

Table II
 $k_{o\text{-obs}}/k_{o\text{-exd}}^a$ and $k_{o\text{-obs}}/k_{p\text{-exd}}$ Values for Reactions of
 2,4-Dinitrophenyl Ethers with MeO^- and MeS^-

Substituent	MeO^-		MeS^-	
	A	B	A	B
NO_2	0.12	0.16	0.18	0.26
OCH_3	0.58	0.39	0.77	0.58

^a $k_{o\text{-exd}}$ was calculated from ρ and σ^o ortho values.

studies,¹² based upon reactions between halogenbenzothiazoles and thioalkoxy ions, high steric retardation occurred only with α -branched nucleophiles; in contrast, when the bulky group was moved further away in β position, there was an increase of reactivity owing to increasing basicity. In addition, substituting¹³ oxygen for sulfur in these hindered nucleophiles caused a higher steric effect.

Since geometry at the reaction center closely approximates tetrahedral structure and free rotation exists around the linkage between the reaction carbon center and leaving group in the transition state, the distance between the displaced group on one side and both the entering group and the benzenoid substrate ring on the other side must be approximately the same. This mitigates against assigning the observed effects exclusively to steric compression during the transition state either between leaving group and entering group or between leaving group and hydrogen and carbon atoms of the substrate.

Nevertheless, the observed lessening of steric phenomena, when the nucleophile is thiomethoxide ion, strongly suggests that in this case the interaction with benzenoid substrate ring is less important.

Finally, assuming complete lack of steric effects for thioethers, σ^o ortho values of *o*-nitro (+0.93) and *o*-methoxy groups (-0.26) can be calculated.¹⁴

Thus we can estimate the actual steric retardation as expressed by $k_{o\text{-obs}}/k_{o\text{-exd}}$ ratio, where $k_{o\text{-exd}}$ represents the expected rate constant in the absence of steric phenomena and $k_{o\text{-obs}}$ is the experimental one. In Table II these ratio values are compared with $k_{o\text{-obs}}/k_{p\text{-obs}}$ values, which would represent a more immediate, but an approximate valuation of steric effects. $k_{o\text{-obs}}/k_{o\text{-exd}}$ ratios are somewhat higher for the nitro group and somewhat less for the methoxy group. This can be taken as additional evidence that contribution of electronic effect should be accounted for in order to evaluate steric effects with a high degree of accuracy.

Experimental Section

Materials. Methanol (reagent grade) was purified by distillation over magnesium. 2,4-Dinitrophenyl ethers were prepared by refluxing a mixture, prepared from 0.2 mol of the appropriate phenol and 0.1 mol of NaOH in 50 ml of methanol, with 0.1 mol of 2,4-dinitrochlorobenzene in 50 ml of methanol. The mixture was diluted with a large amount of alkaline water and then quickly filtered. The precipitated product was washed and crystallized from ethanol. Thioethers were prepared by the same procedure from 0.1 mol of the appropriate thiophenol and 0.1 mol of 2,4-dinitrochlorobenzene by performing the reaction at room temperature.

Rate Measurements. Reactions of Diphenyl Ethers with MeO^- . For all derivatives kinetic experiments were performed by following the appearance of phenoxide ions. The same titrimetric procedure as described by Ogata¹⁷ was used. When possible, a spectrophotometric procedure was also applied. This was for example the case of *Z'*-nitro substituted compounds. These reactions (performed under pseudo-first-order conditions) were run in the thermostatic cells of a Gilford automatic spectrophotometric apparatus, by following the appearance of the developed nitrophenoxide ion at the appropriate wavelength.

Reactions of Diphenyl Thioethers with MeO^- . Kinetic experiments were performed by following the appearance of thiophenoxide ions by the iodimetric method.¹⁸

In the case of nitro-substituted compounds an additional spectrophotometric procedure, as above described, was also applied.

Reactions of Diphenyl Thioethers with MeS^- . A spectrophotometric procedure was used for all kinetic experiments, by following the appearance of reaction products (2,4-dinitrophenyl methyl thioether) except in the case of nitro derivatives, in which the appearance of nitrophenoxide ions was again followed. For this very fast system the Durrum-Gibson stopped-flow apparatus was used.

In all cases, in which two different kinetic procedures were applied, a good agreement of calculated second-order rate constants was obtained.

