Addition of Arylsulfinic Acids to N,N-Dialkylquinone Diimines[1]

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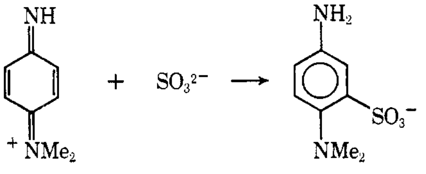
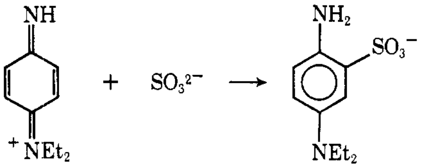
The addition of arylsulfinates (**2**) to N,N-dialkylquinone diimines (**1**) under anaerobic conditions can result in four products. Sulfonamide **3** is produced in good yield under a variety of conditions (pH 5–9; temperature 0–50°). One of the possible sulfones (**4**, the 3 isomer) is found in significant amounts at pH 5–6 at room temperature and below; the 2 isomer is not found. At pH 7–9 detectable quantities of the N′,N′-disulfonamide (**5**) and *p*-phenylenediamine (**6**) are obtained from the reactions of benzenesulfinate and sulfinates with electron-donating substituents. Significantly larger amounts of **5** and smaller amounts of **3** were obtained at 0 and 50° than at 24°. The relationship of product yield to acidity is discussed in terms of the mechanisms of analogous reactions. The reported yields were obtained from the uv spectra of reaction mixture extracts by novel matrix methods involving characteristic vectors. A linear regression technique and a calibration with the spectra of pure compounds were required. The errors in yield lie in the range of 1–5% based on starting material.

N,N-Dialkylquinone diimines are ambident cations which show a high degree of specificity in reactions with anionic nucleophiles. Thus, dye-forming reactions with phenolates give only the product arising from attack at the unsubstituted imino nitrogen,[2] reaction with hydroxide ion gives only the product resulting from displacement of the substituted imino group,[3] and reaction with sulfite ion appears to give only ring addition.[4] We have extended these studies to include reactions with arylsulfinates since stable products result from reaction of these nucleophiles at more than one site. We have made systematic variations in structure, reaction pH (5–9), and reaction temperature (0–50°) to learn how these factors influence the competition between the single-step nitrogen attack and the two-step ring addition. The reactants and products are shown in Scheme I.

Sulfite is reported to show a remarkable selectivity in its final orientation on addition to N,N-dimethyl- and to N,N-diethylquinone diimine, giving **9** and **10**, respectively.[5] We find that phenylsulfinate ion, which has a formal resemblance to sulfite ion, gives a single sulfone isomer from both quinone diimines (**4a** and **4f**).



7 **9**



8 **10**

Results

Product Isolation and Identification.—The quinone diimines were generated *in situ* by oxidation of the appropriate *p*-phenylenediamine with stoichiometric amounts of potassium ferricyanide in deaerated phosphate buffer solutions. It was shown that the presence of the sulfinates during the oxidation had no significant effect on the total yield of products; therefore no oxidation of the sulfinate by ferricyanide was taking place. Self-condensation reactions were minimized by using low concentrations of quinone diimine (2×10^{-8} *M*). The competing deamination of the tertiary imino group was not significant in the pH range used in this study.

Because two of the products are sensitive to air (**4** and **6**), nitrogen was constantly bubbled into the reaction solutions. Extractions with chloroform and dilution of the extracts for spectrophotometric analysis were carried out with deaerated solvents in a nitrogen atmosphere. If these precautions were not taken, significant errors in the product analyses resulted.

The products were all poorly soluble in the aqueous buffers and precipitated in large-scale product-isolation experiments. The major products were isolated from such runs and were characterized by elemental analysis and by nmr, ir, and mass spectral analysis.

The ir spectra of the sulfonamides showed a strong single band at approximately 3.1 μ indicative of NH. Several strong bands in the regions, 7.4–7.9 and 8.4–8.9 μ, can be assigned to SO_2 stretching. The sulfones showed a strong split band at approximately 3 μ indicative of NH_2. The SO_2 stretching bands were similar to those present in the sulfonamides. The disulfonamides showed no absorption in the 3-μ region and this was taken as the absence of NH. The strong SO_2 bands were present.

An AA′BB′ pattern (6.7 ppm) which on integration showed the presence of four aryl protons was found with both sulfonamide and disulfonamide. The latter compounds showed twice as many protons associated with the arylsulfonyl group as the corresponding monosulfonamide. The sulfones gave a complicated multiplet between 7 and 8 ppm. The protons of both aryl groups are involved in this absorption pattern.

All three classes of compounds gave a parent peak in the mass spectrum corresponding to the expected molecular weight. In the case of the disulfonamide it was necessary to introduce the sample directly into the ion source. If the sample was allowed to pass through the molecular leak, only the monosulfonamide parent peak was observed although larger amounts of Ar and SO_2 fragments were found. This was attributed to

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(1) Presented in part before the 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 13, 1968.

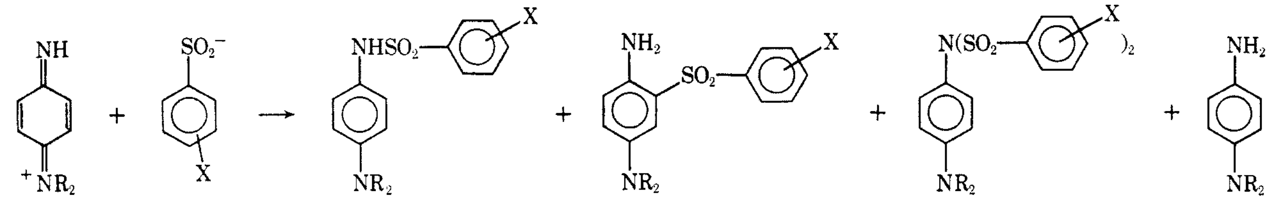
(2) L. K. J. Tong and M. C. Glesmann, *J. Amer. Chem. Soc.*, **90**, 5164 (1968).

(3) L. K. J. Tong, M. C. Glesmann, and R. L. Bent, *ibid.*, **82**, 1988 (1960).

(4) K. T. Finley and L. K. J. Tong in "The Chemistry of the Carbon-Nitrogen Double Bond," S. Patai, Ed., Interscience Publishers, Inc., New York, N. Y., in press.

(5) K. H. Bauer, *J. Prakt. Chem.*, **4**, 65 (1958).

