73.28; H, 3.50; N, 10.61. The degree of CT of 0.62 was deduced from the IR frequency (ω_{CN} = 2187 cm^{-1}).[17]

Iodine Complexes of DTPR and Ph_2DTPR. These iodine complexes were prepared from a CH_2Cl_2 solution of the donors and n-Bu_4NI_3 by electrochemical methods with a current of about 3 μA: DTPR-$I_{2.22}$, black needles, mp 138 °C dec. Anal. Calcd for $C_{18}H_{10}S_2I_{2.22}$: C, 37.79; H, 1.76. Found: C, 37.78; H, 1.79. Ph_2DTPR-$I_{1.8}$, dark green needles, mp 162 °C dec. Anal. Calcd for $C_{30}H_{18}S_2I_{1.8}$: C, 53.70; H, 2.70. Found: C, 53.68; H, 2.71.

DTPY-I_3. To a solution of DTPY (22 mg, 0.092 mmol) in 1,1,2-trichloroethane (50 mL) was added a solution of I_2 (50 mg, 0.20 mmol) in 1,1,2-trichloroethane. The resulting precipitates were collected by filtration and washed with CH_2Cl_2 to give black microcrystals: mp 104 °C dec. Anal. Calcd for $C_{14}H_8S_2I_3$: C, 27.08; H, 1.30. Found: C, 27.06; H, 1.35.

Crystal Structure Analyses. The single crystals of Ph_2DTPR-ClO_4 were obtained from dichloromethane solutions of Ph_2DTPR and n-Bu_4NClO_4 with a current of about 3 μA. The single crystals of $(Ph_2DTPY)_2$-I_3 were prepared by mixing a chlorobenzene solution of Ph_2DTPY and iodine. Intensities were collected by using a Rigaku automated 4-circle diffractometer with the Cu Kα radiation monochromatized by graphite. Numbers of the independent reflections are 3317, 3814, 835, and 3489 for Ph_2DTPR, Ph_2DTPR-ClO_4, DTPY, and $(Ph_2DTPY)_2$-I_3, respectively. The structures were solved by the Monte-Carlo direct method[29] by use of Multan-78 program system[30] and refined by the full-matrix least-squares method. the final R values were 0.042, 0.073, 0.044, and 0.059 for Ph_2DTPR, Ph_2DTPR-ClO_4, DTPY, and $(Ph_2DTPY)_2$-I_3, respectively. The atomic numbering schemes are shown in Figure 8.

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Supplementary Material Available: Tables of atomic and thermal parameters (4 pages). Ordering information is given on any current masthead page.

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Rearrangement of Benzylically Lithiated Methylaryl Alkyl Sulfones[1]

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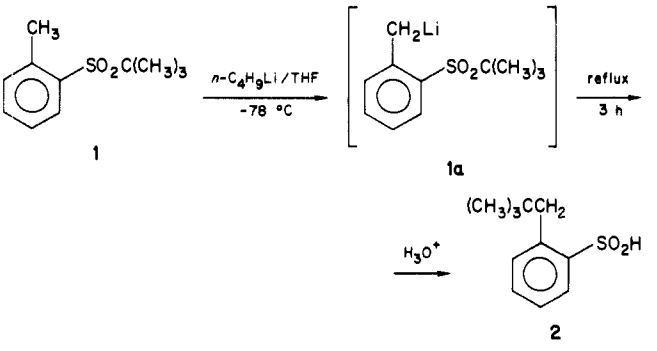
Abstract: Lithiation of appropriate methylaryl alkyl sulfones is followed by migration of the alkyl group from sulfur to the benzylic carbon. Product studies, relative reactivities, and crossover experiments are consistent with a radical-radical anion chain process for this rearrangement.

Directed lithiation[2,3] of aromatic compounds is a phenomenon of broad scope and considerable synthetic utility. Diaryl sulfones,[4] sulfonates,[5,6] and sulfonamides[5,7] are easily metalated, either at an open *ortho* position or at an *ortho* methyl grouping. Each of these three classes of organic sulfur compounds (when metalated at a benzylic site) can undergo rearrangement or coupling condensation, depending upon the starting material.

