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Aromatic Substitution. XXXII.[1] Aluminum Chloride Catalyzed Arenesulfinylation of Benzene and Toluene with Benzenesulfinyl and Substituted Benzenesulfinyl Chlorides in Nitromethane Solution

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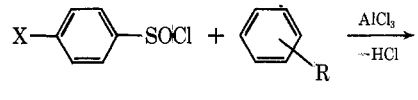
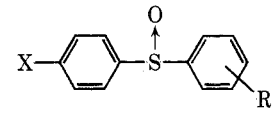
Aluminum chloride catalyzed arenesulfinylation of benzene and polymethylbenzene with substituted benzenesulfinyl chlorides in nitromethane showed that the reaction is of high selectivity. The linear correlation between logarithms of k_{tol}/k_{benz} values and Brown σ^+ substituent constants gives a positive ρ value. These data contrast with previously reported data of sulfonylation and indicate the differing nature of the reactions. The mechanism of the reaction is discussed based on experimental data.

Our preceding work has proved in the case of a series of studied reactions that the transition state of electrophilic aromatic substitutions is not rigidly fixed, resembling the Wheland intermediates (σ complex), but frequently represents a much earlier state on the reaction coordinate resembling starting aromatics (*i.e.*, being of the π-complex character).[3] It was possible to vary in a systematic way the electrophilicity of reagents, such as alkylating agents, by introducing suitable substituents. Thus, a regular change of the transition state of highest energy can be observed from σ-complex to π-complex nature corresponding to the "late" or "early" position of the transition state along the reaction coordinate.

Reactions studied included the titanium tetrachloride catalyzed benzylation of benzene and toluene with substituted benzyl chlorides, giving k_T/k_B rate ratios varying between 2.5 and 136.0 and a correspondingly significant change of the ortho/para isomer ratio.[4] The results of benzoylation of benzene and toluene with substituted benzoyl halides further proved the importance of substituents in the electrophilic substituting agent influencing both substrate and positional selectivity.[5] Aryl thiolcarboxylation also showed the same substituent effect on k_T/k_B and isomer ratio.[6]

Related to these carbocationic reactions, arenesulfonylation of aromatics was also investigated with arenesulfonyl halides.[7] In spite of the fact that the sulfonylation reaction is regarded as an analog of the acylation reaction, it is interesting that the para-substituent effects in arenesulfonyl chlorides on both substrate and positional selectivity show closer similarity to those found in benzylation than in benzoylation reactions. Therefore, from a mechanistic point of view, Friedel–Crafts sulfonylation cannot be considered as a simple analog of the acylation reaction. In order to further study the possible scope and implication of this observation, we undertook a study of the aluminum chloride catalyzed arenesulfinylation of aromatics with benzenesulfinyl and substituted benzenesulfinyl chlorides in which the electron-deficient center of the electrophilic reagent is also on sulfur.





Arenesulfinylation of aromatics giving diaryl sulfoxides was so far little studied. The literature contains but a single report[8] of the preparation of aryl sulfoxides by this reaction. The reaction was found in our hands to be of general utility and allowed us to study the mechanism of arenesulfinylation, including the effect of substituents in the arenesulfinylating agent on the reaction.

Results and Discussion

In order to study the inter- and intramolecular selectivities of Friedel–Crafts arenesulfinylation reactions, we determined, by the use of the competititve method, the relative rates (compared to benzene) of the *p*-toluenesulfinylation of a series of polymethylbenzenes, as well as the related isomer distributions of the alkyl and aryl sulfoxides formed. Data obtained are summarized in Table I.

