene with 3,5-dimethylbenzoyl chloride in carbon disulfide.[9]



The structure of the sulfinic acid X from rearrangement of mesityl 1-naphthyl sulfone was proved by oxidation to sulfonic acid XI and desulfonation to 2-naphthyl-3′,5′-*dimethylphenylmethane (XII) which* was alternately synthesized by Wolff–Kishner reduction of 2-naphthyl 3,5-dimethylphenyl ketone (XIII). This ketone was likewise prepared by the reaction of di(2-naphthyl)cadmium with 3,5-dimethylbenzoyl chloride. The hydrocarbon XII was also synthesized by aromatization of the olefin formed from addition of the Grignard reagent of ω-bromomesitylene to β-tetralone followed by dehydration.



In both cases the rearrangement products were identified by vpc comparison with the alternately synthesized hydrocarbons, as well as by infrared spectra.

The sulfonic acid salt VII was isolated, and its infrared spectrum in the region 650 to 1000 cm^{-1} was found to be very similar to that of hydrocarbon VIII. The same procedure was followed for sulfonic acid salt XI, and its infrared spectrum in the region considered was found to be very similar to that of hydrocarbon XII but unlike that of compounds VII and VIII. These observations indicate that no rearrangements occurred during the desulfonation process.

The discovery of this novel rearrangement prompted a reinvestigation of the earlier findings in the phenyl series. Mesityl *p*-tolyl sulfone (I) had been rearranged with *n*-butyllithium in ether and the desulfonated product (XIV) compared with the hydrocarbon obtained from Wolff–Kishner reduction of ketone XV. The comparison by infrared spectra and refractive indices indicated these hydrocarbons to be identical.[4a] However, an additional proof has now been provided by vpc comparison of the hydrocarbons obtained from repeating these reactions and the alternative hydrocarbon XVI, which would have been expected from an

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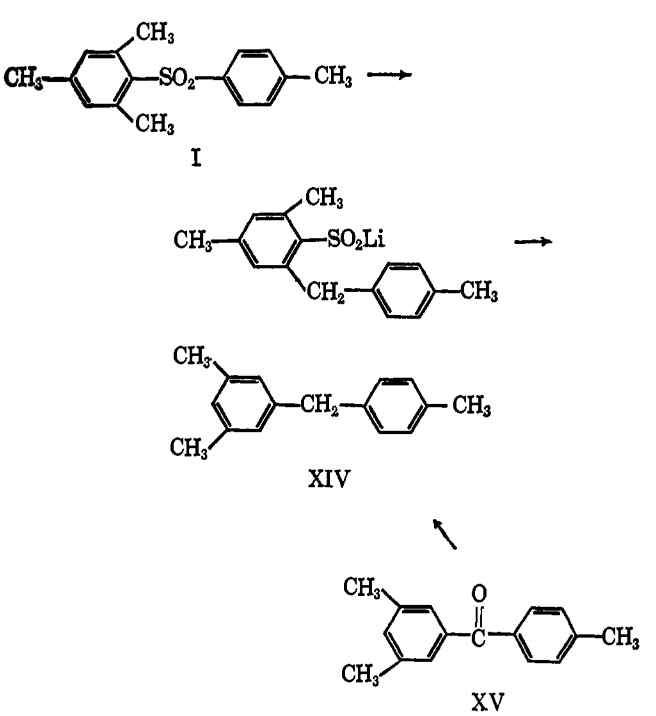
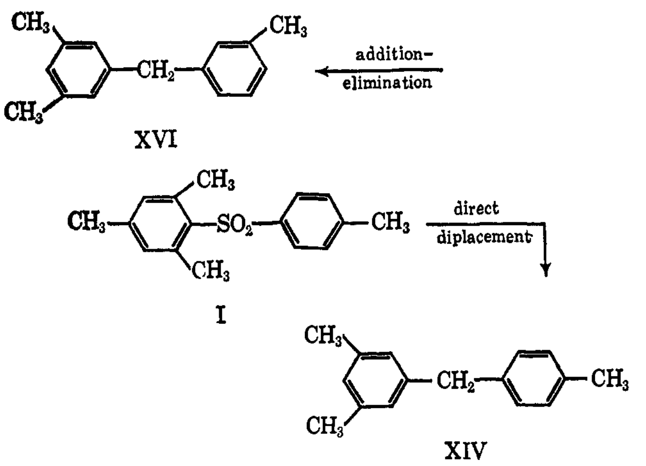
[9] E. Caille, *Compt. Rend.*, **153**, 393 (1911); *Chem. Abstr.*, **5**, 3413 (1911).



addition–elimination mechanism. Each of these hydrocarbons (XIV and XVI) was synthesized by two unambiguous alternate routes, and vpc analysis verified that the product of rearrangement of mesityl *p*-tolyl sulfone was XIV. Hence the rearrangement has clearly been shown to proceed by a different path for a naphthyl migrating group as compared to phenyl.



The novel nucleophilic addition of the carbanion across the 1,2 bond in the naphthalene nucleus, followed by β elimination of the sulfone group, may be explained on the basis that the 1,2 bond in naphthalene has much more double-bond character than benzene bonds, while the 2,3 bond has more single-bond character. This decreased aromaticity, and therefore increased reactivity, of naphthalene is supported by physical and chemical evidence. X-Ray studies show that the bond between carbon atoms 1 and 2 is shorter and nearer to the length of a true olefinic bond than those of benzene, while calculations by both the MO and the Pauling valence bond methods agree that the bond order of the four equivalent α,β bonds in naphthalene is $^2/_3$ while the bond order of the remaining bonds is only $^1/_3$.[10] It is well known that naphthalene undergoes addition reactions more readily than benzene;[11] reactions of naphthols and naphthylamines in particular have frequently been observed to appear to proceed through intermediate addition products. A recent example of the nucleophilic addition of a carbanion across a naphthalene α,β bond was provided by Schriesheim and co-workers[12] who found that treatment of naphthalene with methylsulfinylcarbanion resulted in methylation of the aromatic hydrocarbon. This presumably occurred by addition of the carbanion to naphthalene followed by base-catalyzed elimination of CH_3SO^- and rearomatization to the methylnaphthalene obtained. These workers could not obtain an addition product from benzene, a fact which supports the existing evidence for a difference in the reactivities of benzene and naphthalene toward nucleophilic additions. It is therefore not surprising that while naphthyl sulfones may undergo an addition–elimination sequence, phenyl systems rearrange by direct displacement at the partially positive carbon atom bearing the sulfone group.

