ORIENTATION IN AROMATIC SUBSTITUTION

BY THE BENZENESULFONIMIDO RADICAL

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By

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PREFACE

There is a definite need for more information concerning the products of homolytic substitutions of aromatic nuclei. This need has been emphasized by various authors in recent publications. Hey and Waters (125) have commented

As far as we are aware, the quantitative examination of the total product from such a homolytic reaction in the liquid phase has not yet been attempted.

Loebl, Stein and Weiss (159) wrote in 1949

However, very limited experimental evidence is available regarding substitution by free radicals in the monosubstituted aromatic nucleus, particularly quantitative data, with the exception of some recent work in which it was found that substitution by aryl radicals takes place at all three positions with respect to CO_2Et, Cl and Br.

More recently still the following comment has been made by Hey, Nechvatal and Robinson (122)

The absence of accurate quantitative data with regard to both orientation and to activation or deactivation of the nucleus by the presence of substituent atoms or groups has hitherto made any comprehensive theoretical interpretation of the substitution of free radicals and atoms highly speculative.

It is the purpose of this dissertation to add to the quantitative knowledge concerning the ratio of isomeric disubstituted compounds obtained from radical substitution of monosubstituted aromatic nuclei. After some preliminary investigation of reactions of the types reviewed by Bachman and Hoffman (6) and of acyl peroxides, it was decided to confine the experimental portion of this dissertation to a study of substitutions resulting from the thermal decomposition of benzenesulfonyl azide in aromatic liquids as reported by Curtius and his co-workers (49).

TABLE OF CONTENTS

LIST OF TABLES

LIST OF ILLUSTRATIONS

HISTORICAL

Part I: Experimental Review

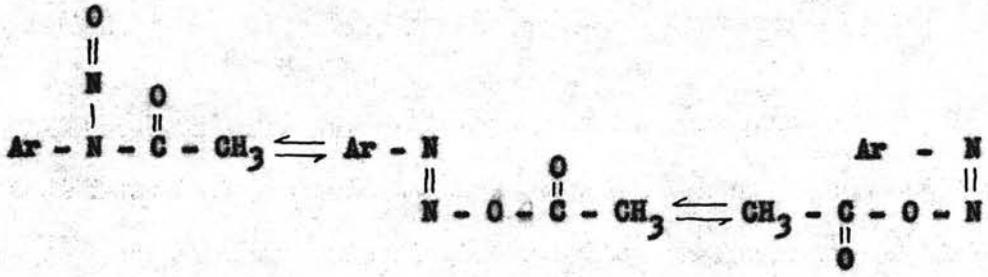
The discussion which follows will be limited to reactions which are more or less generally accepted as proceeding by a radical mechanism. For background material on radicals several good reviews are to be found in scientific publications (1, 17, 70) and in books containing discussions of radicals (6, 68, 180, 207, 214). Such background reading should include the publications of some of the early workers such as Bamberger (8, 9, 10, 11) and Kuhling (154, 155) and the often-cited work of Paneth and Hofeditz (173).

The present discussion will be confined to orientation in radical substitution of aromatic nuclei. The reactions will be discussed only in sufficient detail to identify each and to give the general conditions under which it takes place. Presentation of the results of investigations of numerous workers in the field will be followed by the theoretical considerations which have been advanced concerning radical substitution of aromatic compounds. In accordance with Kharasch's (149) precautionary suggestion that it is profitless to discuss the reactions of a radical independently of its mode of formation, the review of previous experiments will be organized according to the generating reactions.

Radicals from Pyrolysis of Diazotates and Diazoacetates

Perhaps the best known methods of producing aryl radicals are those which might be considered as having for their first step the diazotization of an arylamine. There is evidence to support the belief that these compounds decompose in non-aqueous media to produce free radicals (187, 207). Most of the instances reported wherein these radicals substitute aromatic nuclei indicate a preponderance of formation of the para isomer, but recent investigations as well as recent theoretical treatments of the subject show that the para does not in fact predominate.

Experiments involving N-nitrosoacylarylamines are presented in this portion of the dissertation. It has been shown that these compounds may exist in tautomeric forms analogous to those of diazohydroxides



and it has been found that the thermal decompositions of these substances in aromatic liquids also yield substituted aromatic compounds. Huisgen (136) shows that the rate-determining step in substitution reactions involving N-nitrosoacylanilides is indeed the migration of the acyl group from the nitrogen atom to the oxygen atom of the nitroso group.

Bachman and Hoffman (6) have discussed reactions of this general category in some detail and they have tabulated the results obtained by many experimenters in the field. Tables I and II of this dissertation

supplement their tabulation primarily by the inclusion of work which has been published more recently. In Table II the quantitative data available concerning isomer ratios of the substitution products have been tabulated for easy reference.

It is interesting to note that the isomer ratios tabulated in Table II do not show a preponderance of the para compounds. There is good agreement between two independent investigations of the decomposition of diazotized p-nitroaniline in pyridine, but no other like comparison can be made from the table. It seems reasonable to expect that the work reported in recent years is more reliable if for no other reason than that new tools and new techniques have become available with which to carry on investigations of this nature. This applies particularly to the determination of isomer ratios in the substitution products.

Radicals from the Pyrolysis of Other Diazo Compounds

From Diazosulfides.--p-Nitrobenzenediazosulfide gave p-nitrobiphenyl when decomposed in benzene (11) and the same investigators report the formation of p-nitrophenyltoluene when it was decomposed in toluene. No information was given as to the ratio of isomers in the latter case.

From Diazocyanides.--The decomposition of diazocyanides in non-aqueous media has been reported (199) and although copper powder was used as a catalyst the authors came to the conclusion that the decompositions are exactly similar to the non-ionic decompositions of diazoacetates. The p-chlorobenzenediazocyanide gave 4-chlorobiphenyl (1.5%) by reaction with benzene and the o-isomer produced o-chlorobenzonitrile

TABLE I

COMPOUNDS PRODUCED FROM DIAZOTATES AND DIAZOACETATES

The procedures are designated by letters and numbers:[a]

- A-1 Diazohydroxide reaction (NaOH)
- A-2 Sodium diazotate procedure
- A-3 Sodium acetate modification
- A-4 Stabilized diazonium salt procedure
- A-5 Pyridine method
- A-6 Pyrimidine method
- B-1 Nitrosoacetylamine reaction (N_2O_3)
- B-2 Nitrosoacetylamine reaction (NOCl)

Product	Component A	Component B	Method	Yield, %	Ref.
		Monosubstituted Biphenyls			
Biphenyl	Acetanilide	Benzene	B[b]	--	139
2-Benzoylbiphenyl	2-Aminobenzophenone	Benzene	A-1	15	66
2-Methoxybiphenyl	Aniline	Anisole	A-2	15	73
2-Phenoxybiphenyl	2-Aminodiphenyl ether	Benzene	A-1	25	66
2-, 3- and 4-Nitrobiphenyls	Aniline	Nitrobenzene	A-1	30	67
2-, 3- and 4-Nitrobiphenyls	Acetanilide	Nitrobenzene	B-2	39-53	67
2- and 4-Nitrobiphenyls	Aniline	Nitrobenzene	A-1	18	67

Product	Component A	Component B	Method	Yield, %	Ref.
3-Nitrobiphenyl	m-Nitroaniline	Benzene	A-1	21	142
3-Trifluoromethylbiphenyl	3-Acetamidobenzotrifluoride	Benzene	B-1	35	175
4-Methylbiphenyl	p-Toluidine	Benzene	A-1	14	33
Disubstituted Biphenyls					
2- and 4-Methyl-3'-nitrobiphenyls	m-Nitroaniline	Toluene	A-3	--	122
2,4'-Dimethoxybiphenyl	p-Acetanisidide	Anisole	B-1	--	73
2-, 3- and 4-Nitro-4'-bromobiphenyls	p-Bromoaniline	Nitrobenzene	A-1	16-25	122
2-, 3- and 4-Nitro-4'-bromobiphenyls	p-Bromoacetanilide	Nitrobenzene	B-2	34-44	122
3-Nitro-2'-methoxybiphenyl	m-Nitroaniline	Anisole	A-2	50	73
3-Nitro-2'-methoxybiphenyl	m-Nitroacetanilide	Anisole	B-1	47	73
2-, 3- and 4-Nitro-4'-methylbiphenyls	p-Toluidine	Nitrobenzene	A-1	27-45	122
2-, 3- and 4-Nitro-4'-methylbiphenyls	p-Acetamidotoluene	Nitrobenzene	B-2	28-32	122
4-Methyl-(2'- and 4'-nitro)biphenyls	p-Toluidine	Nitrobenzene	A-2	--	122

Product	Component A	Component B	Method	Yield, %	Ref.
4-Nitro-3-trifluoromethyl-biphenyl	5-Amino-2-nitrobenzotrifluoride	Benzene	A-3	22	175
	Polysubstituted Biphenyls				
Methyl biphenyl-3,4,5-tricarboxylate	Methyl 5-Acetamidohemimellitate	Benzene	B-2	--	176
	Substituted Furans				
2-p-Bromophenylfuran	p-Bromoaniline	Furan	A-1	15	143
2-m-Chlorophenylfuran	m-Chloroaniline	Furan	A-1	16	143
2-p-Chlorophenylfuran	p-Chloroacetanilide	Furan	B-2	19	143
2- and 3-p-Chlorophenylfurans	p-Chloroaniline	Furan	A-1	29	143
2-α-Naphthylfuran	α-Naphthylamine	Furan	A-3	18	143
2-p-Nitrophenylfuran	p-Nitroaniline	Furan	A-3	19.7	143
2-Phenylfuran	Aniline	Furan	A-1	22	143
	Substituted Naphthalenes				
1- and 2-Phenylnaphthalenes[c]	Acetanilide	Naphthalene	B[b]	37.5	139
1-, 3- and 6-Phenyl-2-ethoxynaphthalenes	Acetanilide	2-Ethoxynaphthalene	B[b]	--	139
Phenyl-2-methylnaphthalenes[d]	Acetanilide	Naphthalene	B[b]	--	139

Product	Component	Component	Method	Yield, %	Ref.
1-Phenyl-2, 6-dimethyl-naphthalene[e]	Acetanilide	2,6-Dimethyl-naphthalene	B[b]	(49.5)[f]	139
Substituted Pyridines and Pyridyl Compounds					
2-n-Butoxy-5-phenyl-pyridine	5-Amino-2-n-butoxy-pyridine	Benzene	A-1	--	2
8-Bromo-6-(α-, β- and γ-pyridyl)-quinolines	8-Bromo-6-amino-quinoline	Pyridine	A-5	--	38
α-, β- and γ-(3,-4-Dibromophen-yl)pyridine	3,4-Dibromo-aniline	Pyridine	A-5	--	111
2-Chloro-3-phenylpyridine	2-Chloro-3-acetamido-pyridine	Benzene	B-2	--	2
2-Chloro-5-phenylpyridine	2-Chloro-5-acetamido-pyridine	Benzene	B-2	--	2
2-Chloro-5-phenylpyridine	2-Chloro-5-amino-pyridine	Benzene	A-3	--	2
α-, β- and γ-(3,-4-Dichlorophen-yl)pyridine	3,4-Dichloro-aniline	Pyridine	A-5	42	111
4-p-Dimethyl-aminophenyl-pyridine	p-Amino-dimethyl-aniline	Pyridine	A-5	--	152
6-(3'- and 4'-2', 6'-dimeth-ylpyridyl)-quinolines	6-Acetamido-quinoline	2,6-Lutidine	B-2	--	41
Ethyl 4-(α-, β- and γ-pyridyl)-phthalates	Ethyl 4-amino-phthalate	Pyridine	A-5	40	111

Product	Component A	Component B	Method	Yield, %	Ref.
6-Methoxy-8-(α-, β- and γ-pyridyl)-quinolines	6-Methoxy-8-amino-quinoline	Pyridine	A-5	--	37, 38
8-Methoxy-6-(α-, β- and γ-pyridyl) quinolines	8-Methoxy-6-amino-quinoline	Pyridine	A-5	--	38
2-Nitro-4-t-butyl-(α-, β- and γ-pyridyl)-benzenes	2-Nitro-4-t-butyl-aniline	Pyridine	A-5	--	37
3-Nitro-4-t-butyl-(α-, β- and γ-pyridyl)-benzenes	2-Nitro-4-amino-t-butylbenzene	Pyridine	A-5	--	37
α-, β- and γ-(2-nitro-5-methoxy-phenyl)pyridines	4-Nitro-p-anisidine	Pyridine	A-5	22	37
2-p-Nitrophenyl-pyridine	p-Nitro-aniline	Pyridine	A-5	15.4	81
3-p-Nitrophenyl-pyridine	p-Nitro-aniline	Pyridine	A-5	5.3	81
4-p-Nitrophenyl-pyridine	p-Nitro-aniline	Pyridine	A-5	2.4	81
4-p-Nitrophenyl-pyridine	p-Nitro-aniline	Pyridine	A-5	28	206
Phthalo-3-(α-, β- and γ-pyridyl)-p-anisidines	Phthalo-3-amino-p-anisidine	Pyridine	A-5	--	37
1,3-Di(α-, β- and γ-pyridyl)benzenes	α-, β- and γ-(3-Aminophenyl)-pyridines	Pyridine	A-5	--	39

Product	Component A	Component B	Method	Yield, %	Ref.
1,4-Di(α-, β- and γ-pyridyl)-benzenes	α-, β- and γ-(4-Amino-phenyl)pyridines	Pyridine	A-5	--	39
4-(α-Pyridyl)-diphenylamine	4-Aminodi-phenylamine	Pyridine	A-5	--	40
3-(α-, β- and γ-Pyridyl)-phthalimides	3-Amino-phthalimide	Pyridine	A-5	85	111
4-(α-, β- and γ-Pyridyl)-phthalimides	4-Amino-phthalimide	Pyridine	A-5	56	111
Tetrapyridyl-phthalocyanines	Tetraamino-phthalo-cyanines	Pyridine	A-5	--	102
4-(α-, β- and γ-Pyridyl)-phthalonitriles	4-Amino-phthalo-nitrile	Pyridine	A-5	--	111
3-(α- and β-Pyridyl)-quinolines	3-Amino-quinoline	Pyridine	A-5	--	36
5-(α- and other Pyridyl)-quinolines	5-Amino-quinoline	Pyridine	A-5	--	36, 38
8-(α-, β- and γ-Pyridyl)-quinolines	8-Amino-quinoline	Pyridine	A-5	--	36, 38
8-(α-, β- and γ-Pyridyl)-6-α-pyridyl-quinolines	8-Amino-6-α-pyridyl-quinoline	Pyridine	A-5	--	39

Product	Component A	Component B	Method	Yield, %	Ref.
Substituted Pyrimidines					
2-p-Nitrophenylpyrimidine	p-Nitroaniline	Pyrimidine	A-6	10	161
4-p-Nitrophenylpyrimidine	p-Nitroaniline	Pyrimidine	A-6	14	161
Substituted Thiophenes					
Dibenzothiophene	2-Aminodiphenylsulfide		A-1	10	66
2-p-Chlorophenylthiophene	p-Chloroaniline	Thiophene	A-1	33	32
2,5-bis(p-Chlorophenyl)-thiophene	p-Chloroaniline	Thiophene	A-1	2	32
2-o-Nitrophenylthiophene	o-Nitroaniline	Thiophene	A-3	51	193
2-p-Tolylthiophene	p-Toluidine	Thiophene	A-1	12.5	32
2,5-bis(p-Tolyl)-thiophene	p-Toluidine	Thiophene	A-1	3.4	32
Other Compounds					
Ethyl 4-phenylphthalate	Ethyl 4-acetamidophthalate	Benzene	B-2	--	111

Product	Component A	Component B	Method	Yield, %	Ref.
Ethyl 2-phenyl-pyrrole-N-carboxylate	Acetanilide	Ethyl pyrrole-N-carboxylate	B-1	29	182
Fluorenone	2-Aminobenzophenone	--	A-1	1	66
4-(o-, m- and p-Methoxyphenyl)-phthalonitriles	4-Aminophthalonitrile	Anisole	A-1	--	111
4-Phenylphthalonitrile	4-Aminophthalonitrile	Benzene	A-1	--	111
4-Phenylphthalonitrile	4-Acetamidophthalonitrile	Benzene	B-2	--	111
3-Phenylquinoline	3-Acetamidoquinoline	Benzene	B-2	--	2
p-Tolylterphenyls	p-Toluidine	Benzene	A-1	--	33

(a) Designation of methods follows that of Bachman and Hoffman (6). The designation A-6 has been added to signify the use of pyrimidine as component B.

