g. of an oil which was saponified for 1.5 hours in a refluxing solution of 0.85 g. of 86% potassium hydroxide in 10 ml. of ethanol. The solvent was removed, water added and the solution acidified and extracted with ether. After drying, the ether was removed to give 1.760 g. (73%) of an oil which solidified completely after seeding and removing all volatiles, m.p. 103–104°. Crystallization from carbon disulfide–pentane raised the m.p. to 107–108°.

Methoxydiphenylacetanilide.[17]—A solution of 100 mg. (0.41 mmole) of methoxydiphenylacetic acid in 1 ml. of methylene chloride was treated with 0.5 ml. (7 mmoles) of methoxyacetylene. The reaction mixture was allowed to stand for one hour at room temperature, volatiles were removed, and the residue was heated at 90° for 2 hours with a slight excess (45 mg., 0.48 mmole) of freshly distilled aniline.

(17) *Cf.* H. Klinger, *Ann.*, **389**, 253 (1912).

The product was dissolved in methylene chloride and washed, first with acid, and then with water. The solid obtained by evaporating the methylene chloride was crystallized from methanol at 5° to give 41 mg. (31%) of methoxydiphenylacetanilide, m.p. 150.5–151.5°, reported[17] 149–150°; 2.95 and 5.88 μ (CCl_4).

Action of Thionyl Chloride on Benzilic Acid.—A solution of 500 mg. (2.2 mmoles) of benzilic acid in 15 ml. of carbon tetrachloride, containing 1.0 ml. (14 mmoles) of thionyl chloride, was refluxed for 40 hours. The solvent was then evaporated and the excess thionyl chloride removed by adding, and subsequently evaporating, two 5-ml. portions of hexane. The resulting oil was dissolved in hexane and passed through a column of silica gel (11 g.). Elution with 20-ml. portions of 5% ether–hexane yielded 381 mg. (96%) of benzophenone, m.p. 49–50°.

NEW HAVEN, CONN.

Orientation and Relative Reaction Rate Factors in Aromatic Substitution by the Benzenesulfonimido Radical

BY JAMES F. HEACOCK AND MARVIN T. EDMISON

The orientation and the relative reaction rates of homolytic aromatic substitution by the benzenesulfonimido radical have been studied. The benzenesulfonimido radicals were generated by decomposing benzenesulfonyl azide thermally at 105–120° in an excess of the aromatic substrate or substrates. The total and partial relative reaction rate factors were determined by using a competitive method with benzene as a reference solvent. Of the aromatic compounds which were studied, most of those with "*meta*-directing substituents" did not react to produce the expected substitution products. Orientation in the resultant compounds indicated electrophilic substitution and relative reaction rate values were indicative of radical substitution.

Benzenesulfonamidation, by decomposition of benzenesulfonyl azide in aromatic substrates, has previously been studied by Curtius and co-workers[1] and more recently by Dermer and Edmison.[2]

In this study,[3] the competitive method was used to determine the relative rate of benzenesulfonamidation of various aromatic substrates, using benzene as the reference solvent. In the course of this work, it became evident that quantitatively there was some discrepancy between the isomer ratios found by Dermer and Edmison[2] and the isomer ratios found in the competitive determinations. The isomer ratios were reinvestigated and analyzed by an analytical procedure that the authors believe to be superior considering the nature of the reaction products.

Recently, it has been found that an electronegative substituent in the p-position of a phenyl radical imparts to the radical an electrophilic character[4–6]; it then is reasonable to assume that the proximity of the strongly electronegative sulfonyl group in the benzenesulfonimido radical also should render it

electrophilic. The results of this experimentation are consistent with this hypothesis.

Experimental

Analytical Method.—The analyses were accomplished by using an infrared technique similar to that of Augood, Hey and Williams.[7] A Perkin–Elmer, model 12-C infrared spectrophotometer, with a 0.1-mm. fixed-thickness sodium chloride cell, was used. Dioxane was employed as a solvent.