A previous communication[8] from this laboratory described the rearrangement of *o*-tolyl *tert*-butyl sulfone (**1**) after metalation by *n*-butyllithium in THF followed by several hours at reflux. The product *o*-neopentylbenzenesulfinic acid (**2**), was formed in 75-80% yield, constituting a Truce-Smiles rearrangement[9] with an *alkyl* group as the migrating unit.



1 1a 2

Under the influence of amide bases, *p*-methyl groups can also undergo metalation,[10] as with *p*-tolyl *tert*-butyl sulfone (**3**). The

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resulting metalated species (**3a**) readily rearranges to *p*-neopentylbenzenesulfinic acid (**4**) in a manner apparently analogous to the rearrangement of **1a**. In contrast to **1a**, however, the rearrangement of **3a** is facile even at room temperature and is virtually complete in about 2 h.

Mechanistically, such rearrangement of aryl alkyl sulfones appears to be different from that of the diaryl systems, which presumably follow two basic pathways:[9] (1) ipso displacement involving a Meisenheimer complex intermediate or a related transition state (stepwise or concerted); and (2) a cine substitution route, which involves internal Michael addition followed by β-elimination, as for α-naphthyl mesityl sulfone (**5**),[11] which rearranges via either route depending upon the base/solvent system employed. Furthermore, rearrangement of **1a**, via an intramolecular "S_N2-like" attack at a tertiary carbon with displacement of sulfinate, is unlikely considering that sulfinates are relatively poor leaving groups in nucleophilic displacements and few documented examples exist of S_N2-type reactions at tertiary carbons, even with good leaving groups.[12] Such a displacement with the para system **3a** would add the further requirement that the reaction be bimolecular.

A clue to what may be the operative process in these systems can be gained by examining work on nucleophilic substitution reactions proceeding by radical–radical anion chain mechanisms,[13,14] wherein sulfinate is a viable leaving group. Preliminary evidence for *free radical* intermediates in the rearrangements of benzylically lithiated methylaryl alkyl sulfones was developed with *o*-tolyl cumyl sulfone (**6**), which yielded radical combination products (**7** and **9**) in addition to normal rearrangement product **8**. The coupling products **7** and **9** were formed in approximately equimolar quantities, constituting evidence for free radicals playing a role in this process, since bicumyl, **7**, is known[15] to arise via dimerization of cumyl radicals.

$$o\text{-}CH_3C_6H_4SO_2C(CH_3)_2C_6H_5 \xrightarrow[\text{2. reflux, 8 h}]{\text{1. } n\text{-}C_4H_9Li,\ THF,\ -78\ ^\circ C} \underset{\mathbf{6}}{}$$

$$\xrightarrow{\text{3. } H_3O^+} C_6H_5C(CH_3)_2\underset{\mathbf{7}}{C}(CH_3)_2C_6H_5 +$$

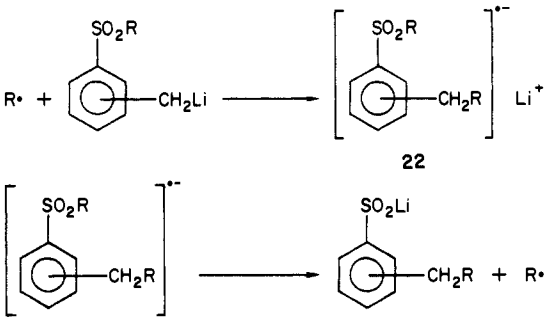
$$[o\text{-}C_6H_5C(CH_3)_2CH_2C_6H_4SO_2H + o,o'\text{-}(HO_2SC_6H_4CH_2)_2]$$
$$\underset{\mathbf{8}}{} \qquad \underset{\mathbf{9}}{}$$

$$\xrightarrow{Ni(R)} C_6H_5C(CH_3)_2CH_2C_6H_5 + C_6H_5CH_2CH_2C_6H_5$$
$$\underset{\mathbf{10}}{} \qquad \underset{\mathbf{11}}{}$$