SCHEME I



1a, R = Me
b, R = Et

2a, X = H
b, X = 4-Me
c, X = 4-Cl
d, X = 3,4-Me$_2$
e, X = 4-CN

3a-j

4a-j

5a,b,d,f,g,i

6a, R = Me
b, R = Et

a, R = Me; X = H
b, R = Me; X = 4-Me
c, R = Me; X = 4-Cl
d, R = Me; X = 3,4-Me$_2$
e, R = Me; X = 4-CN
f, R = Et; X = H
g, R = Et; X = 4-Me
h, R = Et; X = 4-Cl
i, R = Et; X = 3,4-Me$_2$
j, R = Et; X = 4-CN

thermal decomposition and was also observed in glpc. The most significant fragment ions from sulfonamide and sulfone were rationalized as M − SO_2Ar and as Ar. The sulfones also showed a peak corresponding to M − Me.

The mass spectra of the sulfones are of special interest in connection with the question of structure. The only sulfones for which a rigorous chemical proof was carried out are **4a** and **4f**. In the former case the alternative 2 isomer (**23**) was also prepared. The mass spectra of these two compounds differed in some important details as shown in Table I. The other sulfones containing a dimethylamino group gave spectra analogous to those of **4a** and **19**. The mass spectra of **4f** and **25** were identical and the other sulfones containing a diethylamino group showed similar fragmentation patterns.

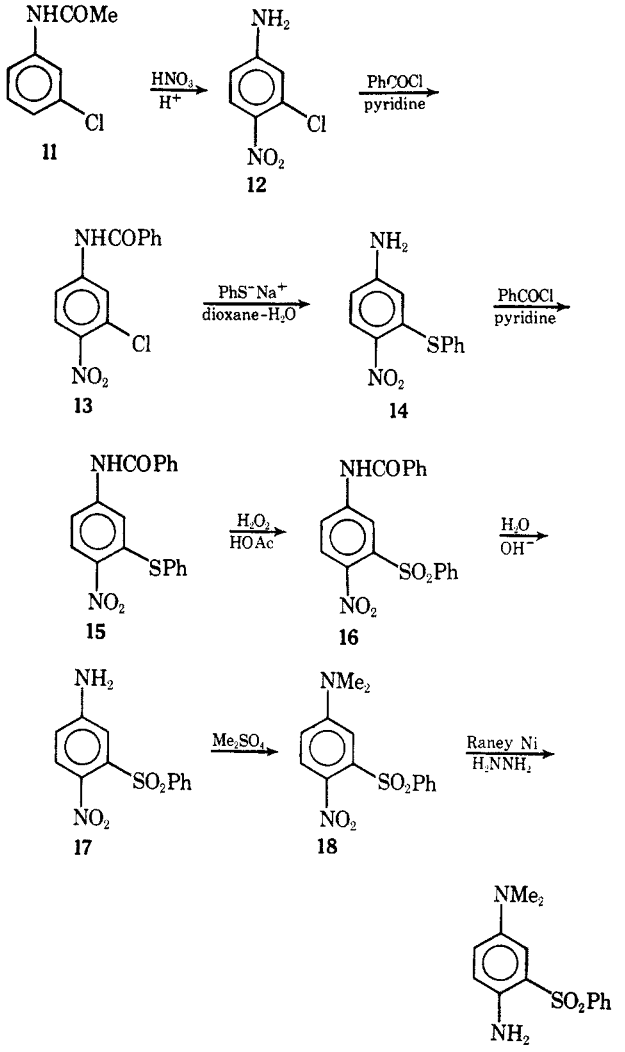
TABLE I

m/e	Probable structure	Rel intensity		
		4a	**19**	**23**
276	M	100	100	100
261	M − Me	12.3	12.4	12.4
259	M − OH	0.2	0.2	7.9
135	M − O_2SPh	18.8	19.3	9.0
134	M − HO_2SPh	3.8	3.9	27.8
133	M − H_2O_2SPh	3.6	3.6	45.7

In addition to being isolated from reaction mixtures, all of the sulfonamides (**3a–j**) were prepared from the appropriate *p*-phenylenediamine and arylsulfonyl chloride in pyridine. These products were shown to be identical with those formed in the addition reaction by melting point, tlc, and spectra.

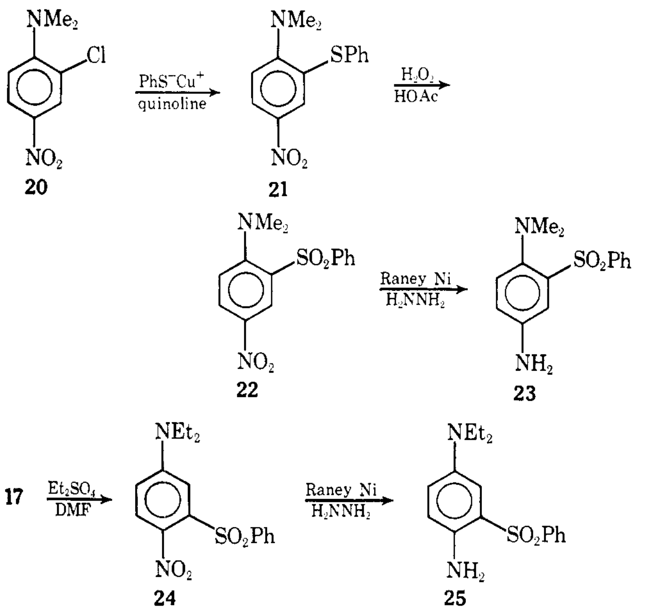
The structure of the sulfone produced by the addition of benzenesulfinate to N,N-dimethylquinone diimine was demonstrated by unambiguous synthesis. By analogy with the reported addition of sulfite, the expected product would be 4-amino-N,N-dimethyl-2-phenylsulfonylaniline (**23**). For comparison we prepared 4-amino-N,N-dimethyl-3-phenylsulfonylaniline (**19**) according to Scheme II. The synthetic compound **19** proved to be identical in all respects with the sulfone isolated from the corresponding addition reaction. The isomeric material **23** and the N,N-diethyl compound **25** were prepared by a similar sequence of reactions shown in Scheme III. Compound **25** proved to be identical with the sulfone isolated from the addition of sodium benzenesulfinate to N,N-diethylquinone diimine.

SCHEME II



The pair of isomeric sulfones of known structure (**19** and **23**) are separated by tlc on alumina when developed with 20% ethyl acetate in benzene. Furthermore, on standing in air, the isomer corresponding to the isolated product (**19**) rapidly becomes colored (magenta) while the 2 isomer does not. The authentic N,N-diethyl structure **25** turns cyan on standing. Since tlc of the

SCHEME III



isolated sulfones (**4a–j**) showed only a single material and all gave the characteristic color on standing, we take this together with the mass spectral evidence as confirmation that all have structure **4**. The 2 isomers, if formed at all, must be below the limit of detection, which we established as 0.3 μg (0.5% yield).[6] The R_f values of the reaction products were within experimental error of those for purified analytical samples (±0.03).