(b) Whether the method was B-1 or B-2 was not clearly indicated.

(c) The 2-isomer comprised 16.6% of the phenylated product.

(d) The 1-phenyl isomer predominated.

(e) Smaller amounts of two other isomers were present; one was thought

to be the 3-isomer.

(f) Numbers enclosed in parenthesis indicate percentages of arylated product rather than of theoretical yield.

Table II

ISOMER RATIOS IN COMPOUNDS PRODUCED FROM DIAZOTATES AND DIAZOACETATES

Product	Component A	Component B	Method[a]	Isomer, % 2-	3-	4-	Ref.
p-Bromophenyl-anisoles	p-Bromo-aniline	Anisole	A-1	20	0	7	106
Nitro-biphenyls[b]	Aniline	Nitrobenzene	A-1	(55-61) 12-16	(0-4) 0-1	(39-41) 7-12	67
Nitro-biphenyls[b]	Aniline	Nitrobenzene	A-1	(54±4)	(9±2)	(37±4)	122
p-Nitrophenyl-pyridines	p-Nitro-aniline	Pyridine	A-5	15.4	5.3	2.4	81
p-Nitrophenyl-pyridines	p-Nitro-aniline	Pyridine	A-5	24	9	4.5	108
p-Nitro-phenylpyr-imidines[c]	p-Nitro-aniline	Pyrimidine	A-6	10	0	14	161
4'-Nitro-(2- and 4-methyl)-biphenyls[b]	p-Nitro-acet-anilide	Toluene	B-1	(67)	0	(33)	83
2-, 3- and 4-substituted Terphenyls[b]	4-Nitroso-acetamido-biphenyl	C_6H_5Y	B-1				82
		Y=Cl		(32)	(20)	(48)	
		Y=Br		(33)	(15)	(52)	
		Y=CH_3		(50)	(6)	(44)	
		Y=NO_2		(54)	(0)	(46)	

Product	Component	Component	Method[a]	Isomer, % 1-	3-	6-	Ref.
1-, 3- and 6-Phenyl-2-ethoxynaphthalenes[b]	Acetanilide	2-Ethoxynaphthalene	B[d]	(36)	(6.5)	(4.9)	139

(a) Designation of method explained at the beginning of Table I.

(b) Numbers enclosed in parenthesis indicate percentages of arylated product rather than of theoretical yield.

(c) Statistically there are twice as many chances of forming 4- monosubstituted pyrimidines as 2- substituted products.

(d) Whether the method was B-1 or B-2 was not clearly indicated.

(7%) and 2-chlorobiphenyl (3%). From p-bromobenzenediazocyanide in dry benzene there was obtained some p-bromobenzonitrile (5%) and 4-bromobiphenyl (1%).

From Diazoanhydrides.--Diazoanhydrides were prepared (9) by careful addition of acetic acid to the potassium salts. Decomposition of these compounds in aromatic liquids resulted in formation of biphenyls. When decomposed in aromatic bases these substances reacted with the amino groups by a process of elimination of water to form diazoamino compounds. p-Toluenediazoanhydride was found to react violently with aromatic liquids, the reaction being explosive in nature when toluene was employed as the substrate. p-Chlorobenzenediazoanhydride reacted with benzene to yield 4-chlorobiphenyl, and with aniline to form the corresponding diazoamino compound. With thiophenol an analogous reaction occurred and the diazosulfide was formed. The p-bromoanhydride reacted in benzene and in aniline in the same manner as did the p-chloro-compound. 4-Nitrobiphenyl was isolated as a product of the decomposition of p-nitrobenzenediazoanhydride in benzene, but the yield was low owing to the violent decomposition of the anhydride. Decomposition in aniline formed the diazoamino compound as described above. The m-nitroanhydride reacted with benzene to produce a substance believed to be 3-nitrobiphenyl, and the m-bromo compound was reported to have formed 3-bromobiphenyl.

From Diazo Ethers.--Bamberger (8) reports that biphenyl and substituted biphenyls can be prepared by the decomposition of diazo ethers in aromatic liquids, but that the reactions require more time. He prepared 4-nitrobiphenyl and 4-nitrophenyltoluene from decomposition of the

methyl ether prepared from p-nitroaniline, in benzene and in toluene respectively. No mention was made of isomer distribution in the 4-nitrophenyltoluene.

From Diazocarboxylic Acids.--Potassium benzenediazocarboxylate has been reported to produce 10.5% of benzoylbiphenyls but no mention was made of isomeric forms (169).

From Diazoamino Compounds.--The pyrolysis of cyclic diazoamino compounds (35, 139, 146, 201) with subsequent formation of cyclic structures has long been known. Detailed description of these reactions is not included here since for the most part there is little freedom of choice as to orientation in the compounds thus produced.

The formation of 2-nitro-4-methoxybiphenyl from the diazoamino derivative of 3-nitro-4-aminoanisole in benzene, and the formation of 3,4-dimethylbiphenyl from decomposition in the same liquid of the 1,2-dimethyl-4-aminobenzene derivative formed by interaction with dimethylamine, have been reported (140). Elks and Hey (74) formed N-dimethyldiazoamino compounds by the action of aromatic diazonium chlorides and dimethylamine. They decomposed these substances in aromatic liquids at reflux temperatures in the presence of dry hydrogen chloride gas, in some cases, and glacial acetic acid in others. When the benzene derivative was decomposed in dry benzene, in the presence of dry hydrogen chloride gas, some chlorobenzene was isolated along with a 25% yield of biphenyl. Biphenyl was produced in 37% yield in the presence of glacial acetic acid. From decomposition in nitrobenzene while passing dry hydrogen chloride gas through the mixture they isolated nitrobiphenyls in 35% yield. From the reaction product they were able to separate and

identify 2- and 4-nitrobiphenyl.

There might be some question as to whether a polar mechanism is involved when hydrogen chloride gas is present but it seems unlikely that such would be the case with glacial acetic acid in the absence of water. The production of 3-phenylquinoline is reported (2) from the decomposition in dry benzene of the diazoamino compound which was prepared from 3-aminoquinoline and dimethylamine. In this case also dry hydrogen chloride gas was passed through the boiling mixture.

Radicals from the Pyrolysis of Azo Compounds

The radicals generated by the decomposition of purely aliphatic azo compounds, e.g., dimethyl 2,2'-azoisobutyrate, are not active enough to attack aromatic liquids (21). However, when phenylazotriphenylmethane was pyrolyzed in benzene the products were shown (120) to include tetraphenylmethane, biphenyl and some triphenylmethyl peroxide. The first two compounds could occur by attack on the benzene or by combination of free radicals, and the last by oxidation of the triphenylmethyl radicals. That biphenyl was probably formed through substitution of benzene is indicated by the fact that no biphenyl was found when the decomposition was carried out in chlorobenzene nor in nitrobenzene. Some 4-chlorobiphenyl was found in the former instance, but no biphenyl derivative was identified among the products formed in nitrobenzene. When phenylazotriphenylmethane was decomposed in toluene (219) a mixture of 2- and 4-methylbiphenyls was formed. This is further evidence for the attack of phenyl radicals on the aromatic substrate.

Wieland (219) also found p-benzoyltriphenylmethane as one of the products of pyrolysis of benzoylazotriphenylmethane. In pyridine there was produced some triphenylmethylpyridine (222). The formation of p-benzoyltriphenylmethane involves an apparent rearrangement, probably by way of a free radical, with substitution in the para position. Decomposition of phenylazotriphenylmethane in pyridine (2) produced a mixture from which tetraphenylmethane, triphenylmethane, 2-phenylpyridine, 3-phenylpyridine and 4-phenylpyridine were isolated. The authors report that from decomposition at 65-70° the ratio of isomers was 4->3->2- and when the reaction was carried out at 20° over a period of six weeks the isomers were obtained in the order 3->4->2-. In both cases the 2-isomer was obtained in lowest yield which is in contrast to the corresponding reactions with diazotized aniline, nitrosoacetanilide or benzoyl peroxide. Other workers (219) were able only to isolate 2- and 4-phenylpyridine from the products of this reaction.

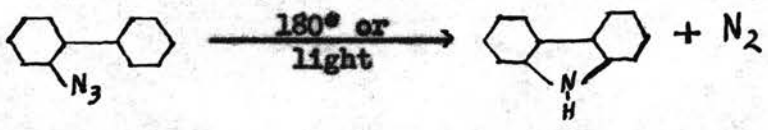
When 2-quinolylazotriphenylmethane was warmed in benzene at 70°, evolution of nitrogen was vigorous and the solution became dark in color. After the evolution of gas had ceased the authors (2) identified triphenylmethane, quinoline, and 2-triphenylmethylquinoline. When the experiment was repeated at the same temperature and the benzene removed under reduced pressure they found triphenylmethyl peroxide in addition. These products are analogous to the ones reported previously except that no attack on the benzene by the quinolyl radical is indicated by the products found.

Radicals from the Pyrolysis of Aliphatic Diazo Compounds

Aliphatic diazo compounds are not known to cause substitution in aromatic nuclei. Schonberg (189) observed no attack of diphenylmethylene (from diphenyldiazomethane) on boiling benzene; and although ethyl diazoacetate causes radical substitution in aliphatic hydrocarbons (172), it adds instead to a double bond in benzene (62).

Radicals from Pyrolysis of Azides

Neither phenyl nor benzoyl azide produces fragments that initiate polymerization of acrylonitrile (134) and phenyl azide accordingly does not cause nuclear substitution of benzene (18). Nevertheless the thermal interaction of hydrazoic acid and p-xylene (19) and the photochemical conversion of benzene and the same acid to aniline (147), coupled with the recent proof (181) that pyrolysis of hydrazoic acid yields imino radicals, show that substitutions of this kind are not impossible. In the very favorable cases of o-azidobiphenyl, 2-(2-azidophenyl)thiophene, and 3-(2-azidophenyl)pyridine, intramolecular ortho substitution (ring closure) does occur very well (193, 194).



However, this cyclization fails with 1-naphthyl azide, 2-phenylethyl azide, some nitroazidobiphenyls, and 2-(2-azidophenyl)pyridine. It is to be noted that Borsche and Hahn (25) obtained nuclear (exclusively

para) substitutions in aromatic compounds with phenyl azide and even wrote a free-radical mechanism for the process, but since they used aluminum chloride in larger amounts than the azide, a polar mechanism is more probable.

Mackey (162) obtained benzenesulfinamide by decomposing benzenesulfinyl azide in petroleum ether, but he did not investigate interaction with aromatic compounds.

From Sulfonyl Azides.--More extensive information is available for the sulfonyl azides. Curtius and his co-workers (49) found that when aromatic sulfonyl azides were heated in various aromatic liquids the ensuing reaction was not a typical Curtius rearrangement. On the contrary, the compounds which they isolated from the reaction mixtures after cessation of nitrogen evolution, which began at approximately 100°, showed that substitution of the aromatic liquid had occurred in nearly every case. The isolable products consisted primarily of aromatic sulfonamides. The reactions can be conceived as follows:

$$ArSO_2N_3 \longrightarrow ArSO_2N: + N_2$$

$$ArSO_2N: + Ar'H \longrightarrow ArSO_2NHAr'$$

$$ArSO_2N: + 2Ar'H \longrightarrow ArSO_2NH_2 + 2Ar'\cdot$$

The fate of the free aryl radicals is not clear, although Curtius (53) had previously reported the formation of a benzidine compound when aniline was used as the aromatic substrate. He was unable to fully characterize the compound, however.

When p-toluenesulfonyl azide was decomposed there was, in addition to the reactions shown above, some formation of the benzylidene radical, $C_6H_5CH:$, through elimination of hydrazoic acid and sulfur dioxide. Evi-

dence for this reaction was found in the fact that sulfur dioxide could be detected and that 4,4'-diaminotriphenylmethane was found when decomposition occurred in aniline, and also some 4,4'-(dimethylamino-)triphenylmethane in dimethylaniline. This is particularly noteworthy since other attempts to cause aromatic substitution by methylene or substituted methylene radicals have failed, as previously noted. Of particular interest also is the statement that substitution occurred only on the nucleus and in the ortho and the para positions exclusively. The statement was made that no side-chain substitution took place, but it was found that with aromatic amines as substrates, where amino hydrogen was available, there was some sulfonanilide formation by elimination of hydrazoic acid. Hydrazine formation did not take place, however.

Benzenesulfonyl Azide. Benzenesulfonyl azide reacts with benzene to form benzenesulfonanilide. With aniline it forms a small amount of benzenesulfonanilide by elimination of hydrazoic acid and it also produces isomeric benzenesulfonamidoanilines through nuclear attack by $C_6H_5SO_2N:$. The corresponding benzenesulfonamido derivatives are formed when methylaniline, dimethylaniline and diphenylamine, respectively, are used as the aromatic substrates. Decomposition of this azide in toluene resulted in the formation of benzenesulfonamidotoluenes along with benzenesulfonamide. When pyridine was the aromatic liquid a product was obtained which was reported to be sulfonamidopyridine. No statement was made as to orientation in this instance, but the general statement was made in the article that β-naphthalenesulfonyl azide caused substitution of pyridine in the β-position but in other cases the attack appeared to be in the β- or γ- position. This statement appears to be in contradic-

tion to the statement previously cited that substitution was invariably o- or p-.