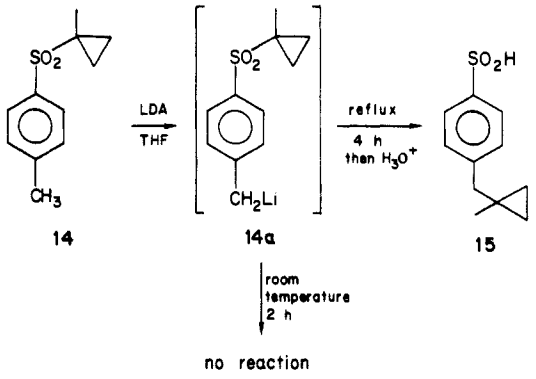
Another experiment supporting the intermediacy of free radicals was the lack of reactivity in a system, *o*-tolyl 1-methylcyclopropyl sulfone (**12**), wherein the "migrating group" corresponds to a less stable free radical.[16-18] Refluxing a THF solution of **12a** for several hours led only to recovery of over 90% starting material; the rearrangement product **13** was not detected.

The para analogue of **12**, *p*-tolyl 1-methylcyclopropyl sulfone (**14**), parallels the ortho system in its diminished reactivity relative

Scheme I



to its *tert*-butyl counterpart. Thus, although the metalated sulfone **14a** rearranges to the salt of sulfinic acid **15** when heated, reaction at room temperature is very sluggish and results in recovery of starting material.



Another *tert*-alkyl sulfone, 2,4-dimethylphenyl *tert*-amyl sulfone (**16**), was found to rearrange to the sulfinic acid **17** in yields comparable to those in the rearrangement of **1**.

When a mixture of **1** and **16** was metalated and refluxed in THF, and the resulting sulfinic acid mixture was desulfurized over Raney nickel, four hydrocarbons were obtained in approximately equimolar quantities. Two of these, **18** and **19**, correspond to the expected rearrangement products of **1** and **16**, respectively. The remaining two, **20** and **21**, are crossover products corresponding to an intermolecular process.

$$o\text{-}CH_3C_6H_4SO_2C(CH_3)_3 +$$
$$\underset{\mathbf{1}}{}$$

$$2,4\text{-}(CH_3)_2C_6H_3SO_2C(CH_3)_2CH_2CH_3 \xrightarrow[\text{2. reflux, 8 h}]{\text{1. } n\text{-}C_4H_9Li,\ THF,\ -78\ ^\circ C}$$
$$\underset{\mathbf{16}}{} \qquad \xrightarrow{\text{3. } H_3O^+}$$

$$\text{mixture of sulfinic acids} \xrightarrow{Ni(R)}$$

$$C_6H_5CH_2C(CH_3)_3 + m\text{-}CH_3C_6H_4CH_2C(CH_3)_2CH_2CH_3 +$$
$$\underset{\mathbf{18}}{} \qquad \underset{\mathbf{19}}{}$$
$$C_6H_5CH_2C(CH_3)_2CH_2CH_3 + m\text{-}CH_3C_6H_4CH_2C(CH_3)_3$$
$$\underset{\mathbf{20}}{} \qquad \underset{\mathbf{21}}{}$$

The absence of bibenzylic coupling products from **1** and **16** obviates a simple fragmentation–recombination sequence.[19] Instead, the fragmentations of radical anions (presumed intermediates in reductive cleavages of sulfones[20-22]) and the analogy of the nitrocumyl systems[13] suggest formation of **22** via attack by a *tert*-butyl radical on **1a**. Fragmentation of **22** would be expected to yield the anion of **2** plus regeneration of *tert*-butyl radical in chain fashion, as depicted in Scheme I. In such a chain reaction, only trace quantities of symmetrical coupling products

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would be formed since the requisite radical species would be present in only a very low concentration. The presence of these radicals could be increased, however, by an increase in the rate of formation (stability) of the radicals and/or factors such as steric effects which would prevent the attack of the free radical on lithiated sulfone. Such might be the case with the cumyl system **6** where, in the proposed chain reaction, the relatively stable cumyl radical would need to attack **6a** at a benzylic position ortho to the extremely bulky cumylsulfonyl unit. By contrast, *p*-tolyl cumyl sulfone (**23**) is metalated by LDA at −78 °C to give **23a**, which rearranges at room temperature to yield **24** in 67% yield (based on isolated, purified benzyl sulfone derivative **25**).