Our discovery of this intramolecular addition of a carbanion at the β position in a naphthyl sulfone prompted us to investigate the possibility of an *inter*molecular addition of a similar nature. Consequently we prepared phenyl 2-naphthyl sulfone and subjected it to treatment with a series of nucleophiles. Table I lists the nucleophiles used, as well as the results. It was

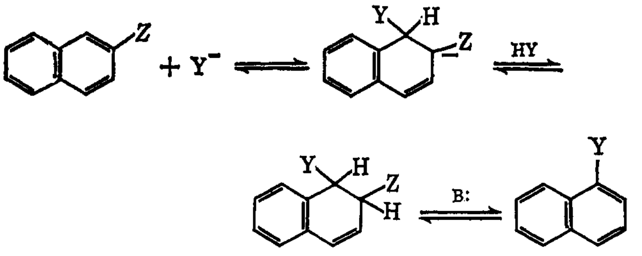


Table I. Treatment of Phenyl Naphthyl Sulfones with Anions

Nucleophile	Sulfone[a]: nucleophile, moles	Product	Yield, %
1 $NaCH(CO_2Et)_2$[b]	1:1.83	Phenyl 2-naphthyl sulfone	80
2 $NaCH(CO_2Et)_2$[c]	1:1.01	Phenyl 2-naphthyl sulfone	65
3 $NaCH(CO_2Et)_2$[c]	1:10	Phenyl 2-naphthyl sulfone	72
4 $NaNH_2$[c]	1:1.03	Phenyl 2-naphthyl sulfone	79
5 *n*-BuSH[c]	1:1.07	Phenyl 2-naphthyl sulfone	77
6 *p*-Toluenethiol[c]	1:10	Phenyl 2-naphthyl sulfone	94
7 Methylsulfinylcarbanion[c]	1:1	Phenyl 2-naphthyl sulfone	62
8 Methylsulfinylcarbanion[c]	1:10	Phenyl 2-naphthyl sulfone (+ oil)	50
9 Methylsulfinylcarbanion[c]	1:10	Methyl 1-naphthylmethyl sulfoxide	17.4

[a] Phenyl 2-naphthyl sulfone for expt 1–8; phenyl 1-naphthyl sulfone for expt 9. [b] In ethanol. [c] In dimethyl sulfoxide.

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(10) D. W. J. Cruickshank, *Tetrahedron*, 17, 155 (1962).

(11) (a) L. F. Fieser in "Organic Chemistry, An Advanced Treatise," Vol. 1, H. Gilman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1941, pp 145–160; (b) N. Donaldson, "The Chemistry and Technology of Naphthalene Compounds," Edward Arnold Ltd., London, 1958, pp 3–12.

(12) P. A. Argabright, J. E. Hofmann, and A. Schriesheim, *J. Org. Chem.*, 30, 3233 (1965).

observed that methylsulfinyl carbanion produced an oil from which only 50% of the starting sulfone could be recovered with difficulty, contrary to the easily obtained high recovery with other nucleophiles. Hence it was considered that some reaction may have occurred and that changing to phenyl 1-naphthyl sulfone might favor reaction by reducing steric hindrance to the incoming carbanion, if indeed attack were occurring at the position β to the sulfone group. A sulfoxide product was obtained from treatment of phenyl 1-naphthyl sulfone with a large excess of methylsulfinyl carbanion. However, this sulfoxide was shown to be the product of direct nucleophilic displacement at the α position, by comparison with authentic samples of the two possible substitution products.

It is felt that this failure to observe intermolecular addition–elimination reactions with the phenyl naphthyl sulfones is an indication of the importance of steric considerations as well as electronic effects in the intramolecular rearrangements observed with mesityl naphthyl sulfones. The benzilic carbanion formed on the mesityl moiety is in a favorable position for attack at the somewhat electropositive β position *via* a six-membered transition state, whereas intermolecular reaction favors attack directly at the more highly electropositive α position of phenyl 1-naphthyl sulfones.

Experimental Section[13]

Mesityl 1-Naphthyl Sulfone. Using a method similar to that of Maclean and Adams,[14] a well-stirred solution of 16.2 g (0.072 mole) of 1-naphthalenesulfonyl chloride, 8.7 g (0.072 mole) of mesitylene, and 200 ml of methylene chloride was treated with 10.0 g (0.075 mole) of aluminum chloride in small amounts over a 15-min period. After refluxing 18 hr, the mixture was cooled and poured onto a mixture of ice and concentrated HCl. The organic layer was separated, washed with water and 10% NH_4OH, filtered, and dried ($MgSO_4$). The solvent was evaporated and the solid product recrystallized three times from ethanol, yielding 10.0 g (50%) of mesityl 1-naphthyl sulfone, mp 154–156°, lit.[15] mp 154–156°.

Anal. Calcd for $C_{19}H_{18}O_2S$: C, 73.51; H, 5.84. Found: C, 73.27; H, 5.55.

Mesityl 2-Naphthyl Sulfone. Using the same procedure, a solution of 49.87 g (0.220 mole) of 2-naphthalenesulfonyl chloride and 33.3 g (0.290 mole) of mesitylene in 200 ml of methylene chloride was treated with 33.3 g (0.250 mole) of aluminum chloride. The mixture was refluxed 16 hr and then hydrolyzed; the product was isolated as described above. Forty grams (60%) of sulfone was obtained, mp 127–128°; lit.[15] mp 126–127°.