No sulfonamido derivatives were isolable from decomposition of benzenesulfonyl azide in nitrobenzene or benzaldehyde. The general statement was made that decomposition of various sulfonyl azides in quinoline, nitrobenzene and benzaldehyde produced only the respective sulfonamide in each case along with tars whose composition could not be determined.

p-Toluenesulfonyl Azide. When p-toluenesulfonyl azide was decomposed in benzene the expected products were found. Decomposition in p-xylene resulted in the formation of p-toluenesulfonamido-p-xylene, but, of course, only one product was possible. The isomer ratio was not given for the product formed by reaction with aniline, but p-toluenesulfonamidoaniline was isolated, and the analogous product was reported from methylaniline, again without indication of isomer ratio. An o- to p- ratio of 2:1 was reported, however, for the p-toluenesulfonamidodimethylanilines produced when dimethylaniline was employed as the aromatic substrate. The expected product was reported from the decomposition of p-toluenesulfonyl azide in pyridine and since its melting point did not agree with the known melting point of the o- isomer, the conclusion was drawn that it must be the β- or the γ- isomer.

p-Chlorobenzenesulfonyl Azide. Only o-(p-chlorobenzenesulfonamido-)toluene was formed when p-chlorobenzenesulfonyl azide was decomposed in toluene. The expected p-xylidide was produced in p-xylene and N-1-naphthyl-p-chlorobenzenesulfonamide was obtained from attack on naphthalene. From aniline only the ortho isomer was obtained and the same result was reported with methylaniline. From the reaction with dimethylaniline both the ortho and para p-chlorobenzenesulfonamido derivatives

were found, but the comparative amounts were not indicated. Decomposition in pyridine was said to cause the expected substitution but again the point of attack was not determined. As previously indicated, only p-chlorobenzenesulfonamide was isolable from decomposition in quinoline.

1,3-Benzenedisulfonyl Azide. The decomposition of 1,3-benzenedisulfonyl azide in p-xylene resulted in the formation of 1,3-benzenedisulfon-di-p-toluidide. The sulfonamide was formed in dimethylaniline, but no sulfonamido substitution product could be found.

Acetylsulfanilyl Azide. When acetylsulfanilyl azide was decomposed in p-xylene the expected p-xylidide was produced.

1-Naphthalenesulfonyl Azide. The p-xylidide was produced when 1-naphthalenesulfonyl azide was decomposed in p-xylene. Owing to the fact that all positions on the nucleus which are subject to attack are equivalent, such examples serve only to emphasize the scope of the reaction.

2-Naphthalenesulfonyl Azide. With p-xylene as the aromatic substrate, the decomposition of 2-naphthalenesulfonyl azide produced 2-naphthalenesulfonamido-p-xylene, and 1-(2-naphthalenesulfonamido)-naphthalene was reported from the reaction with naphthalene. The attack on aniline resulted in the formation of the ortho 2-naphthalenesulfonamido derivative, and the expected product was formed in methylaniline but the isomer ratio was not determined. The decomposition of 2-naphthalenesulfonyl azide in dimethylaniline produced 2-naphthalenesulfonamidodimethylanilines but again the orientation was not indicated. The expected product was reported from the attack on pyridine but, contrary to the general statement previously cited, the orientation again appears to be uncertain. Only 2-naphthalenesulfonamide could be identified as a

product of the reaction with quinoline.

1,5-Naphthalenedisulfonyl Azide. The decomposition of 1,5-naphthalenedisulfonyl azide in p-xylene produced the expected compound by attack on two molecules of the aromatic substrate.

β-Anthraquinonesulfonyl Azide. Decomposition of this substance in p-xylene also gave the expected product, namely β-anthraquinonesulfonamido-p-xylene.

As previously noted Curtius (49) concluded that decomposition of sulfonyl azides in pyridine resulted in attack on the ring carbons. Alamela and Ganapathi (3) studied the decomposition of p-acetamidobenzenesulfonyl azide in pyridine and concluded that the product obtained was N-(3-pyridyl)-p-acetamidobenzenesulfonamide since its melting point was closer to that of the 3-isomer than to that of the 2- or the 4-isomer. Buchanan and his co-workers (5, 27) have shown that the structure of the compounds formed when aromatic sulfonyl azides are decomposed in pyridine is that of a quaternary salt, $C_5H_5\bar{N}-\dot{N}SO_2Ar$, and that C- substitution of the nucleus had not been accomplished by previous workers. Datta (60) substantiated the work of the latter group. He decomposed p-acetamidobenzenesulfonyl azide and p-toluenesulfonyl azide, respectively, in an excess of pyridine. The main reaction products were shown to be N-(p-acetamidobenzenesulfonimino-)pyridine and N-(p-toluenesulfonimino-)pyridine in that order. He was able to hydrolyze the compounds and to prepare other N-iminopyridine derivatives in order to prove the structure. The isolation of N-iminopyridine was reported, but it was found to be very short lived. Thus the decomposition of sulfonyl azides in pyridine is shown not to involve ring substitution but to be analogous to the formation of amine oxides.

$$R_3N + O \longrightarrow R_3N \rightarrow O$$

$$\diagup\!\!N + ArSO_2N: \longrightarrow \diagup\!\!N \rightarrow NSO_2Ar$$

Radicals from the Pyrolysis of Peroxides

Alkoxy radicals derived from mono- (183) or dialkyl peroxides (153, 202) do not attack aromatic nuclei. Acyl peroxides yield acyloxy radicals, which may substitute as such or decarboxylate to alkyl or acyl radicals which may or may not cause substitution. These reactions can be summarized as follows:

$$(RCO_2)_2 \longrightarrow R\cdot + RCO_2\cdot + CO_2$$

$$R\cdot + R'H \longrightarrow RR' + H\cdot$$

$$R\cdot + R'H \longrightarrow RH + R'\cdot$$

$$RCO_2\cdot + R'H \longrightarrow RCO_2R' + H\cdot$$

$$RCO_2\cdot + R'H \longrightarrow RCO_2H + R'\cdot$$

$$RCO_2\cdot + H\cdot \longrightarrow RCO_2H$$

$$RCO_2\cdot + R'\cdot \longrightarrow RCO_2R'$$

$$R\cdot + H\cdot \longrightarrow RH$$

$$R\cdot + R'\cdot \longrightarrow RR'$$

(Expressions such as $R\cdot$, $H\cdot$ and $RCO_2\cdot$ denote free radicals) Primary interest is in the orientation of the products (RR') or (RCO_2R') where R' is an aromatic nucleus. Alkyl radicals produced from peroxides do not attack aromatic nuclei (151, 207) unless such nuclei are unusually activated toward radical substitution, i.e., polynitro compounds (78), in which case orientation is practically meaningless because so many positions are blocked.

Table III presents a literature summary of arylations and acylations by aroyl peroxides.

The work of De Tar (67) and that of Hey (122) on the decomposition of benzoyl peroxide in nitrobenzene probably represent the only really quantitative data available on isomer ratios from substitution reactions of this type. Dannley and co-workers (57, 58a) applied to radical substitution, the Ingold (142) competitive method for comparing rates of reaction. Benzoyl peroxide was decomposed in equimolar mixtures of pyridine and various other solvents. They arranged the substances in the following order of decreasing reactivity toward substitution by phenyl radicals: nitrobenzene, 7> benzonitrile, 4.1> methyl benzoate, 3.7> methyl benzenesulfonate, 1.8> chlorobenzene, 1.7; pyridine, 1.7> bromobenzene, 1.6> toluene, 1.4> benzene, 1.0 .

Although the phenyl radicals generated were from N-nitrosoacetanilide, it is interesting to note here that De Tar (67) also found that chlorobenzene was attacked preferentially in a mixture of benzene and chlorobenzene and Huisgen and Sorge (139) found that twenty-two molecules of naphthalene were attacked for every molecule of benzene in a mixture of these two compounds.

Radicals from the Pyrolysis of Polyacetates

Carboxylic acid "salts" of elements in an abnormally high state of valence can lose RCOO• radicals and thus return to a more usual valence condition. Fieser and Chang (77) have generated radicals of this kind from lead tetraacetate and Sandin (185) likewise has generated acetate

Table III

SUBSTITUTIONS EFFECTED BY AROYL PEROXIDES

Peroxide	Aromatic Substrate	Ring-substituted Products[a]	Ref.
Benzoyl	Benzene	Biphenyl, phenyl benzoate, terphenyl, quaterphenyl	89
	Benzonitrile	Cyanobiphenyls, 2- (60)%, 3- (10)% and 4- (30)%	58
	Bromobenzene	Bromobiphenyls, 2- (48.5)%, 3- (33.0)% and 4- (18.5)%	58
	Biphenyl	Terphenyl, quaterphenyl	91
	Chlorobenzene	Chlorobiphenyls, 2- (64)%, 3- (23)% and 4- (13)%,	58
		4-isomer in 9% yield	57
	Chlorobenzene containing triphenylmethyl	4-Chlorotetraphenylmethane	220
	o-Cresol	2-Benzoyloxy-m-cresol[b]	42
	m-Cresol	4-Benzoyloxy-m-cresol	42
	p-Cresol	4-Benzoyloxy-m-cresol[b]	42
	Diphenylamine	2-Hydroxy-N-benzoyldiphenylamine	87
	Ethyl benzoate	Ethyl 3- and 4-phenylbenzoates	120
	Mesitol	4-Benzoyloxy-2,4,6-trimethylcyclohexa-2,5-dienone	43
	3-Methoxyphenol	2-Benzoyloxy-5-methoxyphenol	42
	4-Methoxyphenol	2-Benzoyloxy-5-methoxyphenol[b]	42
	Methyl benzenesulfonate	Methyl biphenyl sulfonates, 2- (53)%, 3- (33)% and 4- (14)%	58

Peroxide	Aromatic Substrate	Ring-substituted Products[a]	Ref.
Benzoyl (cont'd)	Methyl benzoate	Methyl 4-phenylbenzoate in 27% yield	57
	Methyl benzoate containing triphenylmethyl	Methyl 4-(triphenylmethyl)-benzoate	220
	Nitrobenzene	2- and 4-Nitrobiphenyls, the 4-isomer in 10% yield;	65, 120
		2- (69, 72 or 76)%, 3- (5, 2 or 0)%, 4- (26, 26, or 24)%;	57
		2- (46.3)%, 3- (0.7)% and 4- (53)%	67
			122
	Phenol	Benzoyloxyphenols, 2- (80)% and 4- (20)%	42
	Pyridine	2- and 4-Phenylpyridines, with 19-24% of the 4-isomer;	172
		the 3- isomer also;	57
		2- (58)%, 3- (27)% and 4- (15)%;	123
		p-phenylbenzoic acid and pyridylbiphenyl (?)	58
			172
	Quinoline	4- and 5-Phenylquinolines and several x-phenyl-quinolines	123
	Toluene	2- and 4-Methylbiphenyls, the 4-isomer in 8% yield;	69, 90
		2- and 4-phenylbenzoic acids and a cresyl benzoate	57
			90
	Toluene containing triphenylmethyl	4-Methyltetraphenylmethane	220
	m-2-Xylenol	5-Benzoyl-m-2-xylenol, 3,5,3',5'-tetramethyl-4,4'-diphenoquinone, 3,5,3',5'-tetramethyl-4,4'-dihydroxy-biphenyl	43
	m-4-Xylenol	4-Benzoyloxy-m-5-xylenol[b]	42
	m-5-Xylenol	4-Benzolyoxy-m-5-xylenol	42

Peroxide	Aromatic Substrate	Ring-substituted Products[a]	Ref.
o-Carbomethoxybenzoyl	Benzene	Methyl biphenyl-2-carboxylate	123
	Pyridine	Methyl x-pyridylbenzoates	123
o-Carboxybenzoyl	Benzene	None	123
	Nitrobenzene	2- and 4-Nitrobiphenyl-2'-carboxylic acids	123
p-Chlorobenzoyl	Benzene	4-Chlorobiphenyl	89
	Pyridine	2- and 4-(p-Chlorophenyl)-pyridines	123
o-Nitrobenzoyl	Benzene	2-Nitrobiphenyl	123
	Pyridine	None	123
m-Nitrobenzoyl	Benzene	3-Nitrobiphenyl	123
	Pyridine	None	123
	Benzoic acid	3-Nitrobiphenyl-3'- and 4'carboxylic acids	123
p-Nitrobenzoyl	Benzene	4-Nitrobiphenyl	123
	Pyridine	None	123
4-Nitro-2-carbomethoxybenzoyl	Benzene	Methyl 4-nitrobiphenyl-2-carboxylate	123
5-Nitro-2-carbomethoxybenzoyl	Benzene	Methyl 5-nitrobiphenyl-2-carboxylate	123
p-Methoxybenzoyl	Benzene	4-Methoxybiphenyl	123
	Pyridine	2- and 4-p-Methoxyphenylpyridines	123
4-Methoxy-4'-nitrobenzoyl	Benzene	p-Nitrobiphenyl, p-methoxybiphenyl	157
	Nitrobenzene	None	

Peroxide	Aromatic Substrate	Ring-substituted Products[a]	Ref.
Cinnamoyl	Benzene	Stilbene	123
	Pyridine	alpha-Stilbazole	123
1-Naphthoyl	Benzene	None	123
	Pyridine	x-(1-Naphthyl)pyridine	123
2-Naphthoyl	Benzene	2-Phenylnaphthalene	123
	Pyridine	x-(2-Naphthyl)pyridines, three forms	123

(a) Numbers enclosed in parentheses indicate percentages of arylated product rather than of theoretical yields.

(b) Benzoyl migration involved in formation of this product.

radicals from phenyliodoso acetate. It seems probable that manganese triacetate could be used in a similar manner.

In the investigation cited above Fieser (77) found that lead tetraacetate, heated in a mixture of 2,4,6-trinitrotoluene and a small amount of acetic acid, caused methylation with the formation of 1,3,5-trinitro-2,4-dimethylbenzene. In a similar fashion 1,3-dinitrobenzene was converted in part to 1,3-dinitro-6-methylbenzene and in part to either 1,3-dinitro-4,6-dimethylbenzene or 1,3-dinitro-2,6-dimethylbenzene. Nitrobenzene itself was methylated to form both the 2- and the 4-isomer. It was believed that the ortho predominated even though the para was easier to separate. With chlorobenzene as the aromatic substrate isomeric chlorobenzyl acetates were formed. It appears that chlorotoluenes were first formed with subsequent attack of the methyl groups by acetoxy radicals. When naphthalene was used in the reaction 1-acetoxynaphthalene was isolated in 25% yield. In the course of the investigation (185) with phenyliodoso acetate it was found that 2,4,6-trinitrotoluene was converted to 1,3,5-trinitro-2,4-dimethylbenzene in 20% yield. This reaction appears to be analogous to that of methylation with lead tetraacetate.

These reactions and the products formed are typical of radical reactions. They may be grouped into three classifications; methylation of the ring, acetoxylation of the methyl group, and acetoxylation of the ring. One sees here, as previously stated for alkyl radicals from peroxides, that the ring must be activated before it is attacked in appreciable amount. The acetoxy radical was shown to attack only the methyl group and the nucleus of naphthalene, which is highly active toward substitutions of this nature.

Radicals from the Pyrolysis of Organometallic Compounds

Ethyl radicals from the decomposition of tetraethyllead do not attack benzene and naphthalene below 300° (48), but certain Grignard reagents cause substitution in aromatic hydrocarbons, presumably by way of radicals (150). Methylmagnesium iodide in benzene gave both toluene and p-xylene, and benzylmagnesium chloride in benzene gave diphenylmethane (29%) and 18% bibenzyl, in mesitylene 20% 4-benzyl-1,3,5-trimethylbenzene, and in m-xylene 17% 4-benzyl-1,3-dimethylbenzene. Phenylmagnesium bromide caused phenylation of toluene in the 4-position and of o-xylene in an undetermined position, probably the 4-position also. In chlorobenzene the decomposition of phenylmagnesium bromide gave 5% chlorobiphenyl and 39% biphenyl. Obviously the high reactivity of Grignard reagents toward most functional groups prevents much extension of this work; similarly the known arylation of pyridines and quinolines by these reagents probably involves a polar, additive mechanism instead of a radical mechanism.