Yields. Method of Analysis and Errors.—Of the various methods tried for obtaining quantitative estimates of product yields from the relatively dilute reaction mixtures, spectrophotometry was most satisfactory. The uv absorption curves for the four products from reaction of **1a** with **2a** are shown in Figure 1 for relative concentrations close to those found in some mixtures. It can be seen that the four curves are rather similar in some wavelength regions. This fact, along with the instability to oxygen of two of the products (**4** and **6**), required a sophisticated method of preparing the solutions and analyzing the absorption curves of the product mixtures.

Initially we were unaware of the presence of the two minor products, **5** and **6**, and attempted to determine the sulfonamide **3** and sulfone **4** by the standard method of solving for the two concentrations from two simultaneous equations, using absorbances at two different wavelengths. We found that the calculated concentrations varied according to the two wavelengths selected. A careful search of the product mixture by tlc led us to the additional compounds. Using the data available from the entire absorption curve seemed to offer hope of resolving this rather complicated product mixture.

It is well known that absorption curves can be written as matrices and, further, that they can be described by characteristic vectors.[7] Absorption curves (225–360 nm) were obtained for each of the pure products. Absorbance values at 28 wavelengths (every 5 nm) throughout each curve were subjected to the matrix transformations needed to derive characteristic vectors and their associated scalar multiples. These derived parameters were used in a linear regression to calculate concentrations of the four components required to give the best fit to the observed absorption curves for mixtures of known composition and for those obtained from the extracts of addition reactions. A comparison of the actual and the calculated concentrations for a typical prepared mixture is given in Table II.

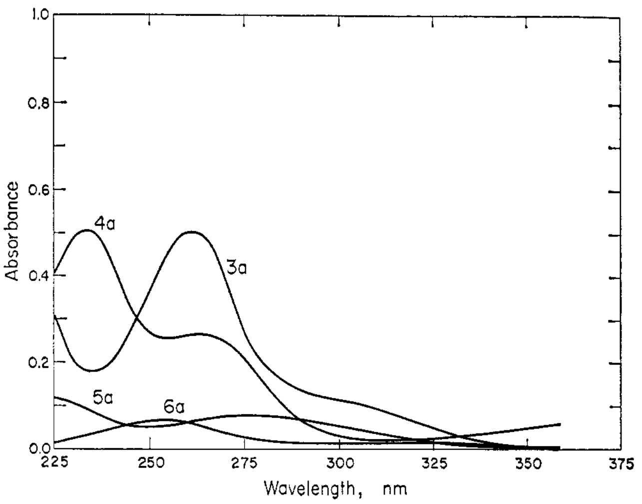


Figure 1.—Spectra of the individual components of a typical reaction mixture. Solvent: 1% chloroform in ethanol–methanol (95:5). Concentration × 10^5 *M*: **3a** = 3.00, **4a** = 2.12, **5a** = 0.48, **6a** = 0.52.

TABLE II

ANALYSIS OF A PREPARED MIXTURE BY CHARACTERISTIC VECTORS

Compd	Concn × 10^7 *M*	
	Actual	Calcd
3a	150	149
4a	64	64
5a	10	8.4
6a	105	99

Similar results were obtained for all pure compounds and analogous prepared mixtures for the other nine pairs of reactants, a total of 94 spectra. The calculated concentrations were then recombined with the vector parameters to calculate a theoretical absorption curve for those concentrations. The theoretical curves always agreed with the observed curves (for pure compounds and prepared mixtures) to within 0.002 absorbance unit, which is well within the error range for spectrophotometry. The differences for reaction mixture extracts were higher, depending upon the reactivity of the sulfinates and the similarity of the absorption curves of the products. With the exception of the reaction of **1b** with **2e**, the greatest difference amounted to 0.015 absorbance unit, which was an acceptable error for determining yields. The extract from the reaction of N,N-diethylquinone diimine (**1b**) with 4-cyanobenzenesulfinate (**2e**) was shown by tlc to contain traces of additional products. The disagreement between the theoretical and observed spectra varied from 0.024 to 0.040 absorbance unit depending on pH.

Since the reconstructed curves for the reaction mixture extracts do not agree with the observed curves to within expected spectrophotometric error, it is difficult

(6) K. T. Finley and R. S. Kaiser, *J. Chromatogr.*, **39**, 195 (1069).

(7) G. Wernimont, *Anal. Chem.*, **39**, 554 (1967).

Table III

Per Cent Product Yields from the Addition of Arylsulfinates to N,N-Dialkylquinone Diimines[a,b]

R X	pH	% product			
		3	**4**	**5**	**6**
Me H	5	31	54		2
	6	54	32	1	4
	7	80	4	2	5
	8	88		4	8
	9	85		4	7
Me 4-Me	5	18	60	2	5
	6	45	46	2	6
	7	74	11	3	10
	8	82		6	12
	9	85		6	13
Me 3,4-Me_2	5	26	54	1	1
	6	45	39		2
	7	74	14	1	2
	8	86	3	2	4
	9	81	3	4	4
Me 4-Cl	5	35	45		
	6	55	23		
	7	82	6		
	8	87	1		
	9	86	2		
Me 4-CN	5	56	25		
	6	71	8		
	7	88			
	8	89			
	9	76			
Et H	5	48	40	1	1
	6	75	16	2	4
	7	94		2	3
	8	90		4	8
	9	92		4	6
Et 4-Me	5	39	43		
	6	67	24		
	7	82	3	2	
	8	86		5	
	9	85	1	4	
Et 3,4-Me_2	5	42	54		
	6	54	24		1
	7	72	7	1	2
	8	83		1	3
	9	81	1	2	1
Et 4-Cl	5	52	22		
	6	72	9		
	7	81	2		
	8	86	2		
	9	83	3		
Et 4-CN	5	64	27		
	6	70	10		
	7	76	3		
	8	75	5		
	9	68	5		

[a] At 24 ± 1°. [b] Where no yield is recorded, the product was not detected by tlc.

to assign exact estimates of errors in the analytical results. We have adopted two estimates as being most informative. First, if we consider the calculated concentrations from single-component solutions prepared from analytical samples, the regression equations show low concentrations of the three absent components. The magnitude of these errors corresponds to yields of ±1%. Second, the calculated concentrations of minor components of the reaction mixture extracts occasionally indicates a negative value which would correspond to a yield error of ±5%. The error in any computed yield should lie within this range, *i.e.*, 1–5% yield based on starting materials.