Anal. Calcd for $C_{19}H_{18}O_2S$: C, 73.51; H, 5.84. Found: C, 73.60; H, 5.87.

Mesityl *p*-Tolyl Sulfone. Following the above procedure, a solution of 46.38 g (0.24 mole) of *p*-toluenesulfonyl chloride and 36.08 g (0.30 mole) of mesitylene in 133 ml of CS_2 was treated with 33.63 g (0.25 mole) of aluminum chloride over a 45-min period. The solution was refluxed 22 hr, the solvent distilled off, and the remaining mixture hydrolyzed with cold 3 *N* HCl. Boiling the water mixture to remove excess mesitylene gave a solid which was filtered off, dissolved in methanol, decolorized, and crystallized to give 50 g (83%) of crude product. Recrystallization from methanol gave white needles, mp 118–120°; lit.[4c,5] mp 119–120°.

General Procedure for the Potassium *t*-Butoxide–Dimethyl Sulfoxide Induced Rearrangements of the Sulfones. The rearrangements were carried out in three-necked, round-bottom flasks equipped with gas inlet, condenser, drying tube, 120-ml vapor bypass addition funnel, and a magnetic stirrer. The glassware was thoroughly dried in an oven, assembled, and cooled in a stream of nitrogen. The potassium *t*-butoxide was introduced through the condenser and dissolved in freshly opened Baker Analyzed dimethyl sulfoxide. The sulfone was dissolved in a minimum amount of dimethyl sulfoxide and was added dropwise to the *t*-butoxide solution. When the addition was completed the reaction was stirred at room temperature for 6–24 hr under N_2 and was hydrolyzed by pouring into water. The aqueous solution was ether extracted and the ether phase washed with water and dried ($MgSO_4$). The material obtained upon evaporation of the ether was purified by recrystallization or column chromatography and was identified as recovered starting sulfone by mixture melting points and infrared spectra.

The aqueous phase was acidified to pH 1 with 50% HCl and extracted with ether. The ether extracts were combined and treated three times with 5% NaOH. The basic extracts were then acidified to pH 1 while cooling with ice. After extracting with ether and drying the ether phase over $MgSO_4$ for 15–30 min at 0°, the solution was filtered and the solvent removed, yielding sulfinic acid.[16] The sulfinic acid products could be purified by recrystallization from acetone–water.

Derivative Formation of the Sulfinic Acids. One-half gram of the sulfinic acid was dissolved in a small amount of methanol and neutralized to phenolphthalein with 1 *N* methanolic NaOH. An equimolar amount of 2-hydroxy-3,5-dichlorobenzyl chloride,[17] mp 83–85°, was dissolved in the minimum amount of methanol and added to the solution of sodium sulfinate. After standing overnight the crystalline product was filtered and recrystallized from ethyl acetate.

Rearrangement of Mesityl 1-Naphthyl Sulfone. To 1.3 g (0.012 mole) of potassium *t*-butoxide in 100 ml of DMSO was added dropwise 3.1 g (0.01 mole) of mesityl 1-naphthyl sulfone in 100 ml of DMSO. The reaction was stirred for 6 hr at room temperature. After hydrolysis as described above, 0.4 g of sulfone (12%) was recovered, and 2.6 g (84%) of sulfinic acid was obtained, mp 98–99° dec. The 2-hydroxy-3,5-dichlorobenzyl chloride derivative of this acid was obtained in 50% yield, mp 175.5–177°.

Anal. Calcd for $C_{26}H_{22}SO_3Cl_2$: C, 64.35; H, 4.54; Cl, 14.60; S, 6.60; mol wt, 485. Found: C, 64.12; H, 4.93; Cl, 14.35; S, 6.40; mol wt, 486.

Rearrangement of Mesityl 2-Naphthyl Sulfone. To 1.3 g (0.012 mole) of potassium *t*-butoxide in 75 ml of DMSO was added dropwise 3.1 g (0.01 mole) of mesityl 2-naphthyl sulfone in 50 ml of DMSO. The reaction was then stirred 6 hr. Hydrolysis yielded 2.66 g of sulfinic acid (84%), mp 108–110.5° dec, neut equiv 333 (calcd 310). The 2-hydroxy-3,5-dichlorobenzyl chloride derivative of this acid melted at 207–209° dec.

Anal. Calcd for $C_{26}H_{22}SO_3Cl_2$: C, 64.35; H, 4.54; Cl, 14.60; mol wt, 485. Found: C, 64.66; H, 4.81; Cl, 14.76; mol wt, 499.

Rearrangement of Mesityl *p*-Tolyl Sulfone. To 1.5 g (0.014 mole) of potassium *t*-butoxide in 100 ml of DMSO was added dropwise 2.82 g (0.01 mole) of mesityl *p*-tolyl sulfone in 50 ml of DMSO. The solution was stirred for 6.5 hr. Hydrolysis yielded 0.2 g (22%) of recovered sulfone and 2.08 g (74%) of sulfinic acid which melted at 94–95° dec after recrystallization. The 2-hydroxy-3,5-dichlorobenzyl chloride derivative of this acid melted at 138.5–140°. The infrared spectrum of the derivative was identical with that of the sulfinic acid produced by *n*-butyllithium-induced rearrangement of mesityl *p*-tolyl sulfone (*vide infra*).

General Procedure for the *n*-Butyllithium-Induced Rearrangement of the Sulfones. These rearrangements were carried out in the same dry apparatus as that described for the potassium *t*-butoxide induced rearrangements. Reactions were carried out under a nitrogen atmosphere with a minimum of exposure to air during addition of reactants and solvent. The solvent used was freshly opened Mallinckrodt anhydrous ether. Commercially available Foote *n*-butyllithium in hexane was used and was analyzed by the titration method of Jones and Gilman.[18] The normality of this *n*-butyllithium reagent was nearly constant throughout the experiments at 1.4 *N*. The calculated volume of reagent was removed from the container and transferred to the addition funnel containing 20 ml of ether, using an oven-dried, 20-ml hypodermic syringe. The diluted *n*-butyllithium was added dropwise at room temperature to a solution of the sulfone in ether. Reverse addition was also used with little change in yields. When the addition was completed

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(13) Microanalyses were carried out by Dr. C. S. Yeh. Melting and boiling points are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 137B spectrometer.