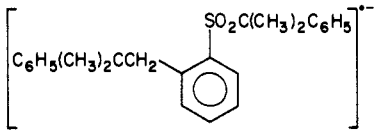
$$p\text{-}CH_3C_6H_4SO_2C(CH_3)_2C_6H_5 \xrightarrow[-78\ ^\circ C]{\text{LDA/THF}} \xrightarrow[\text{then overnight}]{-78\ ^\circ C \text{ to room temp}} p\text{-}C_6H_5C(CH_3)_2CH_2C_6H_4SO_2X$$

23

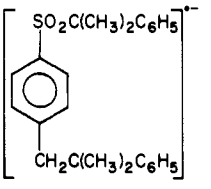
24: X = Li
25: X = $CH_2C_6H_5$

It is interesting to note that bicumyl (**7**) is not formed in more than trace amounts in the rearrangement of **23**, nor is bibenzylic coupling product, **26** (p,p'-$(LiO_2SC_6H_4CH_2)_2$).

The results on sulfones **6** and **23** are reasonable considering the structures of sulfone radical anions formed by attack of cumyl radical on **6a** and **23a** (**27** and **28**, respectively). The sterically more strained structure **27** predicts that approach of cumyl radical to the benzylic position of **6a** would be hindered. The anticipated buildup of cumyl radicals would account for a greater amount of radical coupling. This difficulty does not arise in the formation of **28**.



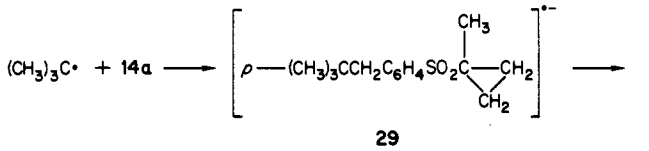
27



28

The most compelling evidence for the chain process shown in Scheme I was obtained by taking advantage of the very different reactivities of the *tert*-butyl (**3**) and 1-methylcyclopropyl sulfones (**14**). As already mentioned, **14a** is relatively unreactive at room temperature while **3a** reacts rapidly under the same conditions. Assuming the unreactivity of **14a** to be due to difficulty of generating 1-methylcyclopropyl radical in the initiation step, another radical source, such as **3a**, should facilitate the rearrangement of lithiated 1-methylcyclopropyl sulfone.

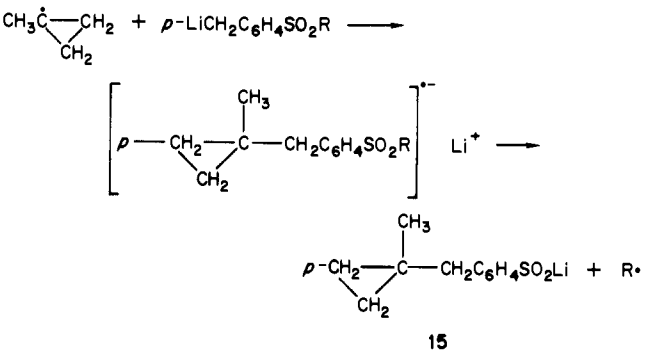
Attack of *tert*-butyl radical should occur unselectively on both **3a** and **14a**, leading readily to radical anion **29** (from **14a**). Upon fragmentation of **29**, the 1-methylcyclopropyl radical necessary to generate **15** becomes available. Probably more reactive[16,17] than *tert*-butyl, it would rapidly attack **3a** or **14a** to give a radical anion which would eventually cleave to give **15** and another radical to continue the chain.



29

$$4^- + CH_3\dot{C}(CH_2)_2$$

On the basis of this reasoning, a mixture of **3a** and **14a** should yield, at *room temperature*, both products **4** and **15**, even though **14a** alone does not react. When a mixture of **3** and **14** was metalated with LDA in THF and the resulting mixture stirred at room temperature for 2 h, followed by extraction with water and derivatization with benzyl chloride, the product was a mixture of the benzyl sulfones of **4** and **15** in an approximately 2:1 molar ratio, respectively.[23]



15

In conclusion, the reaction of **14** in the presence of **3**, under conditions where the former compound alone is unreactive, constitutes evidence for an intermolecular mechanism for these rearrangements. Since other data show that radical intermediates appear to be involved, a plausible pathway appears to be a radical–radical anion chain process.