The average total yield of products for the 62 experiments reported in Tables III and IV is 89%. In view of the scope of the study and the probable errors just discussed, we feel that an acceptable material balance has been achieved. We were unable to detect any disulfonamide (**5**) or *p*-phenylenediamine (**6**) in the reactions of arylsulfinates containing electron-withdrawing substituents. These reaction mixtures were analyzed for two components (**3** and **4**).

Table IV

Effect of Temperature on the Addition of Benzenesulfinate to N,N-Dialkylquinone Diimines[a]

R	pH	% product			
		3	**4**	**5**	**6**
		At 0 ± 1°			
Me	6	30	54	4	3
	7	51	26	13	2
	8	65	6	23	1
Et	6	47	38	8	
	7	76	9	14	
	8	72		26	
		At 50 ± 1°			
Me	6	64	19	9	4
	7	55		15	6
	8	63		20	6
Et	6	75	8	8	
	7	64	1	18	
	8	68	3	24	2

[a] Where no yield is recorded, the product was not detected by tlc.

The effect of temperature on yield was examined for the addition of benzenesulfinate to N,N-dimethyl- and N,N-diethylquinone diimine. These data are presented in Table IV.

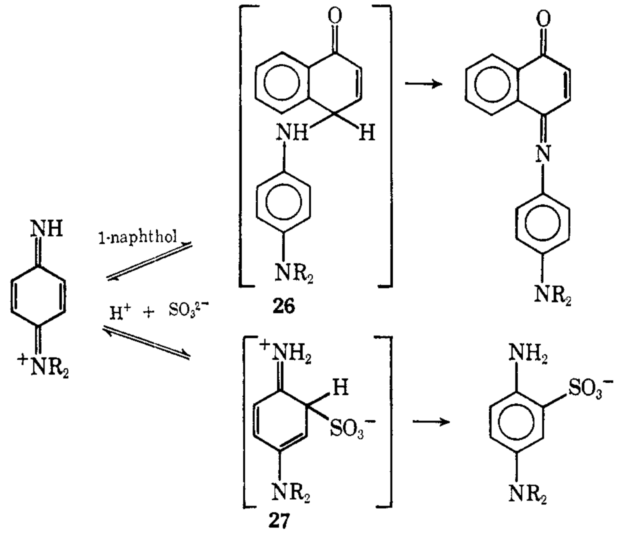
4-Nitrobenzenesulfinate was also added to the two quinone diimines, but the reaction appeared to be relatively slow and tlc indicated the presence of eight to ten minor by-products. Since the 4-cyanobenzenesulfinate reacted more cleanly, and attempts to improve the 4-nitro reaction failed, no yields were measured. The major 4-nitro products are probably the sulfone and sulfonamide as indicated by tlc comparison with authentic samples.

We have shown, in separate experiments, that the reaction products **3**–**5** are not interconverted under reaction conditions.

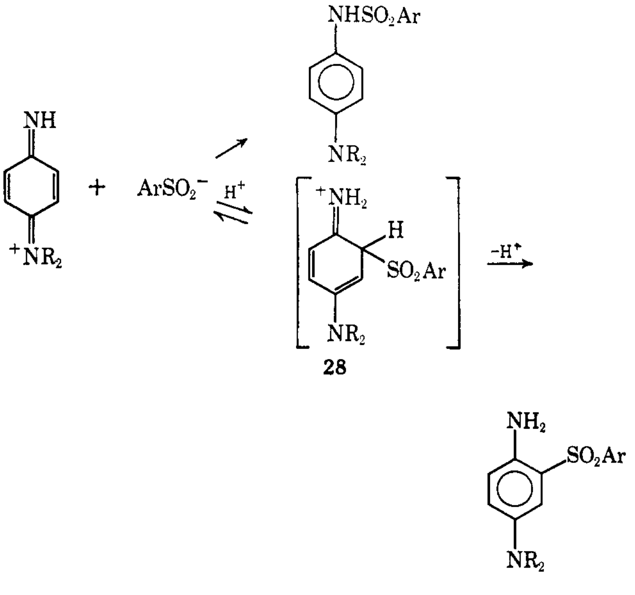
The yield data presented in Tables III and IV indicate certain general trends: (1) sulfone **4** decreases with increasing pH and temperature, (2) sulfonamide **3** and disulfonamide **5** increase with pH, (3) sulfonamide decreases and disulfonamide increases with temperatures either above or below 24°, and (4) sulfone increases with electron-donating substituents in the arylsulfinate and with the N,N-dimethylamino group in the quinone diimine (compared with the N,N-diethylamino group). The fourth trend is less marked than the other three, but is still outside the limits of experimental error.

The addition of phenolate and sulfite ions to quinone diimine provides useful models with which to discuss the mechanisms of the observed reactions (Scheme IV). It seems reasonable that the pathway for sulfone formation might correspond rather closely to that for sulfonation. Similarly we might compare the formation of the coupling intermediate **26** with sulfonamide formation (Scheme V). Kinetic studies of the sulfonation reaction show that the ring addition is subject to general acid catalysis by acid phosphate salts. This has been interpreted mechanistically as base-catalyzed removal of a ring proton from the protonated intermediate **27**. The rate of addition of phenolate ions, on the other hand, is independent of pH. By analogy, it seems reasonable that the sulfonamide:sulfone ratio would change with pH in the direction which we observe.