A solution of 0.5 g. in 5 cc. of dioxane was prepared for each component to be analyzed, and the spectrum of the solution was scanned between 9.5 and 14.5 mμ. A wave length, at which it had a higher absorbance than the other components, was selected for each component. The absorptions at these wave lengths were checked for deviations from the Beer–Lambert law. In every case, the selected wave length had a negligible deviation with the exception of the 11.0 mμ absorption used in the analysis of p-benzenesulfonamidobenzoic acid. In this case, a correction was applied by means of a calibration curve. The weight per cent. was then determined from the absorbance, of the unknown solution, at the five selected wave lengths. Knowns were used in each case to prove that the chemical interactions of the various components were not so great as to give erroneous results.

Synthesis of the Isomeric Benzenesulfonanilides.—Three methods were used in the synthesis of the benzenesulfonanilide derivatives. In all three procedures, the corresponding arylamine was treated with benzenesulfonyl chloride in the presence of a base. When possible, a 10% sodium hydroxide solution was used as the reaction medium, but in a number of syntheses, the alkali caused undesirable hydrolysis or side reactions. In these latter syntheses, pyridine and toluene were used as reaction media. The isomeric benzenesulfonamidoanilines were prepared by the reduction of the corresponding benzenesulfonamidonitrobenzene derivatives with iron and acetic acid. Table I lists the derivatives. The melting points agreed satisfactorily with those reported earlier.

(1) T. Curtius, *J. prakt. Chem.*, **125**, 303 (1930).

(2) O. C. Dermer and M. T. Edmison, THIS JOURNAL, **77**, 70 (1955).

(3) J. F. Heacock, Ph.D. Thesis, Oklahoma State University, 1959; research program supported by a Frederick Gardner Cottrell grant from the Research Corporation of New York. Authors also gratefully acknowledge valuable assistance of Dr. O. C. Dermer, Head, Department of Chemistry, Oklahoma State University.

(4) J. I. G. Cadogan, D. H. Hey and G. H. Williams, *J. Chem. Soc.*, 1425 (1955); Chang Shih, D. H. Hey and G. H. Williams, *ibid.*, 1885 (1958); D. H. Hey, B. W. Pengilly and G. H. Williams, *ibid.*, 1463 (1956); Chang Shih, D. H. Hey and G. H. Williams, *ibid.*, 2600 (1958).

(5) R. L. Dannley and M. Sternfeld, THIS JOURNAL, **76**, 4543 (1954).

(6) D. F. De Tar and A. A. Kazimi, *ibid.*, **77**, 3842 (1955).

(7) D. R. Augood, D. H. Hey and G. H. Williams, *J. Chem. Soc.*, 44 (1953).

Synthesis in 10% Sodium Hydroxide Solution. Hinsberg Reaction.—A 0.15-mole sample of the appropriate arylamine was treated with 250 cc. of a 10% sodium hydroxide solution and 20 cc. of benzenesulfonyl chloride. The reaction flask was stoppered and shaken until the contents cooled to room temperature. The mixture was then placed on a steam-bath and heated to approximately 85° for one hour with occasional shaking, then treated with charcoal and filtered. The derivative was precipitated by the addition of enough concentrated hydrochloric acid to make the solution definitely acid, and this crude product, in most instances, was recrystallized five or six times from dilute ethanol; dilute methanol was found to be a better recrystallization solvent for the isomeric benzenesulfontoluidides and xylene for the isomeric benzenesulfonamidobenzoic acids.

The yields of the purified products varied but were usually around 30–50% of theoretical.

Synthesis in Pyridine.—One-tenth mole of the arylamine, 12.6 cc. of benzenesulfonyl chloride and 150 cc. of pyridine were heated for 2.5 hours under reflux, cooled in an ice-bath, and poured into ice and excess concentrated hydrochloric acid. The crude product was collected and recrystallized three times from dilute ethanol. The yield of purified product was about 50%.

Synthesis in Toluene.—This synthesis was used only to prepare the isomeric benzenesulfonamidophenols, to prevent substitution on the hydroxyl group rather than the amino group. Pollard and Amundsen[8] previously used this method to prepare o-benzenesulfonamidophenol.

Six and four-tenths grams of benzenesulfonyl chloride, 10.9 g. of the corresponding aminophenol and 100 cc. of toluene were treated under reflux for one hour, treated with charcoal, filtered and cooled. The white crystalline product was filtered and recrystallized from toluene.