Free phenyl radicals are thought to be responsible for the ortho- and para- phenylation of ethyl benzoate when that liquid is used as solvent during the Ullmann treatment of iodobenzene with copper (179). The same radicals from diphenyliodonium chloride heated with pyridine and sodium hydroxide give 2-, 3- and 4-phenylpyridines (184).

Radicals from the Pyrolysis of Allylic Compounds

The grouping $Ar_nCH_{(3-n)}$-, like other allylic groups, is easily detached from atoms to which it may be bound, the more so as n increases.

The extreme case is that of Ar_3C joined to itself, wherein the spontaneous homolytic breaking of the bond at ordinary temperatures is familiar. Accordingly radicals are formed, and if the temperature is high enough they may cause aromatic substitution; they would not be expected to do so as easily as aryl radicals themselves, because resonance energy stabilizes allyl and benzyl but not phenyl radicals.

Thus the rearrangement of benzyl phenyl ethers (126, 127) in quinoline produces not only the expected o- and p-benzylphenols, but, by participation of the solvent, benzylquinolines and hydroxyphenylquinolines. The formation of benzyl and phenoxy radicals is postulated, the latter rearranging or undergoing intermolecular hydrogen transfer to yield hydroxyphenyl radicals. Similarly benzyl radicals from the pyrolysis of benzyl p-toluenesulfonate benzylate chlorobenzene in the para position, but do not affect nitrobenzene (171).

Triarylmethyl radicals normally do not attack aromatic nuclei (71, 207, 220). The conversion of phenol to p-hydroxytetraphenylmethane (207) probably involves primary attack on the hydroxyl hydrogen, and that of o-xylene to 4-(3,4-dimethylphenyl)triphenylmethane (221) should be verified, since m-xylene did not behave so. The disproportionation of triphenylmethyl (207) and diphenylamino (207) free radicals to polycyclic structures obviously involves only the ortho orientation of ring attack that is necessary for cyclization. The rearrangement of trimethylphenyl phenyl ketone to p-benzoyltriphenylmethane (222) appears to be substitution by a benzoyl rather than a triphenylmethyl radical. However, a disproportionation of triphenylmethyl leading to p-(triphenylmethyl)-triphenylmethane (221) appears to be a case of free "choice" of the para position.

Radicals from the Pyrolysis of Hypobromites

In all probability phenyl radicals are involved in the decarboxylative bromination of silver salts of aromatic carboxylic acids (12, 116) but no aromatic substitution has been caused by radicals so generated.

Radicals from the Pyrolysis of Halogens and N-Halogen Compounds

Atomic halogens, according to the picture being developed, should not obey usual orientation rules for polar substitution in even a side-chain-free aromatic nucleus. They might themselves substitute:

$$ArH + Cl\cdot \longrightarrow ArCl + H\cdot \qquad (I)$$

or they might pick up hydrogen and transmit the radical state to the ring:

$$ArH + Cl\cdot \longrightarrow Ar\cdot + HCl \qquad (II)$$

The chief examples of reactions of type I are the high-temperature halogenations done by Wibaut and his students (118, 192, 215, 216, 217, 218). It is sufficient to say here that such halogenations above 400° give isomer ratios approaching the statistical (for monosubstituted benzenes, 40% ortho, 40% meta, 20% para) as the temperature is raised; and such an amount of meta-isomer from, say, bromobenzene is accountable only on the hypothesis of radical attack.

The sole example found of type II reactions is the production of a little N-phenylsuccinimide from N-bromosuccinimide and benzene (135).

Radicals from Irradiation or One-electron Reduction of Hydrogen Peroxide

It has been demonstrated that in the oxidation of aromatic compounds by hydrogen peroxide in the presence of ferrous ions both free hydroxyl and free aryl radicals are involved. Thus Merz and Waters (166) summarized the reactions as follows:

$$Fe^{++} + HOOH \longrightarrow Fe^{+++} + HO:^{-} + \cdot OH$$

$$Fe^{++} + \cdot OH \longrightarrow Fe^{+++} + OH^{-}$$

$$ArH + \cdot OH \longrightarrow Ar\cdot + HOH$$

$$2Ar\cdot \longrightarrow ArAr$$

$$Ar\cdot + \cdot OH \longrightarrow ArOH$$

They found no evidence of attack on water by aryl radicals, but these radicals did dimerize in part and did combine with free hydroxyl radicals. From toluene there was formed bibenzyl (side-chain attack), benzaldehyde (also side-chain oxidation), and cresols by ring substitution of hydroxyl radicals. Some o-nitrophenol was isolated as a result of the oxidation of nitrobenzene and polyphenolic compounds were also produced. There was no evidence of the formation of dinitrobiphenyls, however. Oxidation of chlorobenzene produced some chlorophenol and polyhydroxy compounds, but again no evidence of the corresponding biphenyls was found. Benzoic acid gave some salicylic acid and salicylamide was produced from benzamide. The isomeric hydroxybenzamides were not found. Oxidation of benzenesulfonic acid gave a product which yielded tribromophenol upon treatment with bromine water. From phenol a good yield of catechol was produced along with some quinone and dihydroxybiphenyls.

Andersen (4) oxidized benzene in presence of ferrous ion and hydro-

gen peroxide. He found that phenol was formed, followed by oxidation to dark-colored compounds (probably quinones) and finally to carbon dioxide and oxalic acid. He postulated the formation of atomic oxygen from the decomposition of hydrogen peroxide. Baudisch (16) found that mixtures of benzene and aqueous solutions of sodium nitroprusside and hydrogen peroxide do not change color in the dark. When these mixtures were exposed to light the benzene layer became green and o-nitrosophenol was determined to be a product of the oxidation. The hydroxylation of nitrobenzene by the ferrous ion - hydrogen peroxide method was further reported (159). The relative amounts of isomers were: o-, 25-30%; p-, 50-55%; m-, 20-25%. Some 3,3'-dinitrobiphenyl was found along with small amounts of another substance thought to be a different dinitrobiphenyl.

The investigations of Davis and his co-workers (61) should be mentioned. They were interested in the formal similarity between oxidations with hydroxylamine in the presence of divalent chromium and oxidations with hydrogen peroxide in the presence of ferrous ion. The main aim of the investigation was the attempt to decide whether the oxidations involved amino radicals, hydroxyl radicals, or both. It suffices to say further only that they were able to isolate biphenyl from oxidation of benzene and that they concluded that a $C_6H_6 \cdot NH_2$ addition complex was involved.

Stein and Weiss (195, 196) reported that irradiation of benzene in water with X-rays and with γ-rays resulted in the formation of phenol and biphenyl. Catechol was produced by γ-rays and a trace of terphenyl resulted from X-ray irradiation. They found that like irradiation of benzoic acid resulted in the production of salicylic acid, p-hydroxybenzoic

acid, phenol and biphenyl. The last two compounds were presumably formed by decarboxylation. They estimated that the ortho to para ratio was 1:2.5. Another report (160) by the same group of investigators on the X-ray treatment of aqueous benzoic acid solutions shows the formation of all three hydroxybenzoic acids in the ratio o-: m-: p- approximately 5:2:10. The same ratio for phenol (197) is given as 1:0:2 in neutral solution and 1:0:8 in acid, and this report shows that ferrous ion - hydrogen peroxide oxidation of nitrobenzene also favors the 4-position since all three isomers are found in approximately equal amounts. For a more detailed report covering both the peroxide - ferrous ion and X-ray treatment of phenol the reader is referred to the source (198). A similar report (144) on chlorobenzene oxidations should be consulted for details of conditions and results. This portion of the dissertation can best be concluded with a statement from Stein and Weiss (197) to the effect that in such widely different reactions as the catalytic decomposition of hydrogen peroxide, the action of ionizing radiations on water, the photochemical decomposition of water by certain metal ions involving single-electron transfer processes, and apparently also some well-defined cases of electrolytic oxidations, evidence points to a mechanism involving the formation of free hydroxyl radicals.

Radicals from the Electrolytic Oxidation of Anions

When ions are discharged at an electrode the formation of free radicals must result. The fate of these radicals is dependent upon their nature. In many instances the final products and the course of the re-

action can only be explained as resulting from attack of these radicals upon the solvent or other materials present. As an example of this type of reaction one can cite the electrolysis of benzoic acid in pyridine (76). The products isolated included biphenyl, 4-phenylpyridine, 2-phenylpyridine, and 4-phenylbenzoic acid. The same products were obtained when benzoyl peroxide and benzoic acid in equal weights were placed in the cell containing the pyridine. Fieser and co-workers (78) observed that electrolysis of sodium acetate in acetic acid in the presence of trinitrotoluene gave small yields of trinitro-m-xylene.

Radicals from Chain Propagation in Vinyl Polymerization

Price (177, 178) in studying the action of mononitro aromatic compounds as inhibitors of styrene polymerization, supposed that the polystyrene radicals attack nitrobenzene in the para position and 2-nitrothiophene in the 5 position. However, no proof of such orientation was given.

Part II: Review of Theories

The preceding portions of this historical review have been limited to the presentations of factual material resulting from experimentation by a large number of investigators. The theoretical considerations that have appeared may well be discussed in relation to three questions. Are radicals involved? Are they free radicals? Why do they orient as they do?

Do the Reactions Previously Discussed Really Involve Radicals?

It is generally agreed that the mode of decomposition of diazo compounds and acyl peroxides depends upon the environment. In a nonpolar environment, particularly in the absence of acids, radicals are believed to be intermediates in the reactions. De Tar (65, 66, 67) draws these conclusions for diazo compounds from the nature of the products they yield. Bartlett (13, 170) and Leffler (157) have made similar deductions for aroyl peroxides. Hodgson (130, 131) rejects the concept of radical intermediates in aqueous solutions but his views are not accepted by Hey and Waters (125) as relevant to mechanisms of decomposition of diazo compounds in non-aqueous media. Indeed the whole trend of British thought in this matter has been an acceptance and extension of the free radical mechanisms reviewed by Waters (207).

Are the Intermediate Radicals Really Free?

This question may be stated more explicitly. Do the radicals exist independently of other entities in the solution, capable of detached though temporary existence, or do they participate in reaction only within a complex wherein the old bonds are broken and new ones formed simultaneously?

The English school of thought has considered, ever since enunciation of the original theory (100), that the radicals are truly free, and that aromatic substitutions by them should be represented by the equation

$$ArH + R\cdot \longrightarrow ArR + H\cdot$$

Besides the emphasis given this view by Waters (207), we may note its more recent adoption by Loebl, Stein, and Weiss (159, 160).

This view has been disputed for some time in continental Europe. Formation of a solvent - acyl peroxide complex which then disproportionated was suggested by Gelissen and Hermans (92) and more or less explicitly stated by others (24, 75, 117, 223, 224). Recently Huisgen and Horeld (137) have adduced serious evidence against the participation of free radicals in decompositions of diazoacetates, notably (a) the failure of the acetate radical to decarboxylate, (b) the failure of the aryl and acetate radicals to combine to give phenolic esters and (c) the absence of arylamines, to be expected from the reaction of aromatic nitro compounds with the atomic hydrogen displaced (224). Huisgen and Horeld (137) proposed a "kryptoradical" mechanism, i.e., a diazoacetate - aromatic compound complex that decomposes into an arylated aromatic compound, nitrogen, and acetic acid; but they consider radicals as much involved here as ions are in an acid-catalysed bromination. This view is echoed by Huisgen and Sorge (139). In this country, the failure of diazotized aminobicyclic compounds to cyclise further (though they do undergo intermolecular Gomberg reaction) led De Tar and Sagmanli (66) also to doubt the freedom of radicals involved, which they noted would be thermochemically improbable. For arylations with acyl peroxides, they suggested that a radical-induced chain decomposition (170) is responsible:

$$PhCOO\cdot + ArH \longrightarrow Ar\cdot + PhCOOH$$

$$Ar\cdot + (PhCOO)_2 \longrightarrow ArPh + CO_2 + PhCOO\cdot$$

How Can the Orientation in Radical Substitutions be Explained?

The dominance of ortho-para substitution in all the work cited previously is obvious; but the independence of such orientation from the nature of the so-called directive group already present, first pointed out by Grieve and Hey (100), has come to be considered characteristic of substitution by radicals. Curtius (49) had already remarked the specificity of free radicals from sulfonyl azides for these positions, never the meta nor side-chain positions, but he was unable to isolate substituted products of rings bearing electrophilic (meta-directing) substituents. Further work soon showed, however, that meta-substitution by radicals does occur, though in subordinate amount (108, 110).

Apparently the first attempt at a theoretical accounting for observed isomer ratios in radical substitution was made by Wheland in 1942 (213). He undertook to account for the facts by molecular-orbital calculations and did so for ortho-para predominance, but could not distinguish these. He has interpreted ortho-para orientation of radicals in nitrobenzene as due to the comparative stability of o- and p-quinoid intermediates (214; cf, 68, p. 278) and in toluene as due to a similar stabilization by hyperconjugation. Wheland's calculations have been critized for their neglect of meta orientation (166) and reviewed or imitated by Sandorfy, Vroelant, Yvan, Chalvet, and Daudel (186) and Hartman (107). The alternative explanation (180) that radicals are amphoteric -- nucleophilic toward nitrobenzene, for example, and electrophilic toward toluene -- appears to be an ad hoc assumption. Seel (190, 191) purports to explain reactions of all conjugated systems of

double bonds, but he does not emphasize radical reactions.

Since there is no theory to account for the ratio of ortho to para isomers in even the long-studied electrophilic substitution, it is understandable that none has been developed in the much newer field of radical substitution. However, Coulson (45, 46) finds that calculations of local electron densities in monosubstituted benzenes suggest a predominance of ortho substitution. Of the quantitative results cited in Part I, the majority do show such a predominance. Predominance of the ortho isomer is shown in Table II (67, 81, 82, 83, 103, 122, 139) and in Table III (42, 43, 166). Some para predominance is also recorded however, in Table II (82, 161) and in the sections on irradiation and one-electron transfer (159, 160, 195, 196).

EXPERIMENTAL

ATTEMPTED CHLORINATION OF AROMATIC NUCLEI THROUGH THE USE OF BENZOYL PEROXIDE AND CARBON TETRACHLORIDE

It has been found that free-radical substitution of chlorine for hydrogen of saturated aliphatic hydrocarbons will take place when peroxides are decomposed in the presence of a polychloroalkane and the desired hydrocarbon substrate. For example West and Schmerling (212) heated benzoyl peroxide, a polychloroalkane, and a liquid hydrocarbon, such as n-heptane, at reflux temperature for sixteen hours. The mixture was then washed with dilute alkali to remove benzoic acid, dried with potassium carbonate, and distilled in a fractionating column. They found in each case that some chlorination of the hydrocarbon had occurred. In some cases, particularly when a low-boiling or a gaseous hydrocarbon was employed as the substrate, the mixture of reactants was heated in a sealed tube.