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Registry No.—1-(2-Methoxyphenoxy)-2,4-dinitrobenzene, 2363-29-3; 1-(4-methoxyphenoxy)-2,4-dinitrobenzene, 2363-27-1; 2,4-dinitrophenyl *p*-tolyl ether, 2363-25-9; 2,4-dinitrophenyl phenyl ether, 2486-07-9; *m*-chlorophenyl 2,4-dinitrophenyl ether, 2363-38-4; 2,4-dinitrophenyl *m*-nitrophenyl ether, 2548-97-2; 2,4-dinitrophenyl *p*-nitrophenyl ether, 2363-36-2; 2,4-dinitrophenyl *o*-nitrophenyl ether, 2363-39-5; 1-[(2-methoxyphenyl)thio]-2,4-dinitrobenzene, 42178-88-1; 1-[(4-methoxyphenyl)thio]-2,4-dinitrobenzene, 1871-44-9; 2,4-dinitrophenyl *p*-tolyl sulfide, 20114-05-0; 2,4-dinitrophenyl phenyl sulfide, 2486-09-1; *m*-chlorophenyl 2,4-dinitrophenyl sulfide, 56679-05-1; 2,4-dinitrophenyl *m*-nitrophenyl sulfide, 1657-86-9; 2,4-dinitrophenyl *p*-nitrophenyl sulfide, 20834-66-6; 2,4-dinitrophenyl *o*-nitrophenyl sulfide, 20834-65-5; CH_3O^- , 3315-60-4; CH_3S^- , 17302-63-5.

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Nucleophilic Displacements on Halogen Atoms. VI.¹ Determination of σ^- Values for the Carboxyl, Carboethoxy, and Methylsulfonyl Groups.

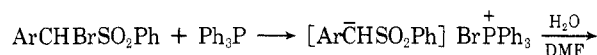
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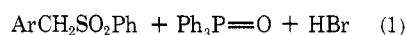
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Recently, we² have shown that the reaction of triphenylphosphine (TPP) with α -halobenzyl phenyl sulfones in

aqueous dimethylformamide (DMF) leads to the reduced sulfone **2** and triphenylphosphine oxide in quantitative yield (e.g., eq 1). The rates of these reactions show excel-



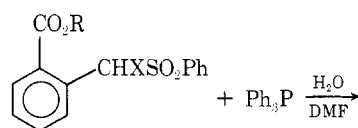
- 1a, Ar = *p*-HOCC₆H₄
 b, Ar = *p*-C₂H₅OCC₆H₄
 c, Ar = *p*-CH₃SO₂C₆H₄



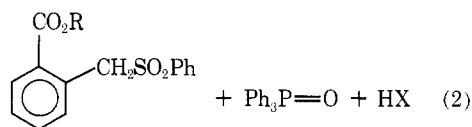
- 2a, Ar = *p*-HOCC₆H₄
 b, Ar = *p*-C₂H₅OCC₆H₄
 c, Ar = *p*-CH₃SO₂C₆H₄

lent correlations with σ^- values (determined from the acidity of phenols)³ and yield large positive values of ρ . An interesting feature of this reaction is that carbanions are generated under neutral and even acidic conditions which then allows the determination of certain quantities which could not be measured under basic conditions. We have utilized this characteristic to determine a σ^- value for the carboxyl group which would not remain un-ionized under basic condition, thus precluding a determination of this value from the ionization of phenols.

The standard reaction used (eq 1) was the reaction of α -bromobenzyl phenyl sulfones with TPP in 90% aqueous DMF at 25° which was shown to give a ρ value of 5.97 ($r = 0.998$).² Three new σ^- values were determined from this reaction: (COOH) $\sigma^- = 0.61$ ($\sigma_a^- = 0.73$);⁴ (COOC₂H₅) $\sigma^- = 0.65$ ($\sigma_a^- = 0.68$);⁴ (CH₃SO₂) $\sigma^- = 0.82$ ($\sigma_a^- = 1.13^5$ and 1.14^6 ; $\sigma_p^- = 0.98^5$). The σ^- value for the carbethoxy group is close to that reported earlier,^{3a} but (COOH) σ^- is significantly lower than the σ_a^- value.^{3a} In fact, for reaction 1, we find the carbethoxy group to be a stronger electron-withdrawing group than is the carboxyl group, a result which is at variance with a number of previous studies.⁷ The α -bromo-*p*-carbethoxybenzyl phenyl sulfone (**1b**) reacts ca. twice as fast as the acid **1a** with TPP at 25° (Table II). This result is not unique in this system. In the reaction of TPP with the ortho isomers **3a** and **3b** (eq 2), the ester also is



- 3a, R = H; X = Br
 b, R = C₂H₅; X = Br
 4a, R = H; X = I
 b, R = C₂H₅; X = I



more reactive than the acid. However, for the corresponding iodides **4**, the reverse holds, i.e., the acid **4a** reacts slightly faster than the ester **4b** (Table III). However, the reactivities of the acids and esters are so similar that subtle differences in solvation could easily account for their behavior.