(14) M. E. Maclean and R. Adams, *J. Am. Chem. Soc.*, **55**, 4685 (1933).

(15) D. E. Hoiness, M.S. Thesis, Purdue University, 1960.

(16) The acids could be dried for 15–20 min at 1 mm over P_2O_5 but decomposed over longer periods. No heat could be applied for solvent removal or for drying without ensuing decomposition of the acid.

(17) C. A. Buehler, *et al.*, *J. Org. Chem.*, **6**, 902 (1941).

(18) R. G. Jones and H. Gilman, *Org. Reactions*, **6**, 339 (1951).

the reaction mixture was refluxed for 18–24 hr, then hydrolyzed by pouring into water. The ether layer was separated and washed with water, dried over $MgSO_4$, and filtered; the solvent was removed on the rotary evaporator. This neutral material was shown to be predominantly starting sulfone by recrystallization or column chromatography, mixture melting points, and infrared spectra.

The aqueous layer was acidified to pH 1 using 50% HCl and extracted with ether. The ether extracts were dried ($MgSO_4$) at 0° for 15–30 min and filtered and the solvent removed, yielding sulfinic acid.[16] Sulfone formation by reaction with 2-hydroxy-3,5-dichlorobenzyl chloride as previously described served as convenient derivatives for identification.

Rearrangement of Mesityl 1-Naphthyl Sulfone. Two grams (0.0064 mole) of mesityl 1-naphthyl sulfone dissolved in 200 ml of anhydrous ether and 30 ml of THF was added slowly to 6.5 ml (0.009 mole) of 1.41 *N* *n*-butyllithium diluted in 20 ml of ether. The mixture was refluxed under N_2 for 24 hr. Hydrolysis as described above yielded 1.02 g of recovered sulfone (51%) and 0.84 g of sulfinic acid (42%). This acid was converted to its 2-hydroxy-3,5-dichlorobenzyl chloride derivative and was shown by its infrared spectrum and the properties of the derivative to be identical with the acid from the potassium *t*-butoxide induced rearrangement of the same sulfone.

Rearrangement of Mesityl 2-Naphthyl Sulfone. To 2 g (0.0064 mole) of mesityl 2-naphthyl sulfone in 150 ml of anhydrous ether was added 6.1 ml (0.0078 mole) of 1.4 *N* *n*-butyllithium diluted in 20 ml of ether. The solution was refluxed for 24 hr and hydrolyzed. Two grams of an oil was obtained which yielded 1.8 g of recovered sulfone (90%) when chromatographed on acid-washed alumina. One-tenth gram of a sulfinic acid (5%) was also obtained, which was too impure for infrared identification, and failed to form the sulfone derivative.

Rearrangement of Mesityl *p*-Tolyl Sulfone. To 5.4 g (0.020 mole) of mesityl *p*-tolyl sulfone in 100 ml of ether was added 14.5 ml (0.022 mole) of 1.4 *N* *n*-butyllithium diluted in 20 ml of ether. The solution was refluxed 18 hr and hydrolyzed to give 0.44 g of recovered sulfone (8.1%) and 4.73 g (88%) of sulfinic acid, which melted at 94–95.5° dec after recrystallization. The 2-hydroxy-3,5-dichlorobenzyl chloride derivative of the acid was synthesized, mp 138.5–139.5°.

Anal. Calcd for $C_{23}H_{22}SO_3Cl_2$: C, 61.45; H, 4.94; Cl, 15.78; S, 7.12; mol wt, 449. Found: C, 61.47; H, 5.23; Cl, 15.87; S, 6.95; mol wt, 441.

Oxidation and Desulfonation of the Sulfinic Acids. Sulfinic Acid IV from Mesityl 2-Naphthyl Sulfone. Four grams (0.0126 mole) of the sulfinic acid obtained from the potassium *t*-butoxide induced reaction of mesityl 2-naphthyl sulfone was dissolved in 100 ml of 5% $NaHCO_3$. Five milliliters of 30% H_2O_2 was added and the solution allowed to stand overnight. From this mixture there was obtained 3.6 g (86%) of the corresponding sodium sulfonate (as indicated by its infrared spectrum). Two grams (0.0063 mole) of the salt was dissolved in the minimum amount of water and treated with 30 ml of concentrated H_2SO_4. After shaking intermittently for 10 min, the solution was poured onto ice and extracted with ether. The ether extracts were examined by vpc and found to contain 0.64 g of 1-naphthyl-3′,5′-dimethylphenylmethane (42%), identified by retention time with the alternately synthesized hydrocarbon (parts A and B below). A sample of this desulfonated material was collected and its infrared spectrum was also superimposable on the spectrum of the authentic sample.

Sulfinic Acid X from Mesityl 1-Naphthyl Sulfone. Ten grams (0.0315 mole) of the sulfinic acid obtained from the potassium *t*-butoxide induced reaction of mesityl 1-naphthyl sulfone was dissolved in 100 ml of 5% $NaHCO_3$. Ten milliliters of 30% H_2O_2 was added and the solution kept at room temperature overnight. Evaporation to dryness produced a residue, which was extracted with hot ethanol. The ethanol was removed, leaving 8.5 g (80%) of solid whose infrared spectrum exhibited characteristic sulfonate absorbances. Of this salt, 6.8 g (0.0195 mole) was dissolved in 35 ml of water and treated with 35 ml of concentrated H_2SO_4. The solution was refluxed for 8 hr, then poured into ice-water. An oil appeared which was extracted with CH_2Cl_2. The organic extract was washed with 5% $NaHCO_3$ until neutral and then dried; the solvent was removed. The residue, a black oil, was taken up in 95% methanol, decolorized, and crystallized to yield 2.47 g (51.5%) of hydrocarbon product, mp 67–68°.