The results summarized in Table I show that the sulfinylating agent obviously is a very weak electrophile, giving reactions of high selectivity with the aromatic substrates. Data of Table I in comparison with known σ basicities[9] (against $HF-BF_3$ as determined by equilibrium studies by Mackor) show good correlation, indicating that the transi-

Table I
Competitive Sulfinylation of Benzene and Polymethylbenzenes with *p*-Toluenesulfinyl Chloride[a]

Registry no.	Substituted benzene	Relative σ-complex stability ($HF-BF_3$)	Relative rate k_T/k_B	Isomer distribution of substituted diphenyl sulfoxides
71-43-2	H	1	1	
108-88-3	CH_3	790	420	8% 2,4, <0.5% 3,4,[b] 92% 4,4
95-47-6	1,2-$(CH_3)_2$	7,600	7,600	0.8% 2,3,4′-$(CH_3)_3$ 99.2% 3,4,4′-$(CH_3)_3$
108-38-3	1,3-$(CH_3)_2$	1,000,000	59,000	100% 2,4,4′-$(CH_3)_3$
106-42-3	1,4-$(CH_3)_2$	3,200	970	100% 2,5,4′-$(CH_3)_3$
108-67-8	1,3,5-$(CH_3)_3$	630,000,000	250,000	100% 2,4,6,4′-$(CH_3)_4$

[a] Reaction conditions: arenes, 0.4 mol; aluminum chloride, 0.01 mol; toluenesulfinyl chloride, 0.01 mol; nitromethane, 10 ml; reaction temperature, 25°; reaction time, 30 min. [b] Small amounts (<0.5%) of meta isomer (if any) could not be separated from the ortho isomer by glc (within the limit of experimental data).

Table II
Concentration Variation of Benzene and Toluene in Competitive *p*-Toluenesulfinylation

Benzene:toluene	k_T/k_B
10:1	440
5:1	390
3:1	380

Table III
Competitive Sulfinylation of Benzene and Toluene with Substituted Benzenesulfinyl Chlorides[a]

Registry no.	XC_6H_4SOCl, X	k_T/k_B	Isomer distributions, % Ortho	Meta	Para
31401-23-7	*p*-CH_3O	460	8	<0.5	92
10439-23-3	*p*-CH_3	420	8	<0.5	92
50986-83-9	*p*-F	560	5	<0.5	95
4972-29-6	H	660	10	<0.5	90
2901-92-0	*p*-Cl	560	5	<0.5	95
50986-84-0	*p*-CF_3	920	11	<0.5	89
13088-17-0	*p*-NO_2	1150	13	<0.5	87

[a] Reaction conditions: benzene-toluene (10:1), 0.4 mol and aluminum chloride, 0.01 mol in 10 ml of nitromethane; substituted benzenesulfinyl chloride, 0.01 mol; reaction temperature, 25°; reaction time, 30 min.

tion states of the reactions resemble closely the corresponding σ complexes.

In order to show that the studied arenesulfinylations were, indeed, kinetically controlled and first order in the aromatic substrates, the competitive *p*-toluenesulfinylation of benzene and toluene was carried out with varying ratios (10:1, 5:1, 3:1) of the substrates shown in Table II. It shows that the reaction, indeed, is first order in aromatics as the k_T/k_B rate ratio is well reproduced in the limit of experimental error in the range of concentration changes studied.

To study the effect of various para substituents in the sulfinylation reaction with benzenesulfinyl chlorides, aluminum chloride catalyzed sulfinylations in nitromethane solution were studied with *p*-methoxybenzene-, *p*-fluorobenzene-, benzene-, *p*-chlorobenzene-, *p*-trifluoromethylbenzene-, and *p*-nitrobenzenesulfinyl chlorides. k_T/k_B reactivity and isomer ratios were determined in the usual way. Results are summarized in Table III.

Isomer ratios of sulfinylated toluene do not vary significantly with the nature of the para substituent in benzenesulfinyl chloride. Data in Table III show that k_T/k_B relative rate ratios in the reaction of benzenesulfinyl chlorides substituted with an electron-donating substituent in the para position are lower than those of reactions with an electron-withdrawing substituent.

From a linear correlation of the logarithms of the k_T/k_B values plotted against Brown σ^+ constants (Figure 1), the value of $\rho = +0.25$ was obtained for the arylsulfinylation