In view of the success attained in chlorination of aliphatic hydrocarbons by the procedure cited above, it was decided to employ this method in an attempt to chlorinate aromatic hydrocarbons. Accordingly benzoyl peroxide and carbon tetrachloride were added to an aromatic liquid and the solution was heated to a temperature somewhat above the decomposition point of benzoyl peroxide. The reaction mixture was then extracted with twenty per cent aqueous potassium carbonate solution in order to remove benzoic acid and this extraction was followed by washing with water to remove the last traces of water-soluble material. The re-

maining material was then dried over sodium sulfate and the lower-boiling portions were removed by vacuum distillation in a multiple-plate column. The higher-boiling residue in each case was then fractionated in the Todd Column.

In no case was the desired product found to be present even though the concentrations of reactants were varied over a considerable range. These experiments are summarized in Table IV.

Table IV

ATTEMPTED CHLORINATION OF AROMATIC NUCLEI

The amounts of benzoyl peroxide and carbon tetrachloride used in each experiment are designated by letters:

A 4.84 g. (0.02 m.) benzoyl peroxide and 61.5 g. (0.4 m.) carbon tetrachloride

B 24.2 g. (0.1 m.) benzoyl peroxide and 61.5 g. (0.4 m.) carbon tetrachloride

C 24.2 g. (0.1 m.) benzoyl peroxide and 385 g. (2.5 m.) carbon tetrachloride

Aromatic Liquid Name	Amount g.	Amount moles	Procedure	Average temp.	Time, hours	Product
Toluene	121	1.31	A	Reflux	16	Trace of benzoic acid[a]
Nitrobenzene[b]	153.5	1.25	A	108°	16	0.5 g., 4-Nitrobiphenyl
Nitrobenzene	153.5	1.25	B	114°	18	Trace of biphenyl
Nitrobenzene[c]	140	1.14	C	84°	25	None isolated

(a) Reaction mixture was not extracted with 20% K_2CO_3 before fractionation.

(b) 14 g. of C. P. K_2CO_3 was added at the beginning (212).

(c) Tarry residue in this experiment was extracted with acetone but no yield of desirable product was obtained.

SUBSTITUTION OF AROMATIC NUCLEI THROUGH THERMAL DECOMPOSITION OF BENZENESULFONYL AZIDE

This portion of the experimental work was based upon results obtained by Curtius and co-workers (49). Benzenesulfonyl azide was thermally decomposed in various aromatic liquids to yield mixtures of substituted benzenesulfonanilides along with varying amounts of benzenesulfonamide. The overall reaction may be represented as follows:

$$C_6H_5SO_2N_3 + ArH \xrightarrow{105\text{-}120^\circ} C_6H_5SO_2NH_2 + C_6H_5SO_2NHAr + N_2$$

Reagents.--All reagents were C. P. grade with few exceptions. In those cases where C. P.-grade materials were not available, purification was accomplished by appropriate means. Liquid reagents were redistilled in a multiple-plate column. A middle fraction was collected and this fraction was stored over anhydrous sodium sulfate before use. Solid reagents were recrystallized. All liquid aromatic amines which showed any signs of deterioration were purified by acetylation, recrystallization, hydrolysis and drying prior to distillation.

Since m-anisidine was commercially unavailable it was prepared in three steps. The first step was the preparation of m-nitrophenol by hydrolytic decomposition of m-nitrobenzenediazonium sulfate. The second step was the preparation of m-nitroanisole by alkylation of sodium m-nitrophenoxide with methyl sulfate, and the third step consisted of reduction of m-nitroanisole to m-anisidine by means of tin and hydrochloric acid. m-Aminobenzoic acid, which was not in stock in our storeroom, was prepared by reduction of m-nitrobenzoic acid with tin and hydrochloric acid.

Benzenesulfonyl azide, which is a clear, colorless, somewhat viscous liquid, was prepared by two different methods. The first method (49) consisted of preparing benzenesulfonhydrazide by reaction of benzenesulfonyl chloride and aqueous hydrazine and converting the hydrazide to the azide by action of nitrous acid. The second method (49), which proved more satisfactory, comprised reacting an alcoholic solution of benzenesulfonyl chloride with an aqueous solution of sodium azide to which alcohol had been added nearly to the point of precipitation of the sodium azide.

Detailed Procedure for Azide Preparation.--To 22 g. of recrystallized sodium azide dissolved in 50 ml. of warm water was added a 90-ml. portion of 95% alcohol and the mixture was cooled in an ice-salt bath. Forty-five grams of benzenesulfonyl chloride, diluted with twice its volume of 95% alcohol, was slowly added, with mechanical stirring, to the cold sodium azide solution. The mixture turned orange and then red in color. Stirring was continued for 30 minutes in the cold and for another 30 minutes at room temperature. At the end of this time the red color had disappeared. The mixture was transferred to a one-liter separatory funnel and 100 ml. of water was added. Upon standing, a clear colorless oil separated at the bottom of the funnel; 48 g. of such crude product was removed. The water layer was extracted with two twenty-five-milliliter portions of ethyl ether and the ether extract was added to the oil in a small separatory funnel. The ether solution was then washed four times with thirty-milliliter portions of water after which the ether layer was separated and dried over sodium sulfate. Removal of the ether by warming on a water bath at 50° under vacuum gave 39 g. of benzenesulfonyl azide (84% based on benzenesulfonyl chloride). Pure benzenesul-

fonyl azide decomposed rapidly but quietly upon being warmed to approximately 105°, but the crude product obtained prior to final thorough washing of the ether solution detonated violently upon heating. A small amount of the crude product was sufficient to cause a shattering explosion.

Preparation of Substitution Products.--Substitution reactions with various monofunctional derivatives of benzene were accomplished by adding benzenesulfonyl azide to the aromatic liquid in sufficient quantity to make a solution of 5-10% concentration. This solution was then heated at 105-120°. in a flask carrying a reflux condenser equipped with a calcium chloride drying tube. Evolution of nitrogen was no longer apparent after approximately 10 hrs. but heating was continued without interruption in each case for a total of 48 hours.

At the end of the 48-hour period the excess aromatic liquid was removed from the reaction mixture by vacuum distillation followed by steam distillation. Steam distillation sometimes caused some hydrolysis of the aromatic liquid to difficultly distillable products, but these were eliminated by subsequent extractive procedures.

The tarry residue remaining in the reaction flask was extracted with copious amounts of 5% aqueous sodium hydroxide solution in order to dissolve all benzenesulfonamide and benzenesulfonanilides. The basic extract, which was very dark in color, was treated with a small amount of decolorizing charcoal, filtered and made acid with dilute hydrochloric acid. The liquid, now containing suspended precipitate, was thoroughly extracted with ether and the ether was then evaporated in order to obtain a crystalline mixture of benzenesulfonamide and isomeric benzenesulfonanilides. The various runs thus made are summarized in Table V.

Table V

PREPARATION OF SUBSTITUTION PRODUCTS

Exp. No.	Aromatic Liquid Name	Aromatic Liquid Wt., g.	Benzenesulfonyl Azide, Wt., g.	Crystalline Product, Wt., g.
1	Toluene	100	10	5.5
2	Toluene	170	15	8.0
3	Chlorobenzene	160	16	15.5
4	Chlorobenzene	200	15	11.5
5	Bromobenzene	300	18	8.0
6	Bromobenzene	300	21	5.5
7	Anisole	200	15	3.5
8	Anisole	200	15	5.0
9	Phenol	200	15	8.5
10	Nitrobenzene	200	10	None
11	Benzonitrile	200	10	2.5
12	Benzonitrile	160	11	3.0
13	Methyl benzoate	200	15	50
14	Methyl benzoate	150	10	36
15	Benzoyl chloride	200	15	55(a)
16	Benzoyl chloride	200	15	40.5

(a) Possibly some benzoic acid remaining; did not give meaningful results in subsequent procedures.

Preparation of Samples for Analysis.--The mixture of amides and isomeric anilides from each experiment was hydrolyzed by refluxing for 48 hours in approximately 10 ml. of 25% hydrochloric acid per gram of crystalline mixture. In every case where the isomeric substituted anilines produced by hydrolysis were steam-distillable, superheated steam was passed into the reaction flask after the solution had been made distinctly alkaline with sodium hydroxide solution. Steam distillation was continued in each case until the distillate being collected no longer gave a positive 2-naphthol coupling test for aromatic amine. The steam distillate was collected in brown bottles to avoid discoloration of the distillate prior to extraction of the amine from the aqueous mixture. As a control a mixture of the synthetic benzenesulfonyl derivatives in known ratio (for the toluidines) or a similarly known mixture of the three isomeric amines (for the other substituted anilines) was refluxed in 25% hydrochloric acid and treated in every way just like the unknown mixture throughout the remaining procedures.

Repeated extraction of the bases was carried out, in some instances with the solvent which was to be used in the spectrophotometric procedure. In others, ether was used for the extraction and evaporated off afterward. Since steam distillation from the hydrolyzed mixture was not feasible in the case of aminophenols and aminobenzoic acids, they were isolated by extraction.

The acid hydrolyzate that contained hydrochlorides of the aminophenols was first freed of any steam-volatile material by passing superheated steam through it for 3 hours. The solution was then transferred to a brown bottle, cooled in an ice bath, neutralized with 20% sodium carbonate solution, and quickly extracted with ether. The ether solu-

tion was dried over anhydrous sodium sulfate in a dark cupboard. It was necessary to accomplish these steps rapidly in order to avoid rapid discoloration of the aminophenol solution.

The acid hydrolyzate containing the hydrochlorides of aminobenzoic acids was freed of steam-volatile material with superheated steam. The solution was then made strongly alkaline by addition of sodium hydroxide solution and super-heated steam was again passed through it for a two-hour period. The mixture was then adjusted to the arbitrarily chosen pH of 5 and the isomeric aminobenzoic acids, which partly precipitated, were removed by repeated extraction with ether. The combined ether solutions were then dried over anhydrous sodium sulfate.

Determination of Isomer Ratios.--All analyses of mixtures of isomeric substituted anilines were done by the method of Vaughn and Stearn (203) using the Beckman Quartz Spectrophotometer, Model DU, with hydrogen lamp and 1-cm. quartz cells. Standard solutions of each of the three isomers involved in any one experiment were carefully prepared. All three solutions were of the same concentration (approximately 0.001 M). The optical density of each solution was then determined at wave lengths 1 mμ apart in the range 240 mμ to 320 mμ. The numerical values for the optical density were then plotted as a function of the wave length. From the curves thus produced, which corresponded closely to those found in the literature (80, 98, 167, 168, 174), four wave lengths were chosen for each set of three isomers such that a maximum and a minimum value for optical density of each isomer were included. Ideally a maximum for one should coincide with minima for the other two. For each of the three isomers, the four values of optical density were separated into two pairs and within each pair one value was subtracted

from the other. The two differences thus obtained were used, one as abscissa and one as ordinate, to determine a point on a graphical plot. When the values for the ortho-, the meta- and the para-isomers were thus plotted a triangle could be obtained by connecting the points with straight lines.

The choice of the wave lengths, the pairing of the optical densities, and the order of the substractions were determined on the basis of two factors. It was desired to obtain the best triangle for later accurate determination of the location of points within the triangle, but it was also desirable to obtain optical density differences of considerable magnitude, either positive or negative, for accurate spectrophotometric measurement of ratios of isomers in the mixtures. Several trials were necessary in each instance before a suitable combination was found. From a mixture of the isomeric compounds, treated in the same manner as each pure isomer, a point was obtained within the triangle and the composition of the mixture could be closely approximated from the location of the point. The composition was finally verified in each instance by preparing a known mixture giving the same point-location.

Actual analyses were accomplished by titrating the solutions of isomeric substituted anilines in order to permit dilution to the same molar concentration as the standard solutions, treating the solutions as previously described for the standard solutions in order to obtain a close approximation of the isomer ratio, and finally matching each solution empirically by mixing standard solutions of pure isomers. The titrations were carried out in glacial acetic acid with perchloric acid in the same solvent using methyl violet as the indicator (163, 225). Verification of the accuracy of dilution was obtained in each case by the

fact that the values obtained for optical density agreed with those of the matching mixture of standard solutions.

The detailed procedure is illustrated by the following typical experiment (No. 3). Sixteen grams of benzenesulfonyl azide was added to 160 g. of dry C. P. chlorobenzene in a 300-ml. three-neck flask equipped with a reflux condenser carrying a calcium chloride drying tube. The temperature was maintained at 105-120° for 48 hours during which time the mixture changed from yellow to light brown and then to very dark brown. Evolution of gas was apparent almost as soon as the temperature reached 105° but was no longer noticeable after six hours. At the end of the 48-hour period the excess chlorobenzene was removed by vacuum distillation followed by steam distillation; a total of three liters of aqueous distillate was collected. The dark residue remaining in the flask was extracted with 200 ml. of 5% sodium hydroxide solution in four portions. All the material in the flask apparently dissolved. To the solution was added 5 g. of decolorizing carbon which was then filtered out by suction and washed with water. The combined filtrate was extracted with 200 ml. of ether which was discarded. The basic aqueous solution was then made distinctly acid by addition of 25% hydrochloric acid and the acid mixture was extracted with three 100-ml. portions of ethyl ether. The ether solution was then dried for 12 hours over anhydrous sodium sulfate.

The sodium sulfate was removed from the ether solution by careful decanting and filtering, after which the ether was removed by evaporation. The yield was 16.25 g. of a light brown crystalline material.

A portion (15.50 g.) of the mixture of benzenesulfonamide and isomeric chloroanilides of benzenesulfonic acid was placed in a 300-ml.

round-bottom flask and 150 ml. of 25% hydrochloric acid was added. The mixture was refluxed for 48 hours. A control mixture of 3.000 g. of o-chloroaniline, 1.500 g. of m-chloroaniline, and 1.000 g. of p-chloroaniline (54.5%, 27.3%, and 18.2% respectively) was refluxed in 25 ml. of 25% hydrochloric acid for the same length of time.

While the above mixtures were being refluxed in hydrochloric acid, standard solutions of o-chloroaniline, m-chloroaniline, and p-chloroaniline, each 0.0006 molar, were prepared in spectrographic-grade isooctane. The optical densities of these solutions were then determined, with results shown in Table VI.

The curves for the pure o-, m-, and p-isomers are shown in Figure 1. From these curves it was determined that wave lengths 265, 274, 285 and 305 mμ would be suitable for establishing a triangle as previously described. The optical densities at these wave lengths were paired and differences taken, (Optical Density_{285} -- Optical Density_{265}) and (Optical Density_{305} -- Optical Density_{274}), and the values obtained are shown in the first part of Table VII. These values were then plotted and the points were connected to determine the triangle shown in Figure 2.