Anal. Calcd for $C_{19}H_{18}$: C, 92.64; H, 7.36; mol wt, 246. Found: C, 92.40; H, 7.39; mol wt, 246.

The infrared spectrum and vpc retention time of this hydrocarbon were identical with those of 2-naphthyl-3′,5′-dimethylphenylmethane, synthesized in parts C and D below, and were clearly distinguishable by these properties from 1-naphthyl-3′,5′-dimethylphenylmethane.

Sulfinic Acid from Mesityl *p*-Tolyl Sulfone. From the *n*-butyllithium-induced reaction of mesityl *p*-tolyl sulfone 3.33 g (0.012 mole) of sulfinic acid was dissolved in 100 ml of 5% $NaHCO_3$. Five milliliters of 30% H_2O_2 was added and the solution let stand overnight. The solvent was then evaporated leaving crystals which were extracted with hot ethanol. The ethanol was removed and 3.0 g (79%) of solid was obtained which was shown to be a sulfonate by its infrared spectrum. The salt (2.5 g, 0.0080 mole) was dissolved in a small amount of water and treated with 40 ml of concentrated H_2SO_4, shaken for 10 min, and poured onto ice. The dark oil was extracted with ether and dried. The ether extracts were examined by vpc and found to contain a hydrocarbon which, when compared with hydrocarbons XIV and XVI by vpc retention times and infrared spectra, was shown to be identical with hydrocarbon XIV, 3,4′,5-trimethyldiphenylmethane.

Alternate Synthesis of 1-Naphthyl-3′,5′-dimethylphenylmethane (VIII). (A) Acylation of Naphthalene. This preparation was adapted from the method of Caille[9] for the preparation of 1-acylnaphthalenes. 3,5-Dimethylbenzoyl chloride was prepared by refluxing 47.4 g (0.40 mole) of thionyl chloride with 25.0 g (0.166 mole) of 3,5-dimethylbenzoic acid for 2.5 hr. The excess thionyl chloride was removed *in vacuo* and the product distilled at 118–120° (15 mm), wt 25.41 g (91%), $n^{30.5}D$ 1.542; lit.[19] bp 109.5° (10 mm). To a solution of 2.37 g (0.019 mole) of naphthalene and 3.15 g (0.019 mole) of 3,5-dimethylbenzoyl chloride in 50 ml of CS_2 cooled to 0° was gradually added 2.44 g (0.019 mole) of aluminum chloride. The solution was stirred at 0° for 6 hr and filtered. The solid was rapidly decomposed with ice and concentrated HCl. The aqueous solution was extracted with ether and dried over $MgSO_4$. Evaporation of the solvent left an oil which crystallized from ether at Dry Ice temperature, yielding 3.0 g (61%) of product. Recrystallization from ether gave ketone melting at 79–80.5°.

Anal. Calcd for $C_{19}H_{16}O$: C, 87.69; H, 6.15. Found: C, 87.63; H, 6.45.

(B) Organocadmium Approach. The Grignard reagent of 1-bromonaphthalene was prepared using 15.5 g (0.075 mole) of 1-bromonaphthalene and 1.82 g (0.075 g-atom) of magnesium turnings. The ethereal solution was cooled in an ice bath until it began to solidify and then 7.0 g of anhydrous cadmium chloride was added over a 5-min period. The reaction mixture was refluxed for 0.5 hr and the ether distilled until the still pot was nearly dry. Anhydrous benzene (75 ml) was added and 25 ml more of solvent was distilled; then 100 ml of benzene was added and the solution heated to reflux. 3,5-Dimethylbenzoyl chloride (8.4 g, 0.05 mole) dissolved in 20 ml of benzene was quickly added to the cadmium reagent. Refluxing was continued for 3 hr, followed by hydrolysis with 15% H_2SO_4. The mixture was extracted with ether, and the ether phase was washed with water and 5% sodium carbonate solution and dried; the solvent was removed. An oil was obtained which crystallized from ether at Dry Ice temperature, giving 6.6 g (51% yield) of 1-naphthyl 3,5-dimethylphenyl ketone. Recrystallization from ether gave a product melting at 79–80.5°. This compound was identical with that prepared in part A.

Wolff–Kishner reduction of the ketone formed in parts A and B using the Huang-Minlon modification,[20] was carried out as follows. A mixture of 13 g (0.05 mole) of 1-naphthyl 3,5-dimethylphenyl ketone, 14 g of NaOH, 14 ml of 99% hydrazine, and 130 ml of diethylene glycol was heated and stirred at 180° for 1 hr. The excess hydrazine and water were distilled from the reaction and the temperature was maintained at 190–200° for 3 hr. The mixture was cooled, poured into water, and extracted with ether. After drying, the solvent was removed and the product distilled, yielding 7.1 g (58%) of VIII, bp 163–165° (0.6 mm).

Anal. Calcd for $C_{19}H_{18}$: C, 92.64; H, 7.36. Found: C, 92.58; H, 7.41.

Alternate Synthesis of 2-Naphthyl-3′,5′-dimethylphenylmethane (XII). (C) From 2-Naphthyl 3,5-Dimethylphenyl Ketone (XIII). The Grignard reagent of 2-bromonaphthalene was prepared from 15 g (0.0725 mole) of 2-bromonaphthalene and 1.82 g (0.075 g-atom) of magnesium turnings in 100 ml of ether. The cadmium reagent was prepared as in part B above using 8 g of cadmium chloride. Ten grams (0.059 mole) of 3,5-dimethylbenzoyl chloride was added to the benzene solution of the cadmium reagent and the mixture was refluxed for 3 hr, then hydrolyzed with 15% H_2SO_4. The

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(19) A Geuther, *Ann.*, **202**, 310 (1880).