Experimental Section

General. All melting points were taken on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Proton magnetic resonance spectra were recorded on a Varian A-60A or a Perkin-Elmer R-32 spectrometer with Me_4Si as an internal standard. Infrared spectra were recorded on a Beckman IR-33 or a Perkin-Elmer 267 spectrometer. Mass spectra were obtained from the Purdue University Mass Spectrometry Center under the direction of R. G. Cooks and staff. *n*-Butyllithium was purchased from Alfa Inorganics (Ventron) or Aldrich Chemical Co. THF solvent was distilled from benzophenone ketyl immediately prior to use. All reactions involving *n*-butyllithium were conducted under an atmosphere of nitrogen or argon.

Sulfones **1**, **3**,[24] and **16** were synthesized by acid-catalyzed alkylation[25] of the appropriate thiophenol by a tertiary alcohol followed by oxidation (30% H_2O_2, acetic acid, reflux).[26]

***o*-Tolyl *tert*-butyl sulfone (1)**: mp 100–100.5 °C (recrystallized from 95% ethanol); NMR ($CDCl_3$) δ 1.35 (s, 9), 2.7 (s, 3), 7.25–7.5 (m, 3), 7.6–8.0 (m, 1); IR (KBr) 1270 and 1110 cm^{-1} (SO_2); EIMS, high resolution, MS, calcd for $C_{11}H_{16}O_2S$ 212.087, found 212.090.

2,4-Xylyl *tert*-amyl sulfone (16): mp 33–35 °C (recrystallized from hexane); NMR ($CDCl_3$) δ 0.9 (t, J = 8 Hz, 3), 1.25 (s, 6), 1.75 (q, J = 8 Hz, 2), 2.35 (s, 3), 2.65 (s, 3), 7.0–7.2 (m, 2), 7.8 (d, J = 9 Hz, 1); IR (KBr) 1260 and 1080 cm^{-1} (SO_2); EIMS, high resolution, MS, calcd for $C_{13}H_{20}O_2S$ 240.118, found 240.117.

***o*-Tolyl 2-phenyl-2-propyl sulfone (6)**: 2-Phenyl-2-propanol (13.3 g, 0.10 mol) in THF (50 mL) was added over 1.5 h to a vigorously stirred solution of *o*-thiocresol (12 g, 0.097 mol) in aqueous sulfuric acid (50% (v/v)). After a further 30 min, the mixture was poured over ice and extracted with ether. The ether extracts were washed with 5% NaOH and water, dried ($MgSO_4$), and stripped of solvent. Next 7.3 g (0.03 mol) of the resulting product was oxidized by *m*-chloroperoxybenzoic acid (2 equiv) in methylene chloride (150 mL) at room temperature for 48 h. The mixture was cooled to 0 °C, filtered, washed with 5% NaOH and saturated sodium thiosulfate, dried ($MgSO_4$), and stripped of solvent. The product was recrystallized from 95% ethanol (yield 6.5 g, 80%): mp 94–95 °C; NMR ($CDCl_3$) δ 1.8 (s, 6), 1.92 (s, 3), 7.0–7.7 (m, 10); IR (KBr) 1270 and 1140 cm^{-1} (SO_2); EIMS, high resolution, MW calcd for $C_{16}H_{18}O_2S$ 274.102, found 274.106.

1-Methylcyclopropyl *p*-Tolyl Sulfone (14). *p*-Thiocresol (21.75 g, 0.175 mol) and 85% crotonaldehyde (20 mL) were dissolved in 250 mL of 95% ethanol at room temperature. Triethylamine (0.7 mL) was added and the solution was stirred 3 h and then cooled to 0 °C. Sodium borohydride (6 g) was added and the solution was allowed to warm to room temperature and stirred overnight. An equal volume of water was added and the suspension was acidified. The ethanol was evaporated and the remaining two-phase mixture was separated. The organic phase was identified (NMR) as crude 3-*p*-toluenethio-1-butanol (34.02 g, 99%).