TABLE I

BENZENESULFONANILIDE DERIVATIVES

o-, m- and p-Benzenesulfonanisidides

o-, m- and p-Benzenesulfonamidobenzoic acids

o-, m- and p-Benzenesulfonamidobromobenzenes

o-, m- and p-Benzenesulfonamidochlorobenzenes

o-, m- and p-Benzenesulfontoluidides

Benzenesulfonanilide

Methyl o-, m- and p-benzenesulfonamidobenzoates[a,b]

p-Benzenesulfonamidobenzonitrile

o-, m- and p-Benzenesulfonamidonitrobenzenes

o-, m- and p-Benzenesulfonamidophenols[c]

o-, m- and p-Benzenesulfonamidoanilines

[a] meta, m.p. 158–160°. Calcd. for $C_{14}H_{13}NO_4S$: C, 57.72; H, 4.50; N, 4.81; S, 11.00. Found: C, 57.53; H, 4.75; N, 4.95; S, 11.00. [b] para m.p. 153–155°. Found: C, 50.09; H, 5.03; N, 4.77; S, 11.46. [c] meta, m.p. 131.0–131.5°. Calcd. for $C_{12}H_{11}NO_3S$: C, 57.81; H, 4.45; N, 5.62; S, 12.86. Found: C, 58.60; H, 4.78; N, 5.66; S, 13.01.

Preparation of Benzenesulfonyl Azide.—Benzenesulfonyl azide was prepared by the procedure described by Dermer and Edmison.[2]

Substitution of Aromatic Nuclei through Thermal Decomposition of Benzenesulfonyl Azide.—In general, the same procedure was used for both the determinations of orientation and the studies of competitive reactions. The main difference between the two was that in order to raise the temperature of the reaction mixture to 105–120° for the competitive experiments which involved benzene, it was necessary to apply a small increase in pressure. This was accomplished by bubbling the escaping nitrogen through a column of mercury. A standard reflux apparatus equipped with a calcium chloride drying tube was used for the orientation experiments.

All substrates used in the investigation were fractionally distilled twice on a 30-plate Oldershaw column and only the middle fraction was used each time. This fraction was stored over anhydrous sodium sulfate until used. For comparative purposes, the decompositions were always

(8) C. B. Pollard and L. H. Amundsen. THIS JOURNAL, **57**, 357 (1935).

carried out in a five mole per cent. solution, and the temperature was maintained between 105 and 120°. Different concentrations (0.05–0.15 mole fractions), different temperatures (105–170°) and dropwise additions were investigated, but no effect on the yield, by-products or isomer ratio was observed.

To the reaction flask were added 13.7 g. (0.075 mole) of benzenesulfonyl azide and 1.5 moles of substrate. In the competitive runs, 0.75 mole of benzene and 0.75 mole of the monosubstituted derivatives of benzene were added. This solution was heated to 105–120° for a period of 48 hours.

At the end of the 48-hour period, the mixture, a black solution with some black solid particles suspended in it, was distilled under reduced pressure to remove the excess substrate, and finally was steam distilled to remove the last traces of substrate. The steam distillation was continued until the distillate was no longer cloudy, and then an additional one liter of distillate was collected.

The residue was cooled, the water content was estimated and enough sodium hydroxide was added to make a 5% solution. All of the residue appeared to go into solution.

In the runs with methyl benzoate, benzonitrile, benzoyl chloride and other derivatives capable of being hydrolyzed to the benzoic acid derivative, this basic solution was refluxed for 12 hours. The other runs did not require this hydrolysis and were used directly.

The basic solution then was extracted with three 200-cc. portions of ether to remove any ether-soluble impurities, treated with charcoal and filtered, and the filtrate was made definitely acidic by the addition of concentrated hydrochloric acid. When aniline was used as the substrate, this solution was neutralized with sodium bicarbonate before subsequent ether extraction.

The acid solution was cooled in an ice-bath and a precipitate formed. The solution was extracted with copious quantities of ether. Most of the precipitate was soluble in the ether, but some remained at the interface between the water and the ether. This portion of the precipitate was removed by filtration and discarded. The water layer was extracted with ether until evaporation of the ether layer left no residue. The extraction usually required 1.5 liters of ether. The ether extract was treated with charcoal, filtered and allowed to evaporate at room temperature. A white crystalline residue, composed of the substitution products and benzenesulfonamide, remained.