(20) Huang-Minlon, *J. Am. Chem. Soc.*, **68**, 2487 (1946).

aqueous solution was extracted with ether; the ether phase was washed with water and 5% $NaHCO_3$ and dried, and the ether was removed. An oil was obtained, which crystallized from ether at Dry Ice temperature, giving 8.5 g (56%) of 2-naphthyl 3,5-dimethylphenyl ketone. Recrystallization from ether gave a product melting at 136.5–138°.

Anal. Calcd for $C_{19}H_{16}O$: C, 87.69; H, 6.15; mol wt, 260. Found: C, 87.41; H, 6.44; mol wt, 258.

This ketone was reduced to the hydrocarbon using the Wolff–Kishner method described above. Seven grams of ketone yielded an oil which was partially purified by crystallization from 95% ethanol. A solid product (0.068 g, 8.8%) was obtained, which melted at 68–69° after several recrystallizations from 95% ethanol.

Anal. Calcd for $C_{19}H_{18}$: C, 92.68; H, 7.32; mol wt, 246. Found: C, 92.73; H, 7.43; mol wt, 245.

(D) From β-Tetralone. This synthesis involved the addition of the Grignard reagent of ω-bromomesitylene to β-tetralone. The product dehydrated during work-up to yield a mixture of olefins. The olefins could then be aromatized with sulfur to the desired 2-naphthyl-3′,5′-dimethylphenylmethane. The procedure used was adapted from that of Fahim, *et al.*,[21] who reported the synthesis of 1-benzylnaphthalenes from α-tetralone.

ω-Bromomesitylene was prepared by the N-bromosuccinimide (NBS) bromination of mesitylene in CCl_4. Equimolar amounts (0.6 mole) of mesitylene and NBS in 150 ml of CCl_4 were treated with two portions, 0.2 g each, of benzoyl peroxide after heating to reflux temperature. After refluxing 8 hr, the solid succinimide was filtered off, the solvent evaporated, and the product distilled. Several fractions were collected, 80–100° (4.5 mm), giving a total of 69.3 g (61%). Vpc analysis showed these fractions to contain only mesitylene and ω-bromomesitylene. When cooled below 40°, the ω-bromomesitylene solidified and was separated from some of the mesitylene by decantation. The solid product (lachrymatory) was used as such.

The Grignard reagent of ω-bromomesitylene was prepared from 0.84 g (0.034 g-atom) of Mg and 6.84 g (0.034 mole) of ω-bromomesitylene in 25 ml of ether. To this solution, 5.0 g (0.034 mole) of β-tetralone in 40 ml of anhydrous benzene was added. The mixture was refluxed for 3.5 hr, hydrolyzed with cold 10% H_2SO_4, and extracted with ether; the ether phase was dried. The solvent was then removed and the product distilled twice. The final distillation through a 6-in. Vigreux column yielded 1 g of recovered β-tetralone (20%), bp 92–95° (1 mm); 0.92 g of olefin, bp 138–144° (1 mm); and 1.92 g of olefin, bp 168–180° (1 mm). The total yield of olefins was 33%. A portion of the higher boiling olefin (1.27 g) was heated with 0.3 g of sulfur at 195–200° for 5 hr. The flask was then cooled and the residue extracted with ether. The ether phase was dried and the solvent removed. A dark oil was obtained which was decolorized and crystallized from 95% ethanol giving a total of 0.30 g (25%) of solid, which when recrystallized several times from 95% ethanol melted at 62–64°. Its infrared spectrum was identical with that of the hydrocarbon synthesized in part C; both were markedly different from the spectrum of the hydrocarbon VIII synthesized in parts A and B. Vpc comparisons confirmed this relationship between the authentic samples.

Alternate Syntheses of 3,4′,5-Trimethyldiphenylmethane (XIV). (E) Friedel–Crafts Acylation of Toluene. The procedure used was that of Eickemeyer.[22] To 21.5 g (0.13 mole) of 3,5-dimethylbenzoyl chloride in 28.6 g (0.30 mole) of dry toluene was added 20.1 g (0.15 mole) of aluminum chloride over 30 min. The mixture was stirred and refluxed for 18.5 hr and then hydrolyzed with an ice–HCl solution. The red oily layer was taken up in ether and dried and the ether removed, leaving an oil which solidified at Dry Ice temperature. The solid was purified and recrystallized several times from methanol at Dry Ice temperature to yield 16.96 g (59%) of 3,5-dimethylphenyl 4-methylphenyl ketone (XV), mp 72.5–74.5°, lit.[22] mp 75–75.5°.

Wolff–Kishner reduction of this ketone using the procedure described in part C above gave a 74% yield of distilled hydrocarbon, bp 100–103° (0.3 mm), n^{26}D 1.5588; lit.[22] bp 114–117° (1.5 mm) and n^{21}D 1.5611.

(F) Grignard Coupling Reaction.[23] The ethereal Grignard reagent of redistilled *p*-bromotoluene was prepared from 2.73 g (0.11 g-atom) of Mg turnings and 27 g (0.158 mole) of halide in 125 ml of ether and 50 ml of benzene. Benzene (50 ml) was added and the ether distilled from the mixture. Then 7.0 g (0.035 mole) of ω-bromomesitylene in 50 ml of benzene was added dropwise and the mixture refluxed for 15 min after addition was complete. Hydrolysis with 4 *N* HCl produced two layers; the organic layer was separated, washed with water and 5% $NaHCO_3$, and dried; the benzene was removed. Distillation of the product gave 5.9 g (80%) of 3,4′,5-trimethyldiphenylmethane, bp 128–133° (2.3 mm), n^{26}D 1.5641. The infrared spectrum and vpc retention time of this compound were identical with those of the product in part E.