SCHEME IV

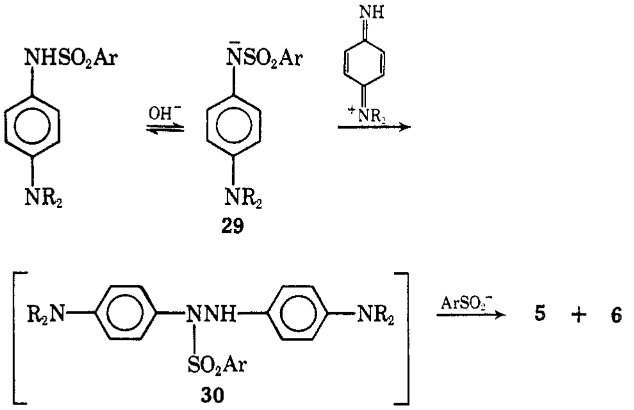


SCHEME V



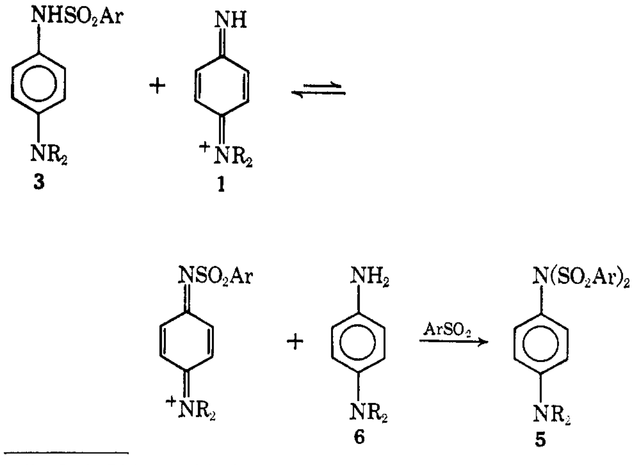
While the disulfonamides **5** are very minor products, they are intriguing because the reaction by which they might be formed is less obvious. We noticed that the disulfonamides were obtained at high pH and that the yields of sulfonamide often dropped slightly above pH 8. The effect of temperature on the yields of sulfonamide and disulfonamide also suggest a connection between these two products. At temperatures both above and below 24° the sulfonamide yield drops and the disulfonamide yield increases. We have considered Scheme VI to account for these facts. This scheme predicts the observed products and the pH dependence. It has been suggested that the formation of hydrazobenzenes from partially oxidized *p*-phenylenediamines involves the reaction of quinone diimines with ionized *p*-phenylenediamines.[8] The subsequent attack of a second arylsulfinate would be expected to occur at the nitrogen bearing the electron-withdrawing arylsulfonyl group. The scheme requires that the rate of addition of sulfonamide anion to unreacted quinone diimine be comparable to the rates of addition of sulfinate. Attempts to investigate this route have been unsuccessful in that we were unable to prepare the intermediate **30**. An earlier study of such compounds indicated that the addition of sulfinic acids to azobenzenes is not a general reaction.[9]

SCHEME VI



An alternative reaction path to the disulfonamide would involve a cross oxidation of the sulfonamide **3** by quinone diimine **1** (Scheme VII). We have found that

SCHEME VII



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[8] C. A. Bishop and L. K. J. Tong, *Phot. Sci. Eng.*, **11**, 30 (1967).

[9] W. Bradley and J. D. Hannon, *J. Chem. Soc.*, 2713 (1962).

treatment of **3** with ferricyanide gives only recovered starting material. Therefore the quinone diimine–quinone diimide equilibrium must lie very far to the left, *i.e.*, toward reactants, and would not be a feasible mode of formation for **5**.

Experimental Section[10]

Materials.—Mono-, di-, and tribasic potassium phosphate and potassium ferricyanide (Baker and Adamson Reagent Grade) were used as received. N,N-Diethyl-*p*-phenylenediamine hydrochloride was recrystallized to a constant melting point of 237–238.5°. N,N-Dimethyl-*p*-phenylenediamine dihydrochloride (Eastman Grade), chloroform (Eastman Spectro Grade), and absolute ethanol denatured with 5% methanol were used as received. Sodium benzenesulfinate and *p*-toluenesulfinate (Eastman Grade and Practical Grade) were used without further purification. The other sulfinic acids were prepared by the reduction of the appropriate sulfonyl chlorides with sodium sulfite.[11-13] 4-Chloro- and 4-nitrobenzenesulfonyl chlorides (Eastman Technical and Eastman Grade) were used without purification. 4-Cyano- and 3,4-dimethylsulfonyl chlorides were prepared by chlorosulfonation as described in the literature.[14,15] All of these compounds were recrystallized to the literature melting points. Solvents for reactions and recrystallizations were Eastman Grade and were used without further purification except as specifically indicated.

Determination of Products.—The appropriate *p*-phenylenediamine (0.2 mmole) was dissolved in 110 ml of deaerated phosphate buffer solution ($I = 0.75\ M$) containing a fivefold excess of the arylsulfinate. Ten milliliters of a deaerated solution containing 0.4 mmole of potassium ferricyanide was added and the reaction was allowed to proceed for approximately 15 min during which time nitrogen was bubbled through the reaction mixture. The products were extracted in 50 ml of deaerated chloroform and after dilution of the solution with deaerated alcohol, the uv spectrum (225–360 nm) was recorded. The reaction vessel was a 250-ml separatory funnel fitted with a long, narrow delivery tip. The extractions were carried out under nitrogen and the extract was delivered directly into a volumetric flask being flushed with nitrogen.

Isolation of Products.—To keep the concentrations of reactants low and still obtain enough product for isolation and analysis large-scale reactions were run at high dilution. Solutions ($4 \times 10^{-3}\ M$) of the *p*-phenylenediamine and ferricyanide were added slowly from separate addition funnels to a well-stirred solution of the appropriate arylsulfinate in the desired buffer. At pH 7 it was possible to isolate the sulfonamides in purified yields of approximately 80%. More acidic conditions (pH 4 or 5) gave lower, but still useful, yields of sulfones. The sulfones were generally chromatographed on silica gel and eluted with 15% ethyl acetate in benzene. The same procedure was employed at pH 9 to obtain samples of N′,N′-disulfonamides.

Preparation of Products.—The various sulfonamides **3a–j** were prepared by the reaction of the appropriate *p*-phenylenediamine and arylsulfonyl chloride in pyridine which had been distilled from BaO.[16] It was very important to keep the reaction cold in most cases since warming produced only a deep purple dye. Some of the sulfonamides appeared to be appreciably more soluble in acid than others and it was necessary to neutralize the aqueous mixture before they could be isolated. A number of the sulfones were prepared by the ferric chloride oxidation of the *p*-phenylenediamines in the presence of sulfinates under acidic conditions.[17] The physical properties and elemental analyses of the sulfonamides and sulfones studied are presented in Table V.

N-Benzoyl-3-chloro-4-nitroaniline (13).—3-Chloro-4-nitroaniline (**12**) was prepared[18] and 20.4 g (118 mmoles) was treated with benzoyl chloride in pyridine. Recrystallization from ethanol gave 24.2 g (74%) of **13**, mp 161.5–163°.

Anal. Calcd for $C_{13}H_9ClN_2O_3$: C, 56.4; H, 3.3; Cl, 12.8; N, 10.1. Found: C, 56.3; H, 3.5; Cl, 13.0; N, 9.9.

4-Nitro-3-phenylmercaptoaniline (14).—To a solution of 24.0 g (87 mmoles) of **13** in 90 ml of 1,4-dioxane was added 14.1 g (128 mmoles) of thiophenol and the mixture was made alkaline with 60 g of NaOH in 400 ml of water. The reaction mixture was then refluxed for 16 hr and poured over cracked ice and water. The precipitate was collected, dried, and recrystallized from ethanol–water giving 17.8 g (83%) of **14**, mp 162–163°.