The σ^- value for the *p*-methylsulfonyl group is significantly lower than the σ^- values determined either from the acidity of phenols or anilinium ions. Somewhat surprisingly, our value agrees with the σ^- value determined from the ionization of thiophenols ($\sigma^- = 0.82$).⁹ The relative magnitude of the σ^- value(s) of a substituent often is taken as a measure of the resonance interaction between the substituent and the reaction center.¹⁰ The σ^- values reported for

Table I
Rate Constants for the Reaction of α -Bromobenzyl Phenyl Sulfones **1** with TPP in 90% Aqueous DMF

Compd	Temp, °C ($\pm 0.05^\circ$)	$k, M^{-1} \text{ sec}^{-1}$
1a	20.00	2.25×10^{-3}
	30.00	5.05×10^{-3}
	40.00	9.19×10^{-3}
1b	10.00	2.40×10^{-3}
	20.00	5.33×10^{-3}
	30.00	1.15×10^{-2}
1c	25.00	8.29×10^{-2}

Table II
Rate Constants and Activation Parameters for the Reaction of α -Bromobenzyl Phenyl Sulfones **1a** and **1b** with TPP in 90% Aqueous DMF at 25°

Compd	$k, M^{-1} \text{ sec}^{-1}$	$\Delta H,^\ddagger \text{ kcal/mol}$	$\Delta S,^\ddagger \text{ eu}$
1a	3.38×10^{-3}	12.1 ± 0.7	-32 ± 2
1b	7.89×10^{-3}	12.8 ± 0.8	-25 ± 2

Table III
Rate Constants for the Reactions of α -Bromo- and α -Iodo-*o*-carboxybenzyl Phenyl Sulfones (**3a** and **4a**) and α -Bromo- and α -Iodo-*o*-carbethoxybenzyl Phenyl Sulfones (**3b** and **4b**) with TPP in 90% Aqueous DMF at 60.0°

Compd	$k, M^{-1} \text{ sec}^{-1}$
3a	3.46×10^{-3}
3b	8.09×10^{-3}
4a	1.18×10^{-3}
4b	7.03×10^{-4}

these substituents are significantly higher than the normal σ^- values,⁷ which indicates a strong resonance interaction between the reaction site (a carbanion)¹¹ and the substituent. The σ^- values tend to have some degree of spread depending upon the reaction system,^{3,7,10} and this appears to be particularly true of the *p*-methylsulfonyl group. We find that for reaction 1, a plot of $\log k/k_0$ vs. σ^- gives an excellent correlation with the σ^- values determined from the ionization of phenols for NO₂, CN, CH₃CO, and COOC₂H₅, but for *p*-COOH and *p*-CH₃SO₂, the σ^- values reported earlier give a rather poor fit with our rate data (Tables I and II).

Experimental Section

Melting points reported in this section were taken on Fisher-Johns and Mel-Temp apparatus and are not corrected. The NMR spectra were recorded on a Varian Associates A-60D and Varian Associates EM 360 NMR spectrometer operating at ambient temperature. All spectra were taken in carbon tetrachloride or deuteriochloroform with tetramethylsilane (δ 0.00) as an internal standard. The ir spectra were taken on a Perkin-Elmer 337 or Beckman IR-8 infrared spectrometer. The ir spectra of analytically pure samples were taken in carbon tetrachloride or as KBr pellets. Polystyrene absorptions at 1028.0 and 1601.4 cm⁻¹ were used for calibration of ir spectra. Elemental analyses were performed by Dr. Franz Kasler of the University of Maryland.

α -Carbethoxybenzyl Phenyl Sulfone (2b). To a dry 100-ml round-bottom flask, equipped with a reflux condenser and a drying tube, containing 10 g (65 mmol) of *p*-toluoyl chloride was added 25 ml of sulfuric chloride. Two sun lamps (G. E. 250 W) were placed 0.5 in. from the flask. The course of the reaction was followed by NMR spectroscopy. The reaction was complete after 10 hr of irradiation, and the excess sulfuric chloride was removed in vacuo. To the remaining oil was added 20 ml of absolute ethanol. In a separate flask, thiophenol (7.1 g, 64.5 mmol) was added dropwise to a solution of 4.00 g (71.5 mmol) of potassium hydrox-