(23) We also attempted a similar crossover experiment using the *o*-tolyl sulfones **1** and **12**. Some of the less reactive **12** was consumed, indicating a possibility that a similar process was involved, since **12** alone is unreactive, but the product mixture was complex and it was difficult to determine whether **13** had formed.

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This was converted to the corresponding chloride with thionyl chloride in 89% yield. Oxidation (30% H_2O_2, acetic acid) gave a 64% yield of sulfone, which was converted to **14** by treatment with *n*-butyllithium (2 equiv) in THF (200 mL) at room temperature for 3 h. Water and ether were added and the organic phase was separated and evaporated. The crude product was crystallized from 95% ethanol. This gave 7.33 g (54%) of **14**: mp 80.5–81.5 °C; NMR ($CDCl_3$) δ 0.8 (m, 2), 1.32 (s, 3), 1.57 (m, 2), 2.45 (s, 3), 7.33–7.73 (AB, J = 8 Hz, 4); IR 1280 and 1130 cm^{-1} (SO_2). Anal Calcd for $C_{11}H_{14}O_2S$: C, 62.83; H, 6.71; S, 15.25. Found: C, 63.17; H, 6.99; S, 14.90.

1-Methylcyclopropyl *o*-Tolyl Sulfone (12). The procedure used in the synthesis of **14** was modified as follows. Starting materials were thiophenol (*o*-thiocresol failed to react) and crotonaldehyde. The intermediate 3-(phenylthio)-1-butanol was converted to the chloride with triphenylphosphine/CCl_4.[27] Oxidation and cyclization gave 1-methylcyclopropyl phenyl sulfone which was metalated (*n*-butyllithium, THF, −78 °C) and treated with methyl iodide (excess). Water and ether were added to the solution, the organic phase was dried (saturated NaCl, then $MgSO_4$) and evaporated, and the residue was recrystallized from 95% ethanol to give **12**: mp 60.5–61 °C; NMR ($CDCl_3$) δ 0.75–0.95 (m, 2), 1.27 (s, 3), 1.5–1.7 (m, 2), 2.67 (s, 3), 7.2–7.6 (m, 3), 7.9–8.1 (m, 1); IR 1285 and 1140 cm^{-1} (SO_2). Anal. Calcd for $C_{11}H_{14}O_2S$: C, 62.83; H, 6.71; S, 15.25. Found: C, 62.81; H, 6.95; S, 15.45.

General Procedure for the Rearrangement of Metalated Methylaryl *tert*-Alkyl Sulfones. A THF solution of the sulfone was metalated at −78 or 0 °C with 1–1.5 equiv of *n*-Butyllithium (if ortho substituted) or LDA (if para substituted; *o*-methyl could also be metalated with LDA). Metalated *o*-tolyl sulfones were refluxed 4–8 h, and the para analogues were held at room temperature 2–16 h (with the exception of **14**).

Isolation of the ortho-substituted acids involved pouring the reaction mixture into 5% NaOH, extraction with ether, acidification (HCl) of the alkaline solution, and separation of the precipitated acid. Prolonged storage over P_2O_5 in vacuo did not dry the acid completely. Derivatization was difficult and will be described for each substrate employed.

The para acids were not isolated. The reaction mixture was diluted with ether and extracted with water. The aqueous extracts were combined with an equal volume of 95% ethanol and treated with 1.5–2 equiv of benzyl chloride. Heating the derivatization mixture 15 min followed by cooling led to crystallization of the benzyl sulfone derivative. Analytical samples were prepared by a second recrystallization from 95% ethanol.

Rearrangement of *o*-Tolyl *tert*-Butyl Sulfone (1). The crude **2** (7.20 g, 72%) derived from 10 g (0.047 mol) of **1** according to the general procedure was derivatized by stirring a solution of the sodium salt of **1** (1.0 g, 0.005 mol) in 100% ethanol with 3 g of anhydrous Na_2SO_4 and excess methyl iodide for 1 week. The solution was filtered and evaporated with the residue dissolved in ether. The solution was washed with 5% NaOH, aqueous sodium thiosulfate, and water. Drying ($MgSO_4$) and evaporation gave an oil (0.57 g, 40%), identified by NMR as a mixture of sulfone and sulfinate (3:1, respectively). Chromatography (SiO_2, $CHCl_3$/pentane, 1/1) followed by crystallization (95% ethanol) gave *o*-neopentylphenyl methyl sulfone: mp 58–59 °C; NMR ($CDCl_3$) δ 1.0 (s, 9), 3.02 (s, 3), 3.08 (s, 2), 7.3-7.6 (m, 3), 8.0–8.15 (m, 1); IR (KBr) 1280 and 1120 cm^{-1} (SO_2); MS, high resolution, calcd for $C_{12}H_{18}O_2S$ 226.102, found 226.102.