Anal. Calcd for $C_{12}H_{10}N_2O_2S$: C, 58.5; H, 4.1; N, 11.4; S, 13.0. Found: C, 58.4; H, 4.0; N, 11.2; S, 13.2.

N-Benzoyl-4-nitro-3-phenylmercaptoaniline (15).—By the method used for the preparation of **13**, 17.8 g (72.4 mmoles) of **14** was converted to 20.5 g (81%) of **15**, mp 193–194°.

Anal. Calcd for $C_{19}H_{14}N_2O_3S$: C, 65.1; H, 4.0; N, 8.0; S, 9.2. Found: C, 65.0; H, 4.0; N, 7.8; S, 9.3.

N-Benzoyl-4-nitro-3-phenylsulfonylaniline (16).—A suspension of 23.2 g (66 mmoles) of **15** in 250 ml of glacial acetic acid was treated with 18 g of 30% hydrogen peroxide (*ca.* an eightfold excess) and refluxed for 2 hr. Analysis by tlc showed two substances, neither of which was **15** (silica gel developed with 20% ethyl acetate in benzene). A partial separation on a column of silica gel gave samples whose ir and mass spectra suggested that they were the desired sulfone **16** and the corresponding sulfoxide. The addition of 85 g of 30% peroxide in portions over a reflux period of *ca.* 56 hr gave 19 g (76%) of crystalline product, mp 252–256°. Only a trace of the sulfoxide was found in this material and recrystallization from acetic acid gave an analytical sample of **16**, mp 255–257°.

Anal. Calcd for $C_{19}H_{14}N_2O_5S$: C, 59.7; H, 3.7; N, 7.3; S, 8.4. Found: C, 59.6; H, 3.6; N, 7.4; S, 8.2.

4-Nitro-3-phenylsulfonylaniline (17).—A suspension of 18 g of **16**, containing a trace of sulfoxide, in 700 ml of 1,4-dioxane, was treated with 350 ml of water containing 47 g of NaOH and refluxed for 4 hr. After standing and cooling, a crystalline material was collected and tlc (silica gel, 20% ethyl acetate in benzene) indicated that all of the amide had been hydrolyzed and that a trace of a second product (sulfoxide) was present. Careful recrystallization from ethanol gave 6.8 g (52%) of analytically pure **17**, mp 234.5–236°.

Anal. Calcd for $C_{12}H_{10}N_2O_4S$: C, 51.8; H, 3.6; N, 10.1; S, 11.5. Found: C, 52.0; H, 3.4; N, 10.1; S, 11.2.

N,N-Dimethyl-4-nitro-3-phenylsulfonylaniline (18).—A suspension of 5.0 g (18 mmoles) of **17** in 50 ml of dimethyl sulfate was heated in an oil bath to 90°. After a short time the aniline dissolved and an additional 25 ml of freshly distilled dimethyl sulfate was added. The reaction mixture was heated at 70–90° for 3 hr and then poured over ice. A yellow oil formed which solidified on standing. Recrystallization from chloroform–ethanol (1:1 v/v) gave 2.0 g (36%) of **18**, mp 236–237.5°.

Anal. Calcd for $C_{14}H_{14}N_2O_4S$: C, 54.9; H, 4.6; N, 9.1; S, 10.4. Found: C, 55.1; H, 4.7; N, 8.8; S, 10.7.

4-Amino-N,N-dimethyl-3-phenylsulfonylaniline (19).—A mixture of 500 mg (1.6 mmoles) of **18** and 1 g of wet Raney nickel in *ca.* 75 ml of hot methanol was stirred in a water bath. During a period of 15 min, 3 ml of hydrazine hydrate (64%) was added dropwise. The reaction was continued for about 1.5 hr until no ammonia was detected. The catalyst was removed by filtration and the methanol evaporated under vacuum. Recrystallization from methanol gave 200 mg (44%) of **19**, mp 128–130°; a mixture melting point with the sulfone obtained from the addition of benzenesulfinate to N,N-dimethylquinone diimine showed no depression.

Anal. Calcd for $C_{14}H_{16}N_2O_2S$: C, 60.8; H, 5.8; N, 10.1; S, 11.6. Found: C, 60.5; H, 5.9; N, 10.0; S, 11.3.

N,N-Dimethyl-4-nitro-2-phenylmercaptoaniline (21).—Cuprous thiophenolate was prepared by Adams' procedure[19] and 18.5 g (0.11 mole) was suspended with 20.0 g (0.1 mole) of 2-chloro-N,N-

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(10) The corrected melting points were obtained by using a Thomas–Hoover apparatus. Ultraviolet spectra were recorded with a Beckman DK-2A spectrophotometer, nmr with a Varian 60A instrument operated at 60 MHz (TMS internal standard), ir using a Baird Atomics spectrophotometer, Model NK-1 with NaCl optics, and mass spectra using either a 60° sector-type, or a Consolidated Electrodynamics Model 21-110B mass spectrometer both with an all-glass heated inlet operated at 235°.