The acid mixture from the control, which had been refluxed for 48 hours, was cooled, treated with 3 g. decolorizing charcoal, filtered and rendered distinctly alkaline by the addition of 25% sodium hydroxide solution. It was then steam-distilled in an all-glass system, with no stopcock grease on any of the joints, until the distillate being collected failed to give a 2-naphthol coupling test for aromatic amine. Approximately 2 liters of distillate was collected. This was extracted with 200 ml. of isooctane in three portions. The isooctane solution was

Table VI

OPTICAL DENSITIES OF CHLOROANILINES (X 10^3)

Experimental results and matching solutions are designated by lettered columns:

A Values for solutions obtained from experimental procedures

B Values for matching solutions

Wave length mμ	Isomer			Control Mixture		Exp. No. 3		Exp. No. 4	
	o	m	p	A(a)	B(b)	A	B(c)	A	B(d)
260	156	179	598						
261	166	167	471						
262	179	166	387						
263	196	175	324						
264	213	183	279						
265	234	196	241	247	244	246	244	242	243
266	266	211	223						
267	295	231	203						
268	328	254	202						
269	362	276	202						
270	409	306	206						
271	449	338	219						
272	496	365	223						
273	543	402	242						
274	602	437	257	521	519	470	468	488	486
275	651	476	274						
276	714	512	294						
277	777	551	314						

Wave length mμ	Isomer			Control Mixture		Exp. No. 3		Exp. No. 4	
	o	m	p	A(a)	B(b)	A	B(c)	A	B(d)
278	843	602	343						
279	909	643	369						
280	978	688	402						
281	1060	735	426						
282	1120	782	450						
283	1170	823	485						
284	1230	856	512						
285	1290	892	544	1090	1085	1000	996	1020	1020
286	1340	935	574						
287	1280	957	602						
288	1430	981	637						
289	1470	1020	664						
290	1500	1040	700						
291	1490	1040	728						
292	1470	1020	741						
293	1440	997	763						
294	1390	981	790						
295	1340	935	797						
296	1270	868	805						
297	1230	825	815						
298	1180	795	819						
299	1130	750	818						
300	1030	698	812						
301	939	632	797						
302	782	543	766						

Wave length mμ	Isomer o	m	p	Control Mixture A(a)	B(b)	Exp. No. 3 A	B(c)	Exp. No. 4 A	B(d)
303	612	440	744						
304	459	352	708						
305	348	270	676	407	406	466	462	452	451
306	255	198	632						
307	180	141	593						
308	123	102	556						

(a) Control mixture contained, before treatment, 54.5% o-, 27.3% m-, 18.2% p-.

(b) Matching solution for control mixture contained 55% o-, 29% m-, 16% p-.

(c) Matching solution for Exp. No. 3 contained 57% o-, 13% m-, 30% p-.

(d) Matching solution for Exp. No. 4 contained 53% o-, 18.5% m-, 28.5% p-.

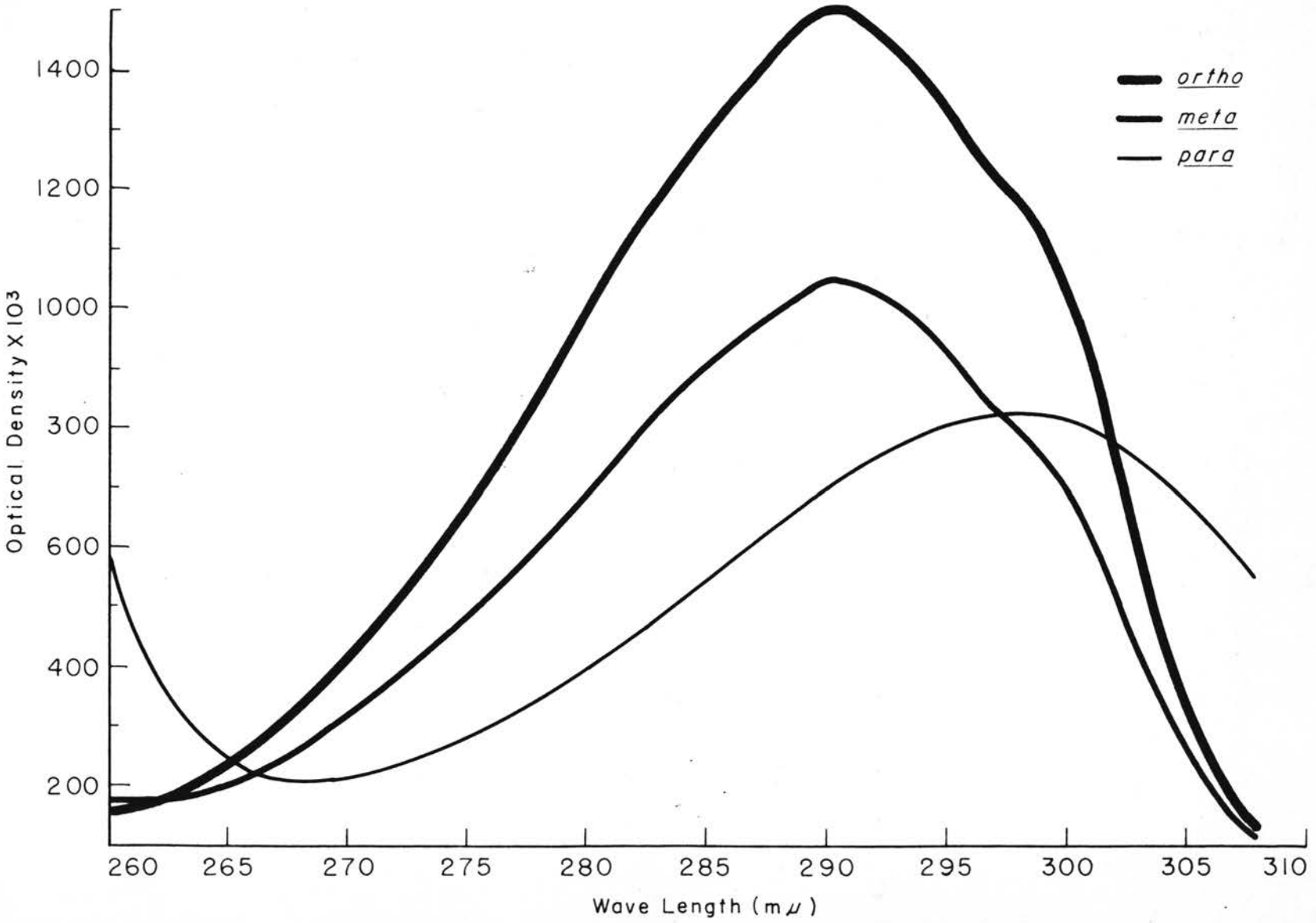


Figure I. Optical Density Curves of the Isomeric Chloroanilines

Table VII

DIFFERENCES IN OPTICAL DENSITIES AT SELECTED WAVE LENGTHS: CHLOROANILINES (X 10^3)

Experimental results and matching solutions are designated by lettered columns:

A Values for solutions obtained from experimental procedures

B Values for matching solutions

Wave length mμ	Isomer			Control Mixture		Exp. No. 3		Exp. No. 4	
	o	m	p	A(a)	B(a)	A	B(a)	A	B(a)
285 minus 265	1056	696	303	843	841	754	752	778	777
305 minus 274	-254	-167	+419	-114	-113	-4	-6	-36	-35

(a) For compositions of control mixture and matching solutions, see footnotes to Table VI.

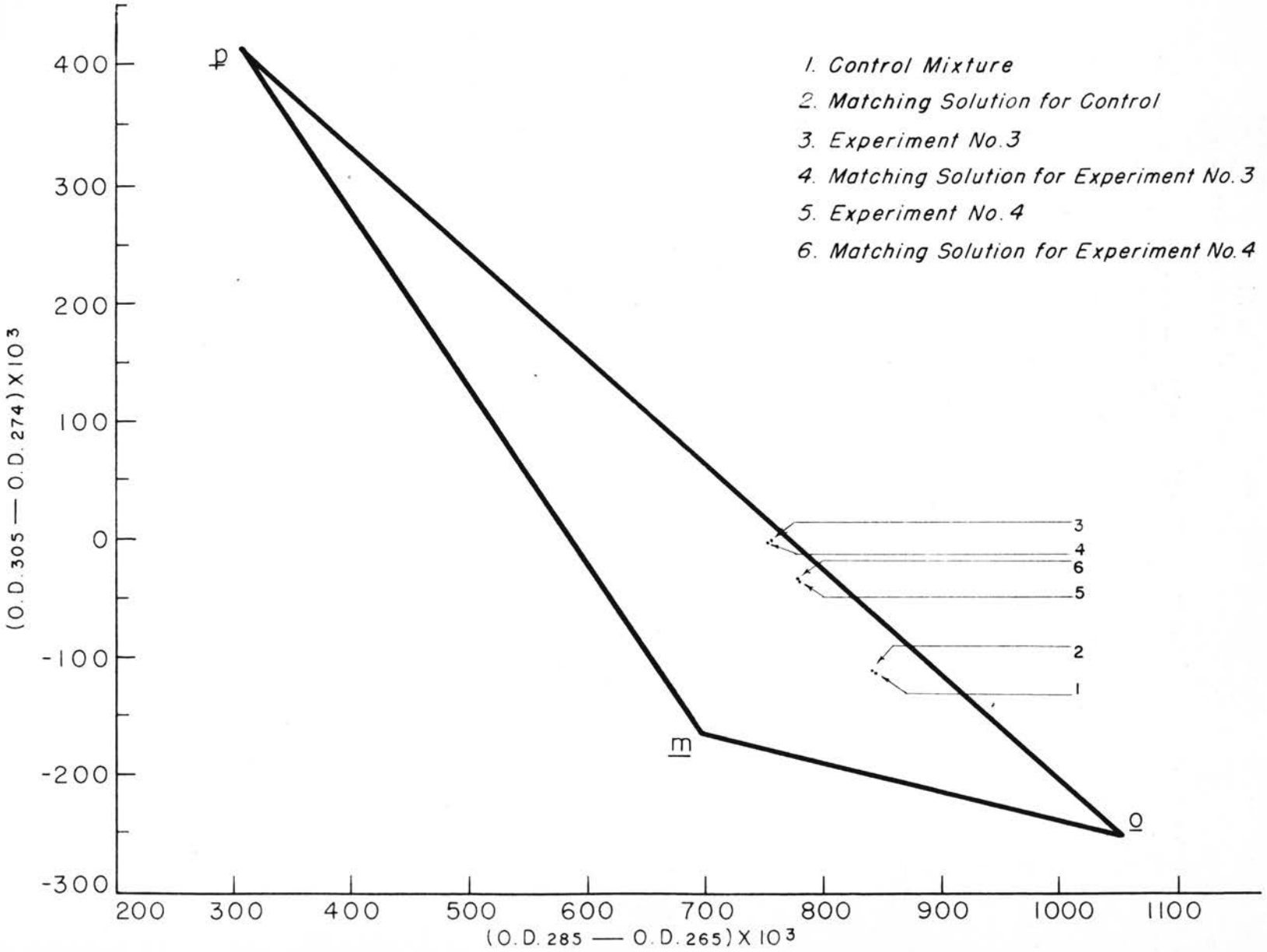


Figure 2. Differences in Optical Density at Selected Wave Lengths: Chloroanilines

then dried over anhydrous sodium sulfate in a dark cupboard for three hours, after which the solution was titrated as previously described and diluted to the same concentration as the standard solutions (0.0006 M). As shown in Table VII, the optical densities were determined at 265, 274, 285 and 305 mμ, and were paired and subtracted as for the standard solutions. The values obtained were plotted in Figure 2 and the approximate ratio was determined graphically from the position of the point on lines drawn in turn from each apex, through the point to the opposite side of the triangle. The actual value was then determined by preparation of a matching solution from pure standards as is also indicated in Table VII and in Figure 2.

Since the results obtained from the control mixture indicated only very slight disturbance of the isomer ratio during steam distillation and subsequent manipulations, the unknown mixture obtained from the experiment was treated in exactly the same manner with results as shown in the last part of Table VII and Figure 2.

The results from the other experiment (No. 4) with chlorobenzene are also shown in Tables VI and VII and in Figure 2. The analytical results obtained from the remainder of the experiments are shown in Tables VIII - XVII and Figures 3 - 12.

Owing to the extreme difficulty encountered in isolating crystalline products from the decomposition of benzenesulfonyl azide in phenol and the great susceptibility of the aminophenols to oxidation and discoloration, only one experiment in this series was completed. Two other attempts were made but no crystalline product was isolable in either case.

It appears that p-aminobenzoic acid was not as completely precipitated at the chosen pH as were m-aminobenzoic acid and o-aminobenzoic.

Table VIII

OPTICAL DENSITIES OF TOLUIDINES (X 10^3)

Experimental results and matching solutions are designated by lettered columns:

A Values for solutions obtained from experimental procedures

B Values for matching solutions

Wave length mμ	Isomer			Control Mixture		Exp. No. 1		Exp. No. 2	
	o	m	p	A(a)	B(b)	A	B(c)	A	B(d)
255	488	692	879						
256	459	615	784	530	530	532	533	531	532
257	438	545	689						
258	422	490	616						
259	412	447	556						
260	411	418	504	408	408	407	408	405	404
261	412	387	459						
262	419	375	430						
263	431	363	400						
264	447	359	379						
265	459	364	367						
266	496	373	356						
267	530	386	352						
268	564	406	354						
269	605	428	362						
270	650	453	372						
271	699	488	391						
272	750	522	412						

Wave length mμ	Isomer o	m	p	Control Mixture A(a)	B(b)	Exp. No. 1 A	B(c)	Exp. No. 2 A	B(d)
273	799	555	431						
274	856	598	457						
275	915	636	487						
276	968	678	518						
277	1030	726	553						
278	1080	774	597						
279	1130	807	634						
280	1170	860	673						
281	1220	900	719						
282	1250	948	761						
283	1290	982	800						
284	1310	1020	844						
285	1325	1040	882	1130	1130	1140	1140	1135	1135
286	1320	1060	926						
287	1290	1070	970						
288	1250	1075	999						
289	1210	1070	1030						
290	1170	1060	1050						
291	1090	1030	1070						
292	1030	990	1080						
293	955	945	1090						
294	860	890	1090						

Wave length mμ	Isomer			Control Mixture		Exp. No. 1		Exp. No. 2	
	o	m	p	A(a)	B(b)	A	B(c)	A	B(d)
295	759	838	1080						
296	648	777	1065	776	775	782	782	778	779
297	538	705	1040						
298	437	625	1005						
299	348	539	955						
300	266	443	900						

(a) Control mixture contained, before treatment, 57.1% o-, 14.3% m-, 28.5% p-

(b) Matching solution for control mixture contained 56.6% o-, 14.5% m-, 28.8% p-.

(c) Matching solution for Exp. No. 1 contained 61.2% o-, 10.6% m-, 28.1% p-.

(d) Matching solution for Exp. No. 2 contained 59.9% o-, 12.7% m-, 27.3% p-.