Table IV
Glc Retention Times of Diaryl Sulfoxides

Registry no.	Diaryl sulfoxide, *p*-$XC_6H_4SOC_6H_4Y$ X	Y	Column conditions	Retention time, min
951-92-8	CH_3O	H	SE-30, 175°	5.7
10381-41-6	CH_3O	*p*-CH_3	SE-30, 175°	9.0
50986-85-1	CH_3O	*o*-CH_3	DE-30, 175°	7.8
948-56-1	CH_3	H	BDS, 200°	8.9
1774-35-2	CH_3	*p*-CH_3	BDS, 200°	12.7
10381-68-7	CH_3	*o*-CH_3	BDS, 200°	10.9
50986-86-2	CH_3	3,4-$(CH_3)_2$	BDS, 200°	24.0
50896-87-3	CH_3	2,3-$(CH_3)_2$	BDS, 200°	21.0
50986-88-4	CH_3	2,4-$(CH_3)_2$	BDS, 200°	21.4
16704-48-6	CH_3	2,5-$(CH_3)_2$	BDS, 200°	22.4
10381-69-8	CH_3	2,4,6-$(CH_3)_3$	BDS, 200°	14.9
945-51-7	H	H	BDS, 130°	7.0
	H	*p*-CH_3	BDS, 130°	11.6
50986-89-5		*o*-CH_3	BDS, 130°	8.5
40154-93-6	F	H	SE-30, 110°	10.0
50986-90-8	F	*p*-CH_3	SE-30, 110°	20.7
50986-91-9	F	*o*-CH_3	SE-30, 110°	13.7
1016-82-6	Cl	H	BDS, 170°	14.3
20608-64-4	Cl	*p*-CH_3	BDS, 170°	21.9
50986-92-0	Cl	*o*-CH_3	BDS, 170°	18.3
50986-93-1	CF_3	H	BDS, 170°	2.9
10381-67-6	CF_3	*p*-CH_3	BDS, 170°	4.0
50986-94-2	CF_3	*o*-CH_3	BDS, 170°	3.4
955-45-3	NO_2	H	SE-30, 180°	7.7
22865-49-2	NO_2	*p*-CH_3	SE-30, 180°	11.8
50986-95-3	NO_2	*o*-CH_3	SE-30, 180°	10.0

reaction. This positive ρ value contrasts with the negative ρ values obtained in previously studied substitutions such as benzylation, benzoylation, aryl thiolcarboxylation, and arenesulfonylation.[3-7] These data clearly indicate the differing nature of sulfinylation from sulfonylation.

The high positional selectivity and predominant para substitution observed in the arenesulfinylation reaction clearly indicate that the reactions involve less reactive (and, therefore, highly selective) sulfinylating reagents. It is highly improbable that "free" arenesulfinyl cations are involved in the reactions (attempts to observe such cations under stable ion conditions were unsuccessful). Even if such sulfinyl cations were involved, their nature would be very different from those of arenesulfonyl cations (examples of which were reported in our preceding work,[7] containing strongly electron-donating para substituents, such as methoxy).

Considering the nature of the sulfonyl cation, it has a highly electron-deficient sulfur center, bound by partial double bonds to two oxygen atoms. The sulfur 3d orbital is, therefore, strongly attracted to the nucleus. This contracted orbital is able to efficiently conjugate with the π system of the aromatic ring, and thus substituent groups (particularly in the para position) can interact with the sulfur center by inductive and/or conjugative effects. A