ide in 50 ml of 95% ethanol. The thiophenoxide solution was added dropwise to the chloride solution with stirring. After 4 hr, the solution was poured into 400 ml of water. The solution was extracted twice with 150-ml portions of ether. The ether layer was washed twice each with 100 ml of dilute potassium hydroxide solution and 100 ml of water and dried (MgSO_4), and the ether was removed in vacuo. The residual oil was dissolved in 100 ml of glacial acetic acid, and the solution was chilled in an ice-water bath. To this solution was added dropwise 20 ml of 30% hydrogen peroxide. After standing overnight at room temperature, the solution was poured into 500 ml of water and extracted twice with 150-ml portions of ether. The ether extracts were combined and washed once with 200 ml of water and twice with 150 ml of saturated sodium bicarbonate solution followed once by 200 ml of water. The ether was dried with anhydrous magnesium sulfate and removed in vacuo. Crystallization from dichloromethane-Skellysolve B gave 8.93 g (45%) of **2b**: mp 112°; ir (KBr) 1700 (C=O), 1310 and 1150 cm^{-1} (SO_2); NMR (CDCl_3) 1.42 (t, $J = 7$ Hz, 3 H), 4.35 (s, 2 H), 4.40 (q, $J = 7$ Hz, 2 H), and 7.0–8.0 ppm (m, 9 H).

Anal. Calcd for $\text{C}_{16}\text{H}_{16}\text{O}_4\text{S}$: C, 63.16; H, 5.26. Found: C, 62.88; H, 5.33.

α -Bromo-*p*-Carbomethoxybenzyl Phenyl Sulfone (1b). One gram (3.0 mmol) of **2b** was dissolved in 15 ml of dry DMF in a dry 50-ml three-necked flask under a dry nitrogen atmosphere. To the solution was added 200 mg (4.15 mmol) of 50% sodium hydride in oil dispersion. The solution turned dark yellow in color and was heated to 60° for 10 min. The solution was cooled to room temperature and transferred via syringe into a solution containing 400 mg (3.78 mmol) of cyanogen bromide in 25 ml of dry DMF. A reddish brown color appeared. After 15 min, the solution was poured into 200 ml of water and extracted twice with 50-ml portions of dichloromethane. The dichloromethane solution was washed twice with sodium thiosulfate solution followed by water and dried (MgSO_4), and the solvent was removed in vacuo. Crystallization from methylene chloride-Skellysolve B gave 460 mg (37%) of **1b**: mp 112°; ir (KBr) 1710 (C=O), 1325 and 1150 cm^{-1} (SO_2); NMR (CDCl_3) 1.42 (t, $J = 7$ Hz, 3 H), 4.40 (q, $J = 7$ Hz, 2 H), 5.81 (s, 1 H) and 7.2–8.1 ppm (m, 9 H).

Anal. Calcd for $\text{C}_{16}\text{H}_{15}\text{BrO}_4\text{S}$: C, 50.13; H, 3.95. Found: C, 50.25; H, 4.12.

α -Bromo-*p*-carboxybenzyl Phenyl Sulfone (1a). To a solution of 500 mg (1.49 mmol) of **1b** in 50 ml of 75% ethanol was added 50 ml of 4% potassium hydroxide in 75% ethanol. After 4 hr, hydrochloric acid was added until the solution was acidic. From this solution precipitated 330 mg (100%) of **1a**: mp 252°; ir (KBr) 3200–2400 (OH), 1690 (C=O), 1300 and 1150 cm^{-1} (SO_2); NMR ($\text{Me}_2\text{SO}-d_6$) 4.3–5 (1 H), 6.94 (s, 1 H), and 7.4–8 ppm (m, 9 H).

Anal. Calcd for $\text{C}_{14}\text{H}_{11}\text{BrO}_4\text{S}$: C, 47.34; H, 3.12. Found: C, 47.22; H, 2.97.

***p*-Methylsulfonylbenzyl Phenyl Sulfone (2c).** In a two-neck 300-ml flask, 3.4 g (0.020 mol) of *p*-methylsulfonyltoluene (Aldrich) was dissolved in 50 ml of dry carbon tetrachloride. The solution was brought to reflux and a bromine solution of 3.5 g (0.022 mol) in 20 ml of carbon tetrachloride was added dropwise (ca. 30 min) while the flask was illuminated with a 275-W sun lamp. After 1 hr, an NMR spectrum showed a mixture of starting material (5%), α -bromo-*p*-methylsulfonyltoluene, (75%) and α,α -dibromo-*p*-methylsulfonyltoluene (20%). The solvent was removed by rotary evaporation and 20 ml of hexane added. The resulting precipitate (2.7 g) was collected and shown by NMR spectroscopy to be a mixture of α -bromo-*p*-methylsulfonyltoluene (60%) ($-\text{CH}_2\text{Br}$, δ 4.47) and α,α -dibromo-*p*-methylsulfonyltoluene (40%) (CHBr_2 , δ 6.69). The mother liquor gave 0.9 g of the monobromide, mp 93–94° (lit.¹² 94–96°).