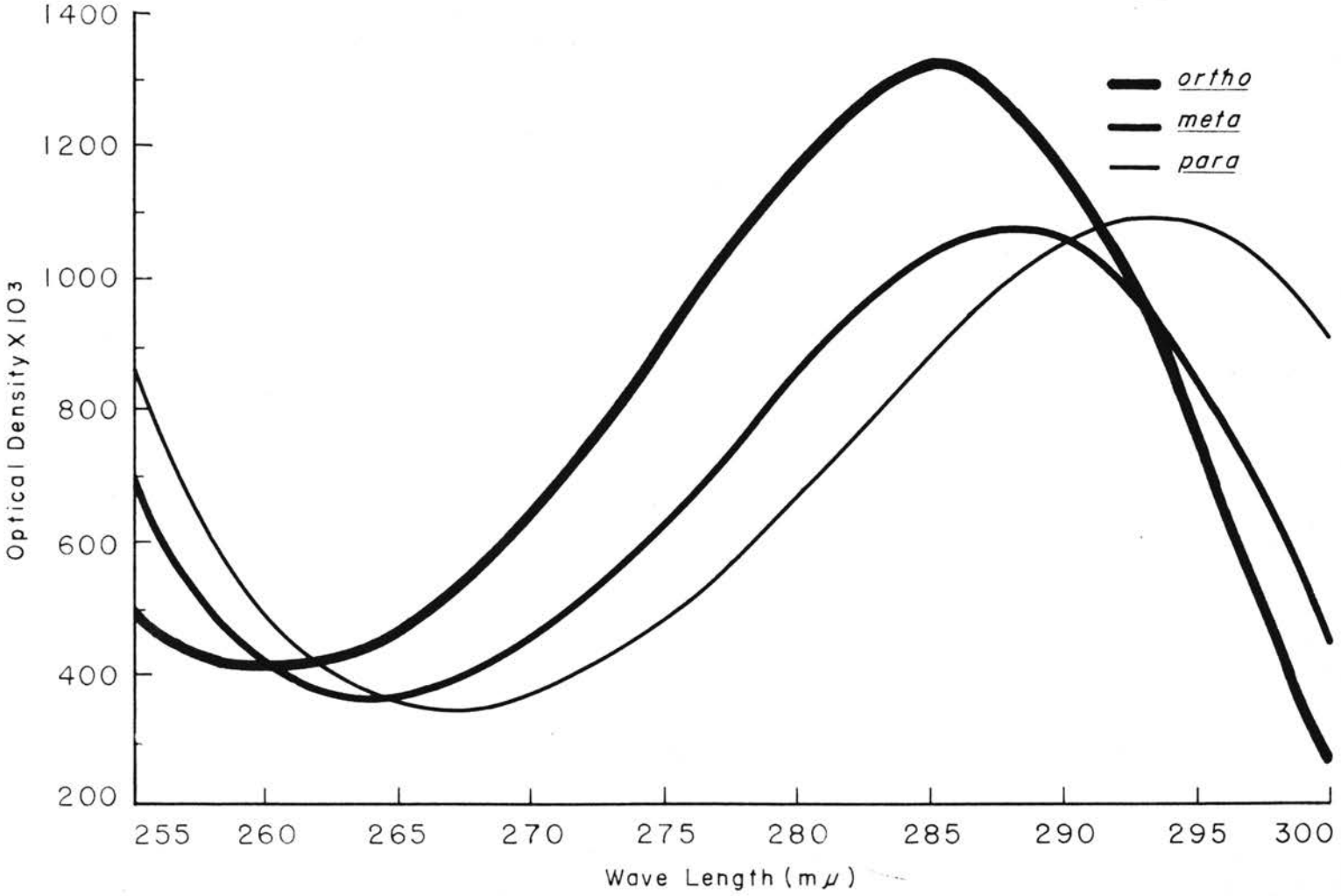


Figure 3. Optical Density Curves of the Isomeric Toluidines

Table IX

DIFFERENCES IN OPTICAL DENSITIES AT SELECTED WAVE LENGTHS: TOLUIDINES (X 10^3)

Experimental results and matching solutions are designated by lettered columns:

A Values for solutions obtained from experimental procedures

B Values for matching solutions

Wave length mμ	Isomer			Control Mixture		Exp. No. 1		Exp. No. 2	
	o	m	p	A(a)	B(a)	A	B(a)	A	B(a)
285 minus 260	919	582	373	722	722	733	732	730	731
296 minus 256	247	165	287	246	245	250	249	247	247

(a) For compositions of control mixture and matching solutions, see footnotes to Table VIII.

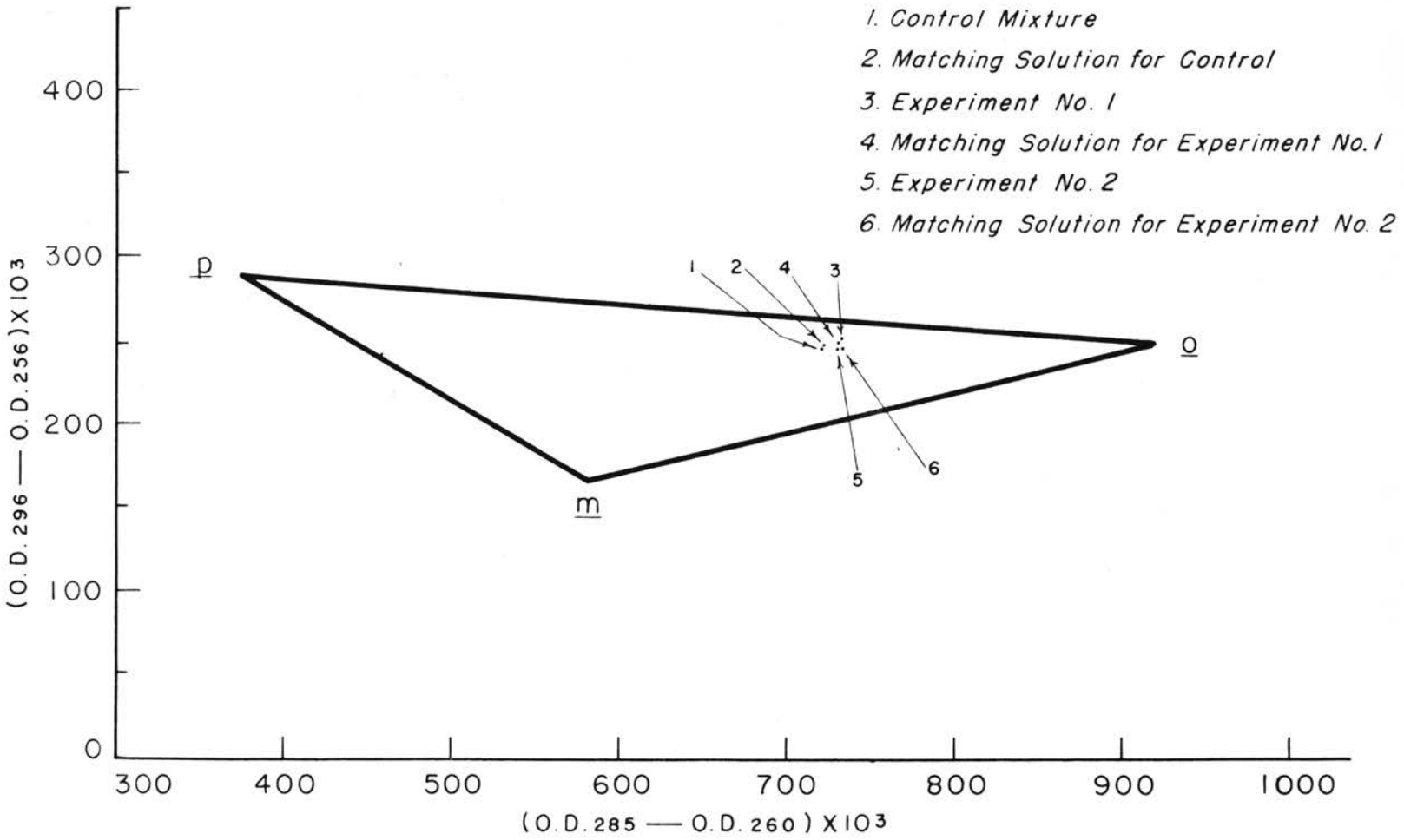


Figure 4. Differences in Optical Density at Selected Wave Lengths: Toluidines

Table I

OPTICAL DENSITIES OF BROMOANILINES (X 10^3)

Experimental results and matching solutions are designated by lettered columns:

A Values for solutions obtained from experimental procedures

B Values for matching solutions

Wave length mμ	Isomer			Control Mixture		Exp. No. 5		Exp. No. 6	
	o	m	p	A(a)	B(b)	A	B(c)	A	B(d)
265	313	196	760						
266	321	204	664						
267	334	218	593						
268	350	234	534						
269	370	254	491	368	369	386	387	394	394
270	400	273	453						
271	429	299	433						
272	461	326	422						
273	493	352	417	437	436	448	450	445	448
274	532	384	419						
275	576	419	423						
276	613	451	433						
277	661	487	446						
278	712	525	463						
279	763	568	488						
280	816	609	514						
281	868	648	538						
282	923	689	567						

Wave length mμ	Isomer o	m	p	Control Mixture A(a)	B(b)	Exp. No. 5 A	B(c)	Exp. No. 6 A	B(d)
283	970	734	598						
284	1020	772	628						
285	1060	800	655						
286	1085	834	687						
287	1140	868	724						
288	1170	885	752						
289	1190	909	789						
290	1220	933	814						
291	1230	950	845						
292	1230	948	867						
293	1210	935	889						
294	1180	918	906						
295	1155	885	922						
296	1130	835	935	1000	1001	1020	1020	1040	1040
297	1060	792	943						
298	1020	757	946						
299	966	731	949						
300	896	679	939						
301	825	635	928						
302	741	562	892	720	721	763	763	767	768
303	638	478	862						
304	538	396	823						
305	438	317	786						

(a) Control mixture contained, before treatment, 49.5% o-, 29.4% m-, 21% p-.

(b) Matching solution for control mixture contained 48% o-, 33% m-, 19% p-.

(c) Matching solution for Exp. No. 5 contained 54% o-, 14% m-, 32% p-.

(d) Matching solution for Exp. No. 6 contained 61% o-, 6% m-, 33% p-.

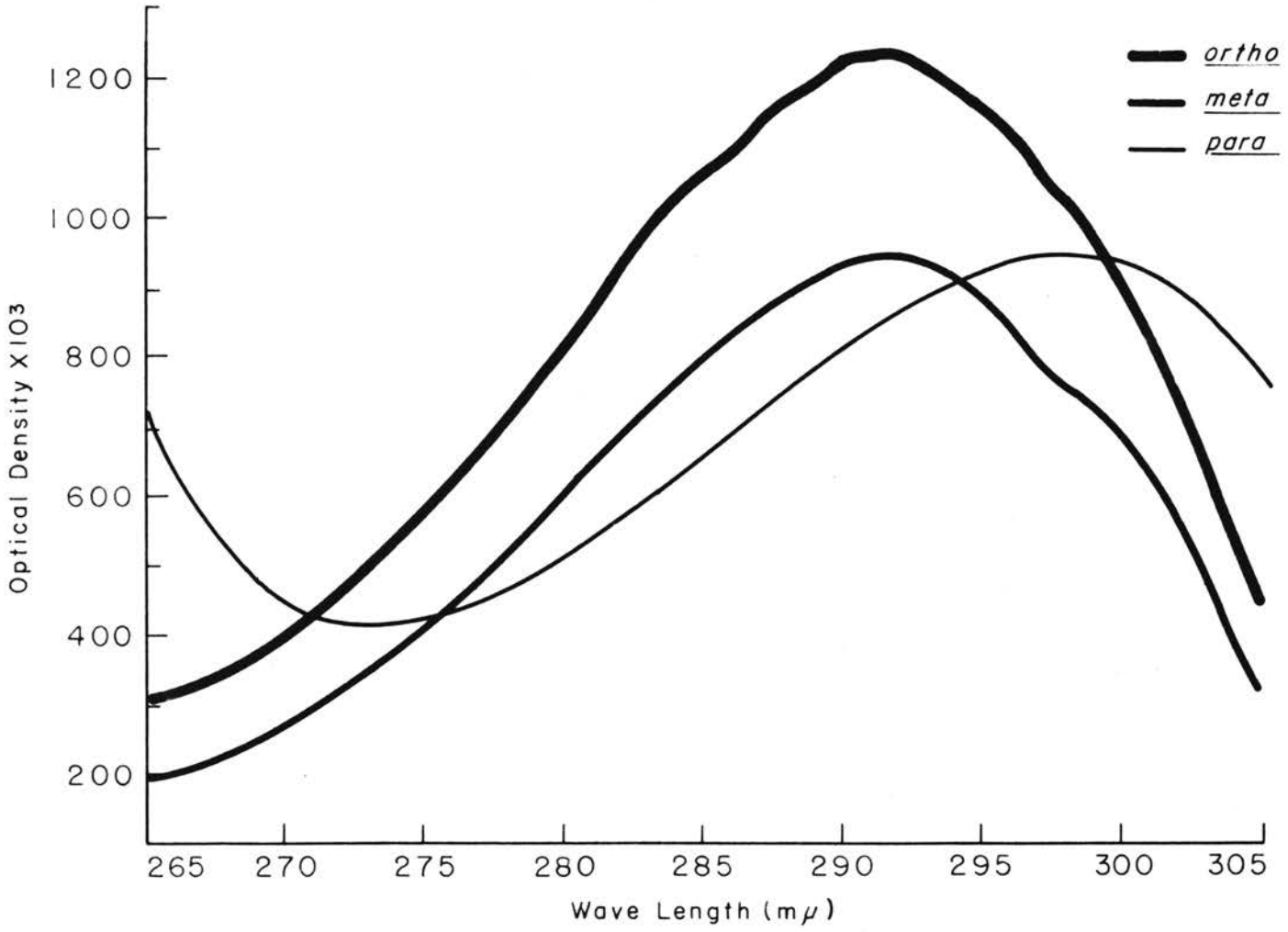


Figure 5. Optical Density Curves of the Isomeric Bromoanilines

Table XI

DIFFERENCES IN OPTICAL DENSITIES AT SELECTED WAVE LENGTHS: BROMOANILINES (X 10^3)

Experimental results and matching solutions are designated by lettered columns:

A Values for solutions obtained from experimental procedures

B Values for matching solutions

Wave length mμ	Isomer			Control Mixture		Exp. No. 5		Exp. No. 6	
	o	m	p	A(a)	B(a)	A	B(a)	A	B(a)
296 minus 269	760	581	444	632	632	634	633	646	646
302 minus 273	248	210	475	283	285	315	313	322	320

(a) For compositions of control mixture and matching solutions, see footnotes to Table X.