Alternate Syntheses of 3,3′,5-Trimethyldiphenylmethane (XVI). (G) Acylation *via* the Cadmium Grignard Reagent. The ethereal Grignard reagent of *m*-bromotoluene was prepared from 2.0 g (0.086 g-atom) of Mg turnings and 21.0 g (0.123 mole) of the redistilled halide. The solution was cooled in an ice bath and 8.5 g of anhydrous $CdCl_2$ was added over 5 min. The mixture was refluxed 0.5 hr, the ether distilled off, and 150 ml of dry benzene added in portions during the distillation. To this cadmium reagent was added 13.98 g (0.083 mole) of 3,5-dimethylbenzoyl chloride in 20 ml of benzene and the mixture refluxed overnight. Hydrolysis with 15% H_2SO_4 was followed by extraction with ether. The ether phase was washed with water and 5% $NaHCO_3$, dried, and evaporated, leaving an oil which was distilled twice through a 12-in. Vigreux column, yielding 11.25 g (60.5%) of product, bp 86–96° (0.3 mm), mp (crystallized from ether) 162–166°. The 2,4-dinitrophenylhydrazone melted at 191–194°.

Wolff–Kishner reduction of this ketone as described in part C yielded the hydrocarbon, bp 114–120° (0.17 mm), 4.45 g (44%), n^{27}D 1.5689. A preparative vpc sample was collected for analysis.

Anal. Calcd for $C_{16}H_{18}$: C, 91.4; H, 8.6; mol wt, 210. Found: C, 91.36; H, 8.73; mol wt, 208.

(H) Grignard Coupling Reaction. This coupling reaction was carried out in the same manner as described in F using 1.83 g (0.075 g-atom) of Mg, 16 g (0.094 mole) of redistilled *m*-bromotoluene, and 7.5 g (0.038 mole) of ω-bromomesitylene. The product obtained by distillation, bp 132–135° (4 mm), $n^{26.5}$D 1.5655, 5.55 g (70%), was shown by infrared spectra and vpc retention times to be identical with the hydrocarbon product in part G, but different from 3,4′,5-trimethyldiphenylmethane (parts E and F).

Reaction of Phenyl 2-Naphthyl Sulfone with Various Nucleophiles. (1) In 11 ml of ethanol distilled from sodium was dissolved 0.44 g (0.019 g-atom) of sodium, followed by 5.4 g (0.033 mole) of diethyl malonate and 4.9 g (0.019 mole) of sulfone. The mixture was refluxed for 23 hr, and poured into water. The yellow precipitate was taken up in ether; the ether phase was washed with a saturated NaCl solution, dried, filtered, and evaporated. The residue was recrystallized from a benzene–hexane mixture to yield 3.91 g (80%) of recovered sulfone, mp 117–118.5°.

(2) Dry DMSO (20 ml) was heated with 0.73 g (0.0187 mole) of $NaNH_2$ at 65–70° until the evolution of NH_3 ceased (10 hr). Three grams (0.0188 mole) of diethyl malonate was added, followed by 5.0 g (0.0185 mole) of sulfone. The mixture was stirred at room temperature for 12 hr, and poured into water. The precipitate was taken up in CH_2Cl_2, washed with a saturated NaCl solution, and dried, and the solvent was removed. Recrystallization of the residue from benzene–hexane gave 3.16 g (65%) of recovered sulfone, mp 117.5–118.5°. Diethyl malonate was observed in the infrared spectrum of the crude residue.

(3) Dry DMSO (200 ml) was heated overnight with 7.3 g (0.187 mole) of $NaNH_2$ at 60–70° under N_2. Thirty grams (0.187 mole) of diethyl malonate was added, followed by 5.0 g (0.0185 mole) of sulfone, and the mixture was stirred at room temperature for 12 hr, then at 60–70° for 12 hr, and poured into water. The white precipitate was dissolved in CH_2Cl_2, washed with a saturated NaCl solution, dried, and evaporated. The residue, mp 117–118° after washing with hexane and drying *in vacuo*, represented a 72% recovery of starting sulfone. The hexane wash solution contained diethyl malonate. Acidification and extraction of the aqueous mother liquor from the initial hydrolysis gave a liquid which contained diethyl malonate and a small amount of a sulfinic acid, probably from cleavage of the sulfone.

(4) To 40 ml of dry DMSO was added 0.70 g (0.018 mole) of $NaNH_2$ and 5.0 g (0.0185 mole) of sulfone. The mixture was stirred at room temperature for 15 min and an additional 0.1 g of $NaNH_2$ was added. Stirring was continued for 23 hr under N_2; then the mixture was poured onto ice and acidified with HCl to pH 1. The precipitate was removed and dissolved in benzene, washed with water, and dried. Evaporation of the solvent gave a

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[21] H. A. Fahim, A. M. Fleifel, and F. Fahim, *J. Org. Chem.*, **25**, 1040 (1960).

[22] D. B. Eickemeyer, Ph.D. Thesis, Purdue University, 1963, p 23.

[23] F. A. Vingiello, S-G. Quo, and J. Sheridan, *J. Org. Chem.*, **26**, 3202 (1961).

solid which, when recrystallized from benzene–hexane, melted at 117–118°; 79% (3.90 g) of the starting sulfone was recovered.

(5) Dry DMSO (35 ml) was heated with 0.78 g (0.020 mole) of $NaNH_2$ under N_2 for 20 hr. Then 2.1 ml (0.020 mole) of *n*-butanethiol was added by syringe, followed by 5.0 g (0.0185 mole) of sulfone. The mixture was stirred at 40° for 43 hr, poured into cold water, extracted with CH_2Cl_2, and dried. Removal of the solvent left a solid which was recrystallized from 95% ethanol. The product weighed 3.85 g (77% recovery of sulfone), mp 117–118°.

(6) Five grams (0.128 mole) of $NaNH_2$ was heated in 75 ml of dry DMSO overnight at 50–60° under N_2. Then 15.9 g (0.128 mole) of *p*-toluenethiol in 50 ml of DMSO was added, followed by 3.43 g (0.0128 mole) of sulfone. The mixture was stirred at 60–70° for 24 hr and hydrolyzed. The brown solid which was filtered off was recrystallized from ethanol and proved to represent a 94% recovery of sulfone, 3.22 g, mp 117–118.5°.