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TABLE V

PHYSICAL PROPERTIES AND ANALYTICAL DATA FOR SULFONAMIDES, SULFONES, AND DISULFONAMIDES

Compd	Mp, °C[a]	λ_{max}, nm[b]	$\epsilon \times 10^{-4}$ [b]	Calcd, % C	H	N	S	Cl	Found, % C	H	N	S	Cl
3a	129.5–130	262, 300 sh	1.71, 0.390	60.9	5.8	10.2	11.6		60.7	6.2	10.2	11.4	
b	127–129	225, 262, 300 sh	1.52, 1.72, 0.370	62.0	6.2	9.7	11.0		61.9	6.4	9.7	11.0	
c	120–121	230, 262, 300 sh	1.82, 1.82, 0.432	54.1	4.8	9.0	10.3	11.4	54.2	4.9	9.2	10.1	11.5
d	148.5–150	228, 262, 300 sh	1.36, 1.70, 0.355	63.1	6.6	9.2	10.5		62.9	6.4	9.0	10.6	
e	158.5–159.5	240, 261, 305 sh	2.06, 2.10, 0.339	59.9	5.0	14.0	10.6		60.0	5.1	14.1	10.8	
f	124–125.5	268, 300 sh	1.80, 0.421	63.2	6.6	9.2	10.5		63.1	6.5	9.2	10.5	
g	160.5–161 dec	226, 268, 300 sh	1.55, 1.98, 0.484	64.2	6.9	8.8	10.1		64.2	6.9	8.6	10.2	
h	153–154.5 dec	230, 268, 300 sh	1.78, 2.10, 0.489	56.8	5.6	8.3	10.5	9.5	56.8	5.4	8.3	10.7	9.6
i	151.5–152.5	228, 268, 300 sh	1.43, 2.07, 0.490	65.1	7.2	8.4	9.6		65.4	7.2	8.5	9.5	
j	135–136.5	240, 268, 300 sh	1.96, 2.56, 0.417	62.1	5.8	12.8	9.7		62.2	5.6	13.0	9.7	
4a	130–131	233, 265	2.44, 1.27	60.9	5.8	10.2	11.6		61.0	5.8	10.2	11.4	
b	173–175	238, 265 sh	2.49, 1.19	62.0	6.2	9.7	11.0		61.9	6.2	9.8	10.8	
c	164.5–166	241, 265 sh	2.85, 1.38	54.1	4.8	9.0	10.3	11.4	53.9	4.8	9.2	10.0	11.3
d	148–149.5	241, 265 sh	2.56, 1.30	63.1	6.6	9.2	10.5		62.8	6.8	9.3	10.4	
e	189.5–190.5	248, 275 sh	2.44, 1.27	59.9	5.0	14.0	10.6		59.8	5.3	13.9	10.7	
f	118.5–120	234, 270	2.06, 1.39	63.2	6.6	9.2	10.5		62.9	6.4	9.0	10.4	
g	156–157.5	239, 270	2.55, 1.60	64.2	6.9	8.8	10.1		63.8	6.7	8.9	9.7	
h	155.5–156.5	242, 270	2.84, 1.60	56.8	5.6	8.3	9.5	10.5	56.9	5.5	8.1	9.5	10.6
i	97.5–99	241, 270	2.08, 1.61	65.1	7.2	8.4	9.6		65.3	7.2	7.9	9.4	
j	118–119.5	248, 275 sh	2.40, 1.61	62.1	5.8	12.8	9.7		61.8	5.8	12.6	9.9	
5a	161.5–162.5	275	1.70	57.6	4.8	6.7	15.4		57.7	5.2	6.7	15.5	
b	208–210 dec	236, 275	2.56, 1.55	59.5	5.4	6.3	14.4		59.9	5.9	6.3	14.1	
d	198.5–199.5 dec	238, 275	2.60, 1.80	61.0	5.9	5.9	13.5		60.8	5.9	5.9	13.6	
f	140.5–142	275	1.63	59.5	5.4	6.3	14.4		59.8	5.2	6.1	14.5	
g	200–202 dec	236, 275	2.90, 2.44	61.0	5.9	5.9	13.6		60.8	5.8	5.8	13.7	
i	196–197.5 dec	238, 280	2.42, 1.99	62.4	6.4	5.6	12.8		62.2	6.1	5.6	12.7	

[a] Corrected. [b] Molar absorptivity measured in 1% chloroform in ethanol (denatured with 5% methanol) with a Beckman DK-2A spectrophotometer.

dimethyl-4-nitroaniline (**20**, Frinton Laboratories) in 100 ml of quinoline containing 2 ml of pyridine. The mixture was refluxed for *ca.* 20 hr and then poured over crushed ice and excess hydrochloric acid. A black tar was decanted and, after air drying, was extracted with ether in a Soxhlet extractor until the extract returning to the pot was colorless. The aqueous mother liquors were also extracted and the ether solutions were combined and washed with 0.1 *N* HCl and then with water. The ether was removed under vacuum after the solution had been dried with anhydrous $MgSO_4$. A dark oil remained which crystallized on cooling. A benzene solution of the product was rapidly passed over a column of Florisil. The benzene was allowed to evaporate and the product was recrystallized from methanol to give 6.6 g (24%) of **21**, mp 69–70°.

Anal. Calcd for $C_{14}H_{14}N_2O_2S$: C, 61.4; H, 5.1; N, 10.2; S, 11.7. Found: C, 61.5; H, 5.5; N, 9.9; S, 11.7.

N,N-Dimethyl-4-nitro-2-phenylsulfonylaniline (22).—A solution of 1.05 g (3.8 mmoles) of **21** and 1.5 ml of 30% hydrogen peroxide in 25 ml of glacial acetic acid was refluxed for 2 hr. The solvent was removed under vacuum and the resulting gum was dissolved in benzene and passed rapidly over a column of Florisil. Three products were successively eluted by benzene; the third was 500 mg (43%) of **22**, mp 89.5–90.5°.

Anal. Calcd for $C_{14}H_{14}N_2O_4S$: C, 54.9; H, 4.6; N, 9.1; S, 10.5. Found: C, 54.9; H, 4.4; N, 9.0; S, 10.8.

4-Amino-N,N-dimethyl-2-phenylsulfonylaniline (23).—By the method used with **19**, 120 mg (0.39 mmole) of **22** was converted to 80 mg (75%) of **23**, mp 132–133°.

Anal. Calcd for $C_{14}H_{16}N_2O_2S$: C, 60.8; H, 5.8; N, 10.1; S, 11.6. Found: C, 60.8; H, 5.7; N, 10.3; S, 11.4.

N,N-Diethyl-4-nitro-3-phenylsulfonylaniline (24).—A suspension of 4.0 g (14.4 mmoles) of **17** in 100 ml of freshly distilled diethyl sulfate was stirred at about 90° for 3 hr. After cooling it was poured over ice and a yellow powder was removed by filtration and recrystallized from chloroform–ethanol (1:1 v/v). Tlc (silica gel, 20% ethyl acetate in benzene) showed it to be **17** containing a small amount of a second yellow material. All of the recovered material was dissolved in 25 ml of dimethylformamide (DMF) and heated to *ca.* 100°. Diethyl sulfate (20 ml) was added with rapid stirring. After 1 hr another 20 ml of diethyl sulfate was added. Stirring and heating was continued for 2 more hr. The reaction mixture was poured over ice and a fine yellow solid and a yellow-brown gum were obtained, the latter solidifying after standing for several days. Tlc indicated that more of the product observed earlier, plus a second component, were present. This mixture of products and **17** were once again dissolved in DMF, treated with two 25-ml portions of diethyl sulfate, and heated (90–100°) for approximately 8 hr. The reaction mixture was poured over ice and the yellow powder which formed was recrystallized from ethanol. All of the starting material (**17**) was gone, but tlc still indicated the presence of two products. Several attempts to separate these by column chromatography failed and preparative tlc was used. The two bands overlapped and both had to be chromatographed a second time. The two products showed only a trace of the other component by analytical tlc and this was removed by recrystallization from ethanol. The major component proved to be **24**, mp 158–159°. The second product was the N-ethyl homolog, mp 182–183°. The mass spectra of both products showed the required molecular ion and fragment ions expected, *i.e.*, M − Me and M − NO.