In some cases, such as the non-competitive runs with methyl benzoate, the products were recrystallized from appropriate solvents, but usually the products were pure enough, after evaporation of the ether, to be analyzed. Excessive recrystallization might change the isomer ratio, but control experiments indicated that there was no significant change caused by the procedure used in this study.

The entire procedure was checked with known compositions of the components, and in each case the extraction and recrystallization was accomplished without appreciable change in composition. However, it was observed that, unless large quantities of ether were used in the extraction, some benzenesulfonamide was not recovered.

In the case of the benzoic acid derivatives, which were prepared by hydrolysis, the products were analyzed for benzoic acid also. Usually the acid was found to be absent, but occasionally it was necessary to correct for this impurity.

Results

Successful experiments and determinations, both competitive and non-competitive, were accomplished with anisole, bromobenzene, chlorobenzene, methyl benzoate and toluene. Although the majority of the experiments with phenol produced an oily tar, one of the competitive runs produced a crystalline product, which was used to determine both the isomer ratio and the competitive constants. The results from this one determination appear to correspond with results from other substrates, but it must be remembered that three non-competitive and five competitive runs were not successful. Purification of this oily product might result in an identical isomer ratio, but as yet this has not been accomplished.

TABLE II

COMPOSITIONS OF ISOLATED PRODUCTS

Substrate	Type experiment	No. runs	Average[b] yield, %	Average[c] mole, % PhSO₂NH₂	Substitution products, mole %[a] Disubstituted products o-	m-	p-	PhSO₂- NHPh
Benzene	Non-competitive	3	30.2	18	..	..	..	100
Toluene	Non-competitive	2	55.3	11	61	1	38	..
Toluene	Competitive	3	25.8	2	30 (60)	0 (0)	20 (40)	50
Anisole	Non-competitive	2	36.0	0	71	2	27	..
Anisole	Competitive	3	38.7	3	32 (65)	0 (0)	17 (35)	51
Phenol	Competitive	1	33.3	15	22 (50)	1 (2)	21 (48)	56
Chlorobenzene	Non-competitive	3	38.2	5	46	2	52	..
Chlorobenzene	Competitive	4	32.5	4	19 (47)	1 (2)	21 (51)	59
Bromobenzene	Non-competitive	4	22.5	6	50	5	45	..
Bromobenzene	Competitive	3	29.4	15	17 (40)	3 (9)	21 (51)	59
Methyl benzoate	Non-competitive	4	31.2	26	43	54	3	..
Methyl benzoate	Competitive	4	60.0	11	12 (40)	17 (57)	1 (3)	70
Aniline	Non-competitive	2	62.0	17	12 (40)	2 (7)	16 (53)	70
Benzoyl chloride	Non-competitive	4	6.8	90	0 (0)	100 (100)	0 (0)	..

[a] Values are given as nearest per cent based on average for the particular experiment; numbers in parentheses show isomer distribution as derived from the other value. [b] Based on benzenesulfonyl azide. [c] Benzenesulfonamide was difficult to remove from the reaction mixture and resulted in poor precision between the various runs; it was therefore mathematically removed from the other products before averaging their values.

TABLE III

SUMMARY OF RESULTS

Substrate	$X_H{}^k$	$X_H{}^k{}_{o-}$ Rate factors	$X_H{}^k{}_{m-}$	$X_H{}^k{}_{p-}$
Benzene	1.00	1.0	1.0	1.0
Toluene	1.00	1.8	0.03	2.3
Anisole	0.96	2.0	.06	1.6
Phenol	.80	1.2	.05	2.3
Chlorobenzene	.69	0.95	.04	2.2
Bromobenzene	.69	1.0	.10	1.9
Methyl benzoate	.38	0.49	.62	0.07

Tables II and III show the percentage yields (based upon benzenesulfonyl azide), mole percentages of the products, the total relative reaction rate $X_H{}^k$, and the partial relative reaction rates with respect to benzene ($X_H{}^k{}_o$, etc.).