(7) Dry DMSO (20 ml) was heated with 0.69 g (0.0177 mole) of $NaNH_2$ at 60–70° for several hours. Addition of 4.78 g (0.0177 mole) of sulfone was followed by heating for 12 hr at 60–70°. Hydrolysis with cold dilute HCl produced a precipitate which was dissolved in CH_2Cl_2, washed with water, dried, and stripped of solvent. The residue was recrystallized from benzene–hexane and melted at 116–118°, 2.95 g (62%) of recovered sulfone.

(8) Dry DMSO (150 ml) was heated with 7.3 g (0.187 mole) of $NaNH_2$ at 60–70° for 6 hr under N_2. Five grams (0.0185 mole) of sulfone was added and the reaction mixture was stirred at 65–70° for 12.5 hr, then poured into cold water. A dark brown solid was removed by filtration and dissolved in benzene, decolorized, and induced to crystallize with hexane. A white solid was obtained, 2.49 g (50% recovery of sulfone), mp 116–117°. The aqueous mother liquor was extracted with CH_2Cl_2; the organic extracts were washed with water, dried, and concentrated, causing an oil to separate. This oil could not be induced to solidify or crystallize from a variety of solvents. Its infrared spectrum, while highly complex due to impurities, contained sulfoxide bands. An attempt at distillation caused extensive decomposition.

Reaction of Phenyl 1-Naphthyl Sulfone with Methylsulfinyl Carbanion. (9) Dry DMSO (120 ml) was heated overnight with 8.8 g (0.225 mole) of $NaNH_2$ at 50–60° under N_2. Six grams (0.0225 mole) of sulfone was added, and stirring at 50–60° was continued for 13 hr, followed by hydrolysis. The aqueous solution was extracted with CH_2Cl_2; the organic phase was washed thoroughly with water and dried. Evaporation of the solvent left a solid which was recrystallized again from benzene–hexane to give finally 0.80 g (17.4%) of methyl 1-naphthylmethyl sulfoxide, mp 89.5–90.5°. The structure of this compound was determined by comparison of infrared spectra and melting points with authentic samples of methyl 1-naphthylmethyl sulfoxide and methyl 2-naphthylmethyl sulfoxide.

Anal. Calcd for $C_{12}H_{12}SO$: C, 70.58; H, 5.92; S, 15.67; mol wt, 204. Found: C, 70.33; H, 6.10; S, 15.58; mol wt, 209.

Methyl 1-Naphthylmethyl Sulfoxide. Sodium methylmercaptide was prepared by dissolving 6.8 g (0.30 g-atom) of Na in 200 ml of anhydrous ethanol, then bubbling in 25 ml of condensed methylmercaptan. Fifty grams (0.283 mole) of 1-chloromethylnaphthalene in 25 ml of ethanol was added dropwise to the solution with ice-bath cooling and stirring. The mixture was allowed to stand overnight at room temperature; then the ethanol was removed and the product distilled, bp 130–138° (3.8 mm), $n^{19}D$ 1.6325. The liquid product crystallized from hexane to give 38.5 g (72.4%) of methyl 1-naphthylmethyl sulfide, mp 48–49.5°.

Anal. Calcd for $C_{12}H_{12}S$: C, 76.57; H, 6.43; S, 17.00; mol wt, 188. Found: C, 76.67; H, 6.21; S, 16.88; mol wt, 189.

Oxidation of the sulfide to the sulfoxide was carried out by Bordwell's procedure.[24] Ten grams (0.05 mole) of the sulfide in 55 g of acetic anhydride was cooled to −5° in an ice–salt bath. Fuming nitric acid (1.5 g) was added slowly and the solution was stirred at 0° for 12 hr, then allowed to warm to 15° overnight. The solution was poured onto ice and neutralized with potassium carbonate, then extracted with chloroform. The $CHCl_3$ extract was washed with water, dried, and stripped of the solvent, leaving an oil which was induced to crystallize only with difficulty from ethyl acetate. The product, 1.80 g (16.4%), melted at 89.0–90.5° and exhibited an infrared spectrum identical with that of the sulfoxide in part 9 above.

Methyl 2-Naphthylmethyl Sulfoxide. Sodium methylmercaptide (0.435 mole) was prepared as before, to which was added 96 g (0.43 mole) of 2-bromomethylnaphthalene in 50 ml of ethanol. The solvent was removed and the product distilled twice, yielding 45 g (55.6%) of methyl 2-naphthylmethyl sulfide, bp 108–117° (0.2 mm), $n^{30}D$ 1.6410.

Anal. Calcd for $C_{12}H_{12}S$: C, 76.57; H, 6.43; S, 17.00; mol wt, 188. Found: C, 76.81; H, 6.31; S, 16.84; mol wt, 187.

Oxidation of this sulfide to sulfoxide occurred in quantitative yield following the procedure of Shriner.[25] To 9.7 g (0.0515 mole) of sulfide dissolved in 65 ml of acetone and cooled to 0° was added 5.9 g of 30% H_2O_2 (0.052 mole). The solution was kept at room temperature for 24 hr; then the solvent was evaporated to give a 95% yield of sulfoxide which when recrystallized from benzene–hexane melted at 126–127°. The fingerprint region of the infrared spectrum of this compound was distinctly different from that of the sulfoxide in part 9.

Anal. Calcd for $C_{12}H_{12}SO$: C, 70.58; H, 5.92; S, 15.67; mol wt, 204. Found: C, 70.04; H, 5.72; S, 15.37; mol wt, 208.

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[24] F. G. Bordwell and P. J. Boutan, *J. Am. Chem. Soc.*, **79**, 717 (1957).

[25] R. L. Shriner, H. C. Struck, and W. J. Jorison, *ibid.*, **52**, 2060 (1930).