4-Amino-N,N-diethyl-3-phenylsulfonylaniline (25).—Since the precursor **24** was proving so difficult to separate from the monoethyl compound, it was decided to reduce the mixture. The method used with **19** was applied to 500 mg of the mixture. Chromatography on a column of Woelm polyamide and elution with DMF gave a solid product with only a trace of a second component. Recrystallization from ethanol failed to remove the impurity. Preparative tlc on silica gel eluted with 20% ethyl acetate in benzene gave **25**, mp 117–118.5°.

Anal. Calcd for $C_{16}H_{20}N_2O_2S$: C, 63.1; H, 6.6; N, 9.2. Found: C, 62.5; H, 6.6; N, 9.1.

Registry No.—**3a**, 19766-54-2; **3b**, 19766-55-3; **3c**, 19770-72-0; **3d**, 19770-73-1; **3e**, 19770-74-2; **3f**, 19770-75-3; **3g**, 19770-76-4; **3h**, 19770-77-5; **3i**, 19770-78-6; **3j**, 19770-79-7; **4a**, 19770-80-0; **4b**, 19789-51-6; **4c**, 19770-81-1; **4d**, 19770-82-2; **4e**, 19789-52-7; **4f**, 19771-02-9; **4g**, 19770-83-3; **4h**, 19789-54-9; **4i**, 19789-55-0; **4j**, 19789-56-1; **5a**, 19770-84-4; **5b**, 19770-85-5; **5d**, 19770-86-6; **5f**, 19770-87-7; **5g**, 19770-88-8; **5i**, 19770-89-9; **13**, 5925-26-8; **14**, 19770-91-3; **15**, 19770-92-4; **16**, 19770-93-5; **17**, 19770-94-6; **18**, 19770-95-7; **19**, 19770-80-0; **21**, 19770-97-9; **22**, 19770-98-0; **23**, 19770-99-1; **24**, 19771-00-7; **24** (N-ethyl homolog), 19771-01-8; **25**, 19771-02-9.

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Linear Free-Energy Relationship Involving *ortho* Substituents in Gas-Phase Reactions. XVII[1]

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Rate constants, and in most cases Arrhenius parameters (E_a and $\Delta S^{\ddagger}$ values), have been determined in the gas-phase pyrolysis of sixteen 1-arylethyl benzoates, sixteen 1-arylethyl acetates, and sixteen 1-arylethyl methyl carbonates. In each case the rates for the pyrolysis of the *meta* and *para* isomers were correlated in a Hammett plot using σ^+ constants. Furthermore, linear free-energy relationships involving *ortho* substituents were obtained in these gas-phase reactions when the log (k/k_0) for the pyrolysis of 1-arylethyl methyl carbonate was plotted as a function of log (k/k_0) for the pyrolysis of 1-arylethyl acetate or 1-arylethyl benzoate, each including *ortho* substituents. This demonstrates that proximity effects are minimal or nonexistent in these reactions. From this study the following σ_o^+ substituent constants have been obtained: *o*-MeO, −0.411; *o*-Me, −0.233; *o*-Br, +0.551; *o*-Cl, +0.452; *o*-NO_2, +0.749.

Equations of the Hammett type have been very successful in correlating equilibrium and rate data for reactions of *meta*- and *para*-substituted benzene derivatives. These equations, however, do not apply for similar reactions of *ortho*-substituted benzene derivatives in the condensed phase because of "proximity effects." Evaluation of *ortho*-substituent constants is extremely difficult since proximity effects for a given *ortho* substituent vary with the nature of the adjacent reaction center, the particular reaction, and especially with the reaction conditions (*e.g.*, solvent). It has been demonstrated, however, that proximity effects are not evident in a study of steric effects in the gas-phase pyrolysis of isopropyl benzoates.[2] From a vapor-phase kinetic study of the pyrolysis of *ortho*-substituted isopropyl benzoates, σ_o^0 constants have been obtained which correlate very well with Taft's calculated values[3] and with other data obtained from reactions thought to be free of the major contributing factor to the proximity effects.[4]

In the present investigation the objective was to evaluate σ^+ values for *ortho* substituents. Previous pyrolysis studies[5,6] have established that the unimolecular vapor-phase pyrolysis of *meta*- and *para*-substituted 1-arylethyl acetates and their methyl carbonates are correlated with the equation log $(k/k_0) = \rho\sigma^+$ using the standard σ^+ values. Assuming that proximity effects for *ortho* substituents in these gas-phase reactions are either negligible or equal, a linear free-energy relationship would result if log (k/k_0) for *ortho*-substituted 1-arylethyl acetates were plotted as a function of log (k/k_0) for *ortho*-substituted 1-arylethyl methyl carbonates. A preliminary report of the data on some of these compounds has been given.[6] In the present study, kinetic data of the gas-phase pyrolysis of sixteen *ortho*-, *meta*-, and *para*-substituted 1-arylethyl benzoates are presented along with some revised data from the gas-phase pyrolysis of the corresponding acetates and methyl carbonates. Linear free-energy relationships for *ortho* as well as *meta* and *para* substituents in these three reactions in the gas phase are reported. From these plots Hammett σ^+ constants are presented for the *ortho* substituents in reactions essentially free of proximity effects.

Experimental Section

Preparation of 1-Arylethyl Alcohols.—All the alcohols, except 1-phenylethyl alcohol, which was purchased from Aldrich Chemical Co., were prepared by sodium borohydride reduction of the substituted acetophenone in 70% aqueous methanol.

Preparation of 1-Arylethyl Benzoates.—The benzoates were prepared by benzoylation of the appropriate alcohols with benzoyl chloride in chloroform in the presence of pyridine. The alcohol (0.1 mole) was mixed with a slight excess of pyridine (0.11 mole) in a three-necked flask fitted with a water condenser and a thermometer. The mixture was cooled externally by an ice-water bath and was stirred by a magnetic bar driven by a motor. Redistilled benzoyl chloride (0.11 mole) in chloroform (80 ml) was added a drop at a time through a dropping funnel, while the temperature of the mixture was kept below 15°. After all the benzoyl chloride was added, the mixture was stirred overnight at room temperature. The reaction mixture was diluted with ether and washed with dilute NH_4OH solution, water, dilute HCl solution, and then again with water. It was dried over magnesium sulfate prior to solvent removal. The desired benzoates were obtained either by fractional distillation at reduced pressure or by recrystallization from pentane. A shorter fractionation column was used in distilling high-boiling benzoates, *e.g.*, 1-*p*-methoxyphenylethyl benzoate [bp 140° (0.09 mm)], to avoid decomposition at the high temperature. Benzoates thus obtained were characterized by infrared and nmr spectra and refractive indices, and where practical the purity was checked by vpc or thin layer chromatography. The physical constants are listed in Table I.

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