Rearrangement of 2,4-Xylyl *tert*-Amyl Sulfone (16): 3.5 g (0.0146 mol) of **16** and 1.1 equiv of *n*-butyllithium in 75 mL of THF (reflux 8 h) gave 2.53 g (72%) of crude **17**. This was converted to its sodium salt and derivatized with 2-bromo-2-nitropropane[29] to give a brown oil which was chromatographed over SiO_2 ($CHCl_3$ eluent). This provided 2-(2,2-dimethyl-1-butyl)-4-methylphenyl α-nitroisopropyl sulfone as a clear oil: NMR ($CDCl_3$) δ 0.8–1.4 (m overlapping sharp singlet at 0.85, 11), 1.96 (s, 6), 2.50 (s, 3), 2.65 (s, 2) 7.1–7.3 (m, 2), 7.7–7.9 (m, 1); IR (neat) 1540 and 1320 (NO_2), 1310 and 1140 cm^{-1} (SO_2); MS exact mass, calcd for $C_{16}H_{25}NO_4S$ 327.151, found 327.156.

Mixed Rearrangement of Sulfones 1 and 16. The mixture of sulfinic acids (7.9 g) derived from the reaction of **1** (5.0 g, 0.0236 mol) and **16** (5.36 g, 0.0236 mol) with *n*-butyllithium in 250 mL of THF (reflux, 8 h) was desulfurized by refluxing **24** with Raney nickel (25 g) in 95% ethanol (50 mL). Filtration and evaporation gave 3.2 g of an oil which was found by GLC (SE-30, 70 °C) to be a mixture of four hydrocarbons in approximately equimolar quantities. The first was identified as 2,2-dimethylpropylbenzene (**18**) by coinjection of an authentic sample. Coinjection of bibenzyl (**11**) confirmed that it was not among the products. The remaining three were identified by NMR (in order of increasing retention times) as 1-(2,2-dimethylpropyl)-2-methylbenzene (**21**) (NMR ($CDCl_3$) δ 0.9 (s, 9), 2.35 (s, 3), 2.48 (s, 2), 6.8–7.1 (m, 4); 2,2-dimethyl-1-phenylbutane[30] (**20**): NMR ($CDCl_3$) δ 0.8–1.3 (m overlapping s at 0.84, 11), 2.5 (s, 2), 7.1–7.3 (m, 5)) and 3-(2,2-dimethyl-1-butyl)-1-methylbenzene (**19**) (NMR ($CDCl_3$) δ 0.8–1.3 (m, overlapping s at 0.84, 11), 2.35 (s, 3), 2.46 (s, 2), 6.8–7.2 (m, 3)).

Rearrangement of *o*-Tolyl 2-Phenyl-2-propyl Sulfone (6). A solution of **6** (3.0 g, 0.011 mol) and *n*-butyllithium (1.1 equiv) in THF (80 mL) was refluxed 8 h. The normal workup was not performed. Instead, 0.2 mL of water was added and the solution evaporated to give a yellow powder which was refluxed with pentane. The pentane was washed with 5% NaOH and dried ($MgSO_4$). Removal of solvent gave 0.40 g (15%) of 2,3-dimethyl-2,3-diphenylbutane (**7**).[31]

The remaining solid was desulfurized with Raney nickel in refluxing ethanol. After the solution was filtered and the solvent removed, the remaining oil was dissolved in ether, washed with 5% NaOH, dried over $MgSO_4$, and evaporated to give 0.95 g of a yellow oil which was separated by GLC (SE-30, 120°) into two components identified as 1,2-diphenyl-2-methylpropane (**10**)[32] and bibenzyl (**11**) in a molar ratio of 70:30, respectively, by NMR integration of the desulfurization product.