In most instances, the deviation from the average values shown for percentages of products was not more than ±1. Based upon experiments with known mixtures, the accuracy of the isolation and analytical methods together is better than 3% of the true value and in a great majority of cases it was within 2%. It then becomes difficult to explain the quantitative differences in isomer distribution between the competitive and non-competitive experiments with some substrates, particularly, with anisole and bromobenzene; qualitatively they do remain the same. The total relative reaction rate factor was calculated from the average ratio of substituted benzenesulfonanilides to benzenesulfonanilide.[9] The partial relative reaction rates were determined by using the total relative reaction rate, along with the average of the mole fractions of each isomer obtained from the non-competitive determinations.

Analysis of the non-competitive experiments with aniline as the substrate revealed that the favored reaction route was not through the radical intermediate but through an ionic mechanism whereby hydrazoic acid was split out to form benzenesulfonanilide. Ammonia was observed as a by-product from these reactions.

(9) C. K. Ingold and F. R. Shaw, J. Chem. Soc., 2918 (1927).

Benzonitrile and benzoyl chloride reacted with benzenesulfonyl azide to produce mainly benzenesulfonamide in poor yields.

Attempts to cause reaction of benzenesulfonyl azide with benzoic anhydride, benzotrichloride, benzamide and benzoic acid were unsuccessful. In each case a very small quantity of benzenesulfonamide was produced and identified by use of the infrared spectrum. The main product was a black amorphous acid. Attempts to identify this product have been unsuccessful. Attempted hydrolysis with concentrated hydrochloric acid or concentrated sodium hydroxide solution at reflux temperature failed to change the appearance or properties of the material.

The material is soluble in any base such as sodium hydroxide or pyridine, but is insoluble in water, acid or the usual organic solvents. The melting point is very high; the substance fails to melt when placed directly upon a hot-plate. If held above a direct flame it seems to char, but does not melt or burn. Elemental analysis shows the presence of both sulfur and nitrogen.

Discussion

The question naturally arises as to whether the substitution is accomplished through a radical or an ionic mechanism. The results of this experimental work at first might seem ambiguous, because the substitution is oriented in a manner similar to an ionic substitution, but the relative reaction rate is similar to that of a radical mechanism. The following mechanism is postulated to explain the results.

Just as in the Curtius rearrangement, the first and undoubtedly the rate-determining step is the decomposition of the azide to form molecular nitrogen and a biradical.

$$C_6H_5SO_2N_3 \longrightarrow C_6H_5SO_2N: + N_2$$
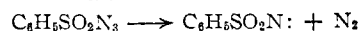
The biradical is supported theoretically since the remaining nitrogen atom would contain six electrons and four atomic orbitals, one 2s, and three 2p orbitals; and the most stable configuration, according to Hundt's rule, would be the biradical with two unpaired electrons.

Dermer[10] has demonstrated that the decomposition of benzenesulfonyl azide produces radicals by decomposing small amounts of freshly distilled vinyl monomers. The benzenesulfonyl azide was found to have a definite catalytic effect in initiating polymerization, and this action could be inhibited by such inhibitors as hydroquinone or p-benzoquinone.

Dannley and co-workers[11] found that p-toluenesulfonyl azide, when thermally decomposed, acts as a weak catalyst in the polymerization of a mixture of styrene and methyl methacrylate.

Hey and co-workers,[4] as well as Dannley and Sternfeld,[5] and De Tar and Kazimi,[6] have demonstrated that an electronegative group in the p-position of a phenyl radical results in ionic character of the radical. This electronic effect is evidently an inductive rather than a resonance effect, because methoxy, as well as nitro, chloro and bromo groups, has been found to impart this electrophilic character. The benzenesulfonimido radical has a sulfonyl group, one of the strongest electronegative groups, adjacent to the reaction site and therefore it would be reasonable to assume that it would show even a greater ionic character than the previously-mentioned radicals.

The relative rate of reaction factors, obtained in this work, demonstrate that the substituents have very little effect on the rate of substitution. This could be explained by assuming that the benzenesulfonimido radical has a very short life and reacts with the first molecule with which it comes into contact. Therefore, the orientation which is observed in benzenesulfonamidation must occur in a transition state of the substitution reaction.