The mixture of 2.7 g of the monobromide and dibromide (vide supra) and 6.0 g of sodium benzenesulfinate in 70 ml of dry dimethyl sulfoxide was heated at 90–100° for 30 min. The progress of the reaction can be followed conveniently by TLC (dichloromethane, silica gel). The mixture was poured into 600 ml of water, and the precipitate was collected and recrystallized from acetonitrile to give 1.9 g (50% based on 2.7 g of the mixture of bromides) of **2c**: mp 261–262°; NMR (CDCl_3) 3.04 (s, 3 H), 4.40 (s, 2 H), and 7.1–7.7 ppm (m, 9 H).

Anal. Calcd for $\text{C}_{14}\text{H}_{14}\text{O}_4\text{S}_2$: C, 54.17; H, 4.54. Found: C, 54.25; H, 4.50.

α -Bromo-*p*-methylsulfonylbenzyl Phenyl Sulfone (1c). Compound **1c** was prepared from **2c** following the same procedure used to convert **2b** to **1b**. One gram of **2c** gave 0.63 g (50%) of **1c**: mp 178–179° (acetonitrile); NMR (CDCl_3) 3.04 (s, 3 H), 5.78 (s, 1 H), and 7.2–7.9 ppm (m, 9 H).

Anal. Calcd for $\text{C}_{14}\text{H}_{13}\text{BrO}_4\text{S}_2$: C, 43.19; H, 3.37. Found: C, 43.31; H, 3.32.

The syntheses of **3a**, **3b**, **4a** and **4b** were reported earlier.²

Kinetic Procedure. The rates for compounds **1a**, **1b**, **3a**, **3b**, **4a**, and **4b** were determined by the conductance method.² The rate of reaction of **1c** was determined by the spectrophotometric technique.² All runs were made in at least duplicate. The precision in the rate constants reported in Tables I–III is $\pm 5\%$. The σ^- values reported were determined from $\log k_X = \sigma^- (5.97) + (-5.970)$ where $X = p\text{-COOH}$, $p\text{-COOC}_2\text{H}_5$, and $p\text{-CH}_3\text{SO}_2$, k_X are the rate constants at 25° reported in Tables I and II, and -5.970 is $\log k_{\text{H}^+}$ at 25°. The σ^- values reported have a precision of ± 0.02 units.

Acknowledgment. Support from the University of Maryland Computer Science Center is gratefully acknowledged.

Registry No.—**1a**, 56571-76-7; **1b**, 56571-77-8; **1c**, 56571-78-9; **2b**, 56571-79-0; **2c**, 56571-80-3; **3a**, 41037-90-5; **3b**, 51229-69-7; **4a**, 41037-91-6; **4b**, 51229-70-0; TPP, 603-35-0; *p*-toluoyl chloride, 874-60-2; sulfonyl chloride, 7791-25-5; thiophenol, 108-98-5; cyanogen bromide, 506-68-3; *p*-methylsulfonyltoluene, 3185-99-7; α -bromo-*p*-methylsulfonyltoluene, 53606-06-7; α,α -dibromo-*p*-methylsulfonyltoluene, 33460-70-7; sodium benzenesulfinate, 873-55-2.

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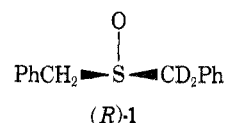
$[\alpha,\alpha\text{-}^2\text{H}_2]$ Dibenzyl Sulfoxide. Synthesis, Reactions, and Chiroptic Properties

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We wish to report on the synthesis, some reactions, and the chiroptic properties of (*R*)- and (*S*)- $[\alpha,\alpha\text{-}^2\text{H}_2]$ dibenzyl sulfoxide (**1**), dissymmetric by substitution of deuterium for hydrogen, two bonds from the asymmetric sulfur atom.



Optical activity in molecules whose dissymmetry arises from isotopic differences is well known and has been observed in compounds containing the isotope pairs ¹H–²H, ¹⁶O–¹⁸O, and ¹²C–¹³C. Chiroptic properties of these com-