Rearrangement of *p*-Tolyl *tert*-Butyl Sulfone (3).[24] The sulfone **3** (4.08 g, 0.019 mol) and LDA (0.027 mol) in THF (40 mL) were stirred at room temperature for 2 h. Derivatization with benzyl chloride gave 3.92 g (67%) benzyl *p*-neopentylphenyl sulfone (**4'**): mp 147–149 °C; NMR ($CDCl_3$) δ 0.86 (s, 9), 2.53 (s, 2), 4.27 (s, 2), 7.2–7.6 (AB, J = 8 Hz, 4), 6.95–7.33 (m, 5); IR 1295, 1152 cm^{-1} (SO_2); MS (EI, 70 eV) m/z (relative intensity) 91 (100), 57 (22), (CI, 70 eV), 303 (100, M + 1), 304 (18), 213 (19), 92 (18). Anal Calcd for $C_{18}H_{22}O_2S$: C, 71.48; H, 7.33; S, 10.60. Found: C, 71.59; H, 7.43; S, 10.77.

Rearrangement of 1-Methylcyclopropyl *p*-Tolyl Sulfone (14). The reaction of **14** (2.39 g, 0.011 mol) and LDA (0.013 mol) in THF (60 mL) at 0 °C for 10 min, then reflux 8 h, was worked up as for the ortho acids (i.e., free acid was isolated) to give crude **15** (1.75 g, 85%), which was then converted to benzyl *p*-(1-methylcyclopropylmethyl)phenyl sulfone (**15'**). An analytical sample was prepared by column chromatography (SiO_2, CH_2Cl_2) followed by crystallization from 95% ethanol: mp 103–105 °C; NMR ($CDCl_3$) δ 0.25–0.50 (m, 4), 0.92 (s, 3), 2.62 (s, 3), 4.29 (s, 2), 7.2–7.6 (AB, J = 8 Hz, 4), 7.2–7.5 (m, 5); IR 1306 cm^{-1} (SO_2); MS (CI, 70 eV) m/z (relative intensity), 301 (100, M + 1), 211 (32), 92 (13). Anal. Calcd for $C_{18}H_{20}O_2S$: C, 71.96; H, 6.71; S, 10.67. Found: C, 71.64; H, 6.74; S, 10.36. Another experiment, identical except for temperature (room temperature) and time (2.5 h), gave recovered **14**.

Crossover Experiment Using Sulfones 3 and 14. A solution of **3** (1.0 g, 0.0047 mol) and **14** (1.0 g, 0.0048 mol) in THF (25 mL) was added to LDA (0.011 mol) in THF (30 mL) at 0 °C. The solution was kept 10 min at 0 °C and then 2.5 h at room temperature and worked up according to the general procedure. The mixture of benzyl sulfones (1.28 g) was found by NMR integration to consist of the derivatives of **4** and **15** (**4'** and **15'**) in an approximate ratio of 2:1, respectively.

A mass spectrum (CI) of the product mixture was also obtained: m/z (relative intensity) 303 (M + 1 of **4'**, 100), 301 (M + 1 of **15'**, 56).[33]

Rearrangement of *p*-Tolyl 2-Phenyl-2-propyl Sulfone (23). Sulfone **23** (1.30 g, 0.0047 mol) in 15 mL of THF was added to LDA (0.005 mol) in 10 mL of THF at −78 °C. The reaction mixture was warmed to room temperature and stirred overnight. Standard workup gave 1-(4-phenylmethylsulfonylphenyl)-2-phenyl-2-methylpropane (**25**): mp 114–115 °C; NMR ($CDCl_3$) δ 1.31 (s, 6), 2.90 (s, 2), 4.25 (s, 2), 6.76–7.41 (AB, J = 8 Hz, 4), 6.96–7.24 (m, 10); IR (Nujol) 1300, 1165 cm^{-1} (SO_2). Anal. Calcd for $C_{23}H_{24}O_2S$: C, 75.79; H, 6.64; S, 8.80. Found: C, 75.63; H, 6.75; S, 9.05.

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