This transition state might be visualized as a π-complex similar to the π-complexes postulated by Dewar[12] for the extremely reactive electron-deficient cations in aromatic substitution. Hammond and co-workers,[13] and later Benkeser and Schroeder,[14] have presented experimental evidence which indicates that certain radicals can also form π-complexes with aromatic compounds. Price and Convery[15] as well as Milyutinskaya, Bagdasar'yan and Izrailevich,[16] using isotope-effect techniques, have postulated that the formation of an additional intermediate is actually the rate-determining step for phenylation of m-dinitrobenzene and of benzene. It should be noted that Eliel, Welvart and Wilen[17] have reported an isotope effect in arylation and alkylation of benzene-d by peroxides; no isotope effect was found with tritium in the systems investigated by Price and Convery.[15] The π-com-

(10) O. C. Dermer, unpublished work.

(11) R. L. Dannley, M. Esayian and H. Essig, Abstracts of papers, A.C.S., Chicago, Ill., Meeting, 1958, p. 28-T.

(12) M. J. S. Dewar, "The Electronic Theory of Organic Chemistry," 1st Ed., Oxford University Press, London, 1949, p. 168.

(13) G. S. Hammond, C. E. Boozer, C. E. Hamilton and J. N. Sen, THIS JOURNAL, 77, 3238 (1955).

(14) R. A. Benkeser and W. Schroeder, ibid., 80, 3314 (1958).

(15) C. C. Price and R. J. Convery, ibid., 79, 2941 (1957); 80, 410 (1958).

(16) R. I. Milyutinskaya, K. S. Bagdasar'yan and E. A. Izrailevich, Zhur. Fiz. Khim., 31, 1019 (1957).

(17) E. L. Eliel, Z. Welvart and S. H. Wilen, J. Org. Chem., 23, 1821 (1958).

plex must have a long enough existence that the electronic effects of the substrate, under the influence of the strong inductive effect of the sulfonyl group at close range, can direct the benzenesulfonimido group to a position favored by high electron density.
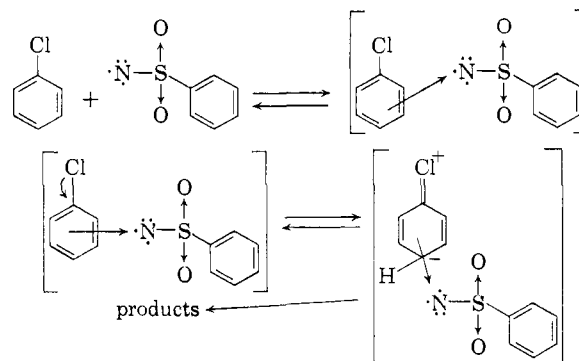
The remainder of the reaction then proceeds as a normal radical substitution.

The failure of the m-directing compounds to produce the expected substitution products could be attributed to complexing of the radical with the electron-rich substituent group, rather than with the electron-poor aromatic nucleus, as previously postulated by Benkeser and Schroeder.[14] Because of this failure to produce significant amounts of N-substituted benzenesulfonamides, no significant conclusions can be drawn concerning the influence of the m-directing groups on either orientation or reaction rate.

If the proposed mechanism is correct, one can explain the difference between the benzenesulfonimido radical and other electrophilic radicals. If the life of the π-complex is sufficiently long, the relative reaction rate will be a function of the difference between the thermodynamic stability of the π-complex of the aromatic substance being studied, and the π-complex of the reference solvent. If the π-complex has a very short existence before being converted to the substitution products, this equilibrium is never attained; the reaction will be kinetically controlled and there will be little difference between the relative reaction rates of the two aromatic substrates. The benzenesulfonimido radical, being very reactive, forms π-complexes with very short lives, and substitutes in various aromatic nuclei at nearly the same rates.

The greater the electrophilic character of the radical the more the orientation in substitution by it should approach that of ionic electrophilic substitution. This explains why the orientation in substitution by the benzenesulfonimido radical, which should be very electrophilic in character, is similar to that in ionic electrophilic substitution.

Benkeser and Schroeder[14] postulated that the surprising lack of suceptibility to steric hindrance of the triphenylmethyl group in attacking the o-position might be due to complexing of the radical fairly close to the negative substituent. The same argument could be applied to explain the similar results found with the benzenesulfonimido radical.