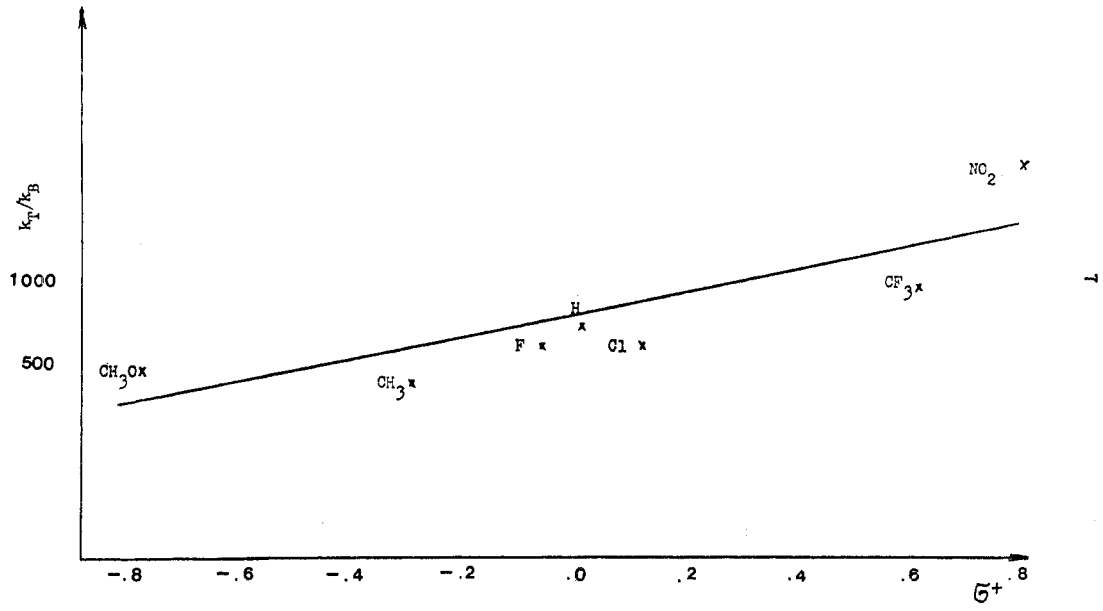


Figure 1. Correlation of relative rates of arenesulfinylation of benzene and toluene with para-substituted benzenesulfinyl chlorides (*p*-XC_6H_4SOCl) with Brown σ^+ constants.

(hypothetical) sulfinyl cation would have only one partially double-bonded oxygen atom bound to its sulfur center, containing also a lone pair of electrons, which thus could inductively donate electrons into the positive site. Thus the sulfinyl cation would be inductively stabilized. However, an interesting point is that the arenesulfinylating agents substituted by electron-withdrawing ring substituents show more selectivity and thus are weaker electrophiles than those substituted by electron-donating groups.

It is reasonable to consider that the sulfur 3d orbital in the sulfinylating agents is more extended than in the related sulfonylating species and, therefore, d_π–p_π overlap is less efficient than in the former cases. An electron-donating group in the ring will tend to inductively decrease the charge on sulfur. At the same time, however, this effect will expand the sulfur 3d orbital and make it less available for d_π–p_π conjugation. Conversely, the presence of electron-withdrawing groups increases the electron deficiency of the sulfur atom and causes the 3d orbital to contract. This results in the possibility of better d_π–p_π conjugation and consequently better conjugative stabilization, giving a less reactive and therefore somewhat less selective substituting agent. Consequently, in sulfinylation substrate selectivity is influenced mostly by the inductive and not by the conjugative effect of substituents.

Differences of physical properties between sulfones and sulfoxides due to differences in the efficiency of d_π–p_π conjugation have been noted.[10] Our present work now presents similar differentiation between reactivities of sulfonylating and sulfinylating systems, which also seem to be due to differences in the d_π–p_π conjugation.

Experimental Section

Materials. Benzene, toluene, and nitromethane were Spectrograde reagents and used without further purification. Commercial sublimed aluminum chloride of high purity was used. Most benzenesulfinyl chlorides were prepared by chlorination of the corresponding acids with thionyl chloride.[11] However, *p*-nitrobenzenesulfinyl chloride was prepared from the related disulfide with chlorine in acetic acid.[12] Substituted diaryl sulfoxides were prepared by literature methods.[13-24]

Competitive Arylsulfinylation. Under a dry nitrogen atmosphere, benzene (28.4 g, 0.364 mol), toluene (3.64 g, 0.036 mol), and aluminum chloride (1.33 g, 0.01 mol) in 5 ml of nitromethane were placed into a 100-ml reaction flask equipped with a dropping funnel, nitrogen seal, and thermometer kept in a constant-temperature bath at 25°. With vigorous stirring, a solution (0.01 mol) of arenesulfinyl chloride in 5 ml of nitromethane was added. After 30 min, the reaction mixture was poured into ice-water and extracted with ether, and the ether solution was washed with water, aqueous NaOH, and again with water and dried over $MgSO_4$. After evaporation of ether and part of excess aromatics, solutions were analyzed by glc.

Glc Analysis. A Varian Aerograph Model 1200 gas chromatograph, equipped with flame ionization detector, was used to analyze reaction mixtures using a SE-30 coated (5% on Chromosorb) packed 3-ft column. Characteristic retention times and conditions are listed in Table IV.

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