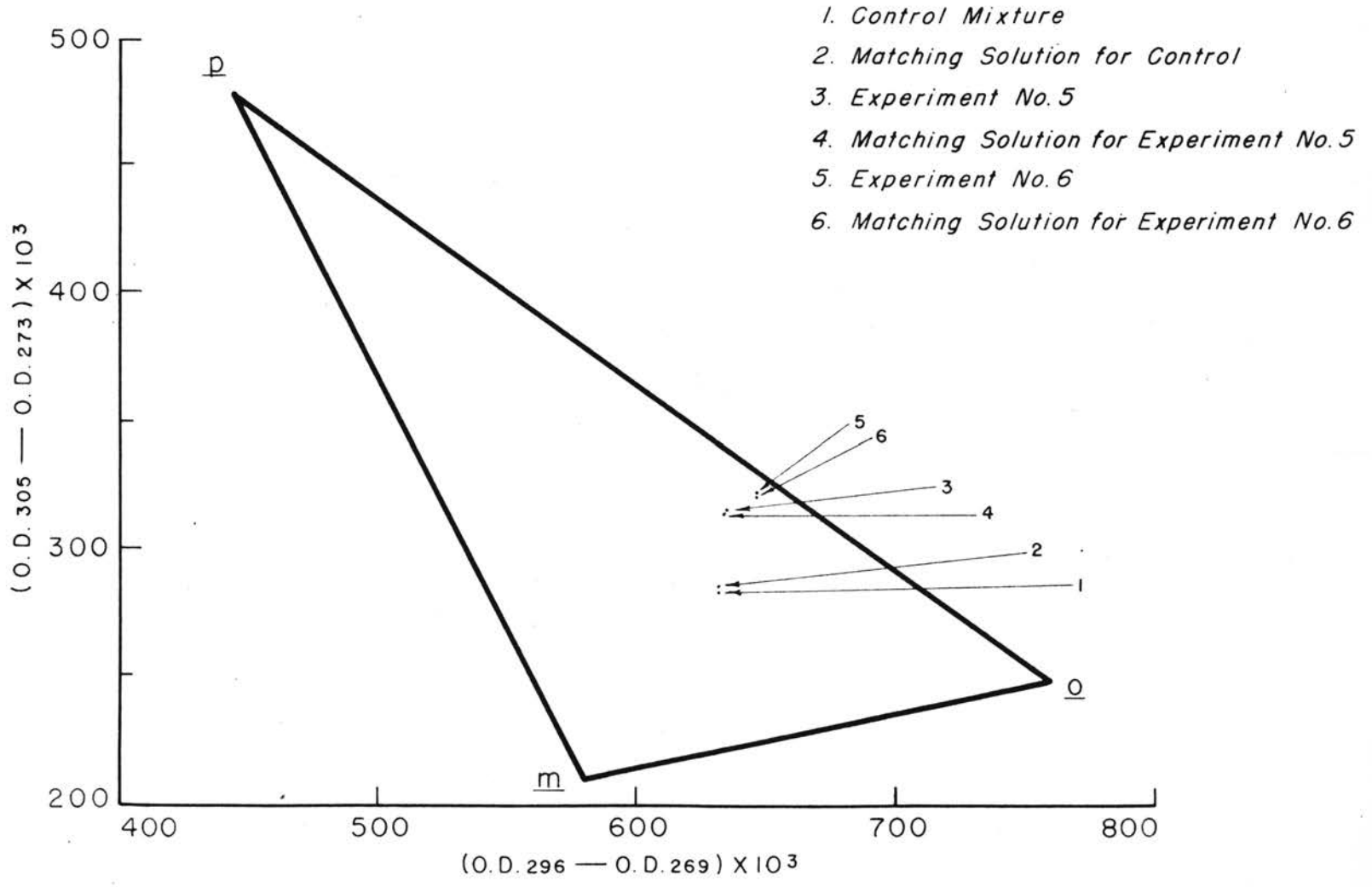


Figure 6. Differences in Optical Density at Selected Wave Lengths: Bromoanilines

Table XII

OPTICAL DENSITIES OF ANISIDINES (X 10^3)

Experimental results and matching solutions are designated by lettered columns:

A Values for solutions obtained from experimental procedures

B Values for matching solutions

Wave length mμ	Isomer			Control Mixture		Exp. No. 7		Exp. No. 8	
	o	m	p	A(a)	B(b)	A	B(c)	A	B(d)
255	648	873	852						
256	552	753	733						
257	478	642	618						
258	424	557	528						
259	397	491	453						
260	381	445	376						
261	374	406	348						
262	372	386	305						
263	384	374	274	418	420	397	392	380	378
264	406	376	253						
265	438	386	238						
266	481	408	232						
267	532	433	231						
268	582	464	236						
269	638	498	242	561	560	528	523	496	494
270	698	540	253						
271	762	585	264						

Wave length	Isomer			Control Mixture		Exp. No. 7		Exp. No. 8	
mμ	o	m	p	A(a)	B(b)	A	B(c)	A	B(d)
272	821	628	279						
273	886	678	300						
274	963	736	320						
275	1030	776	344						
276	1095	826	373						
277	1170	874	401						
278	1230	925	434						
279	1320	990	469						
281	1420	1055	541						
282	1455	1080	589						
283	1495	1105	638						
284	1520	1120	665						
285	1540	1140	711						
286	1560	1140	752	1335	1335	1260	1260	1220	1220
287	1540	1135	796						
288	1520	1110	843						
289	1490	1090	883						
290	1435	1040	932						
291	1380	976	968						
292	1320	909	1010						
293	1220	845	1040						
294	1135	781	1070						
295	1045	728	1095						

Wave length mμ	Isomer o	m	p	Control Mixture A(a)	B(b)	Exp. No. 7 A	B(c)	Exp. No. 8 A	B(d)
296	945	646	1135						
297	857	587	1155						
298	763	521	1165						
299	684	460	1175						
300	601	402	1180						
301	532	351	1180						
302	448	293	1170	536	533	611	609	670	673
303	386	249	1165						
304	328	208	1150						
305	274	174	1130						

(a) Control mixture contained, before treatment, 60% o-, 20% m-, 20% p-.

(b) Matching solution for control mixture contained 48% o-, 35% m-, 17% p-.

(c) Matching solution for Exp. No. 7 contained 48% o-, 26% m-, 26% p-.

(d) Matching solution for Exp. No. 8 contained 50% o-, 17% m-, 33% p-.

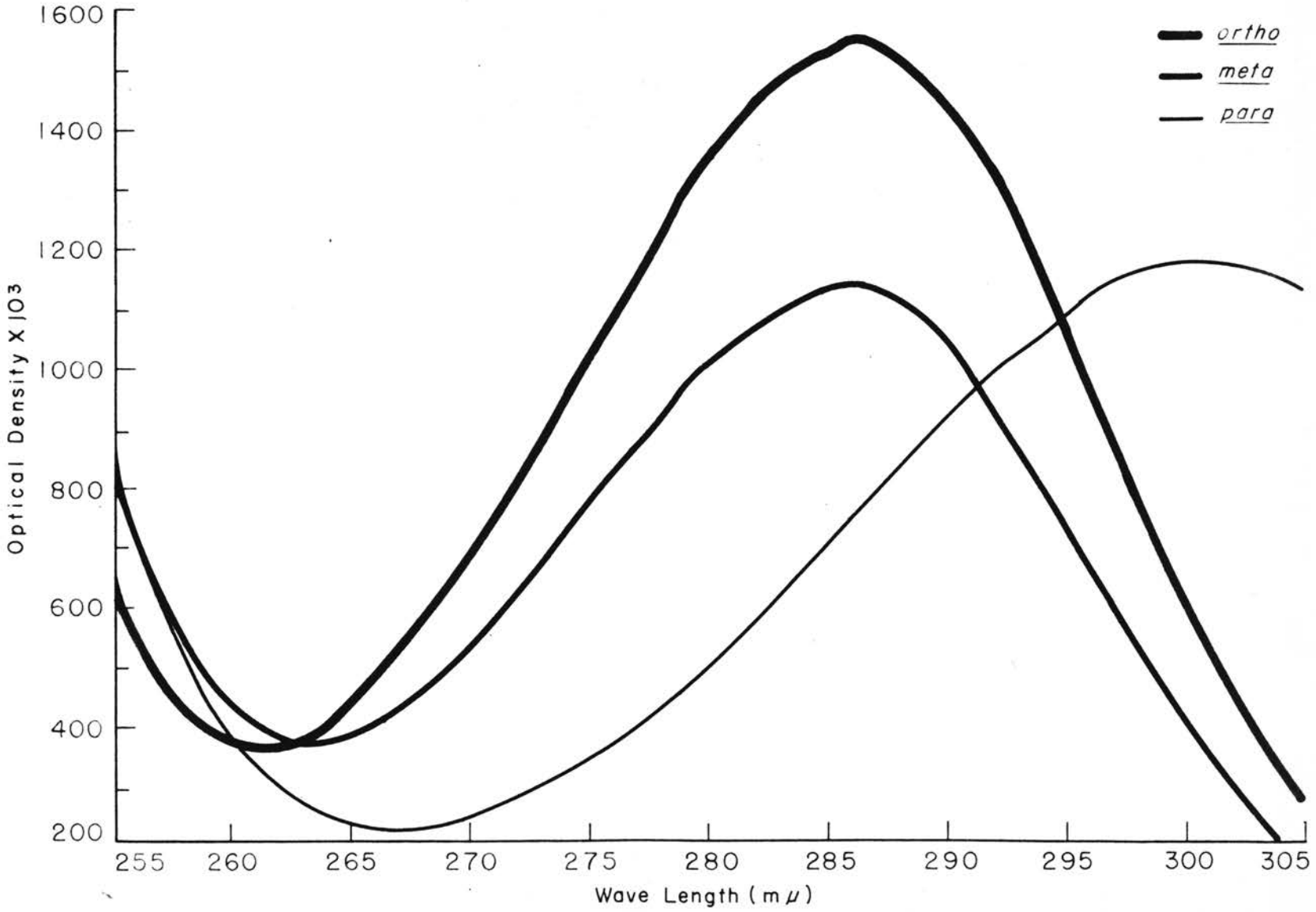


Figure 7. Optical Density Curves of the Isomeric Anisidines

Table XIII

DIFFERENCES IN OPTICAL DENSITIES AT SELECTED WAVE LENGTHS: ANISIDINES (X 10^3)

Experimental results and matching solutions are designated by lettered columns:

A Values for solutions obtained from experimental procedures

B Values for matching solutions

Wave length mμ	Isomer			Control Mixture		Exp. No. 7		Exp. No. 8	
	o	m	p	A(a)	B(a)	A	B(a)	A	B(a)
302 minus 269	-190	-205	928	-25	-27	83	86	174	179
286 minus 263	1176	766	478	917	915	863	868	840	842

(a) For compositions of control mixture and matching solutions, see footnotes to Table XII.

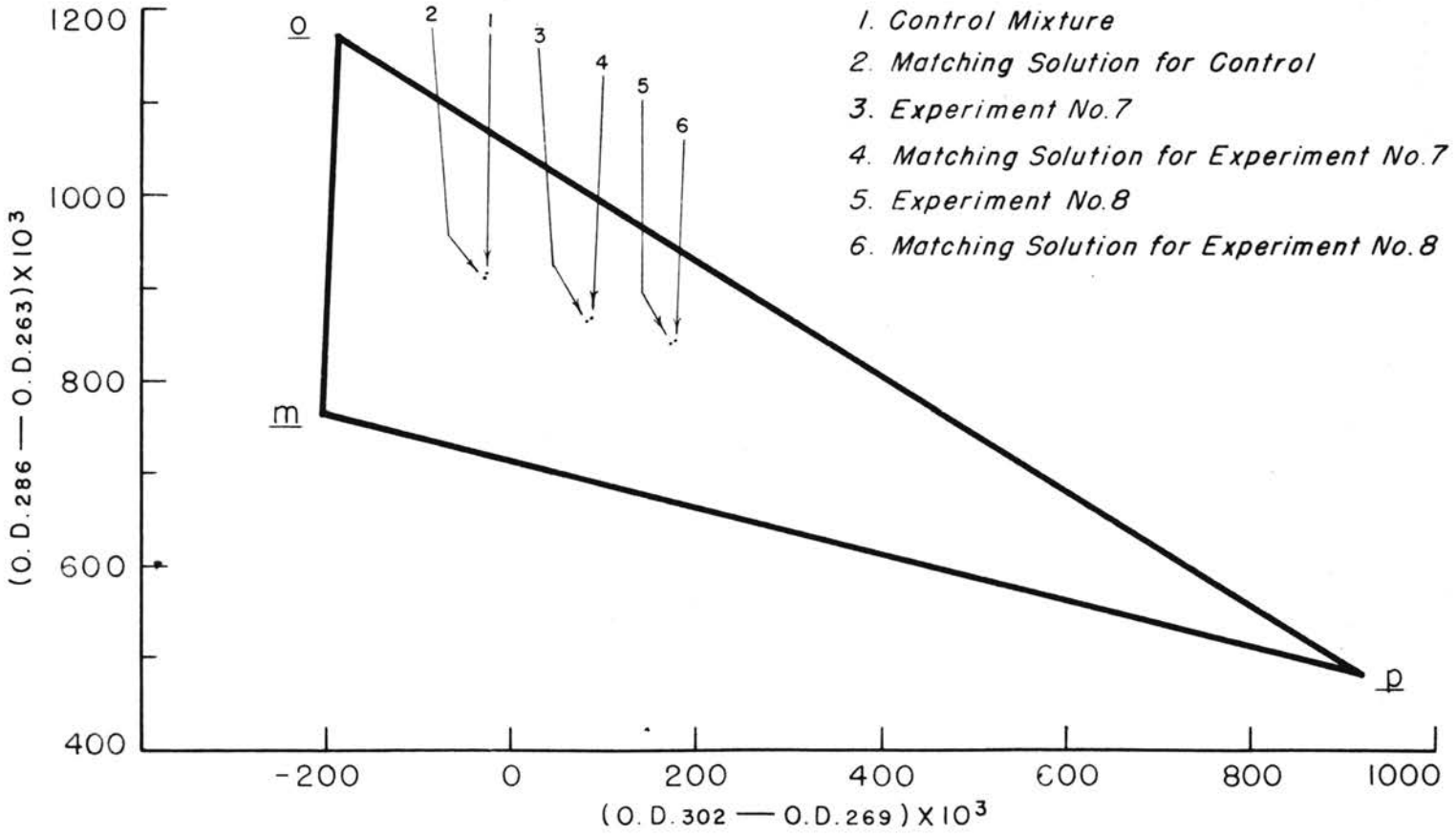


Figure 8. Differences in Optical Density at Selected Wave Lengths: Anisidines

Table XIV

OPTICAL DENSITIES OF AMINOPHENOLS (X 10^3)

Experimental results and matching solutions are designated by lettered columns:

A Values for solutions obtained from experimental procedures

B Values for matching solutions

Wave length	Isomer			Control Mixture		Exp. No. 9	
mμ	o	m	p	A(a)	B(b)	A	B(c)
255	324	489	497				
256	291	411	442				
257	270	354	385				
258	257	322	334	297	298	296	294
259	249	291	298				
260	253	276	266				
261	259	258	242				
262	273	260	223				
263	289	266	205				
264	304	278	188	274	270	293	288
265	330	294	177				
266	358	319	168				
267	393	341	162				
268	430	369	167				
269	475	398	173				
270	522	432	184				
271	570	472	197				

Wave length mμ	Isomer o	Isomer m	Isomer p	Control Mixture A(a)	Control Mixture B(b)	Exp. No. 9 A	Exp. No. 9 B(c)
272	619	509	210				
273	671	550	221				
274	721	589	236				
275	782	626	252				
276	840	667	271				
277	900	707	292				
278	952	741	313				
279	1021	779	340				
280	1080	809	373				
281	1129	830	408				
282	1171	845	437				
283	1213	860	470				
284	1244	871	498				
285	1260	876	534				
286	1270	875	571	1036	1040	1030	1032
287	1268	868	608				
288	1260	852	645				
289	1243	828	683				
290	1220	789	724				
291	1182	740	759				
292	1130	680	785				
293	1070	616	812				
294	1007	555	836				
295	929	493	862				
296	843	438	891				

Wave length mμ	Isomer			Control Mixture		Exp. No. 9	
	o	m	p	A(a)	B(b)	A	B(c)
297	763	389	913				
298	672	335	931				
299	602	296	945	675	669	621	618
300	523	247	954				
301	461	211	954				
302	392	179	951				
303	338	148	946				
304	290	119	938				
305	247	92	929				

(a) Control mixture contained, before treatment, 62.5% o-, 6.25% m-, 31.25% p-.

(b) Matching solution for control mixture contained 58% o-, 13% m-, 29% p-.

(c) Matching solution for Exp. No. 9 contained 58% o-, 20% m-, 22% p-.

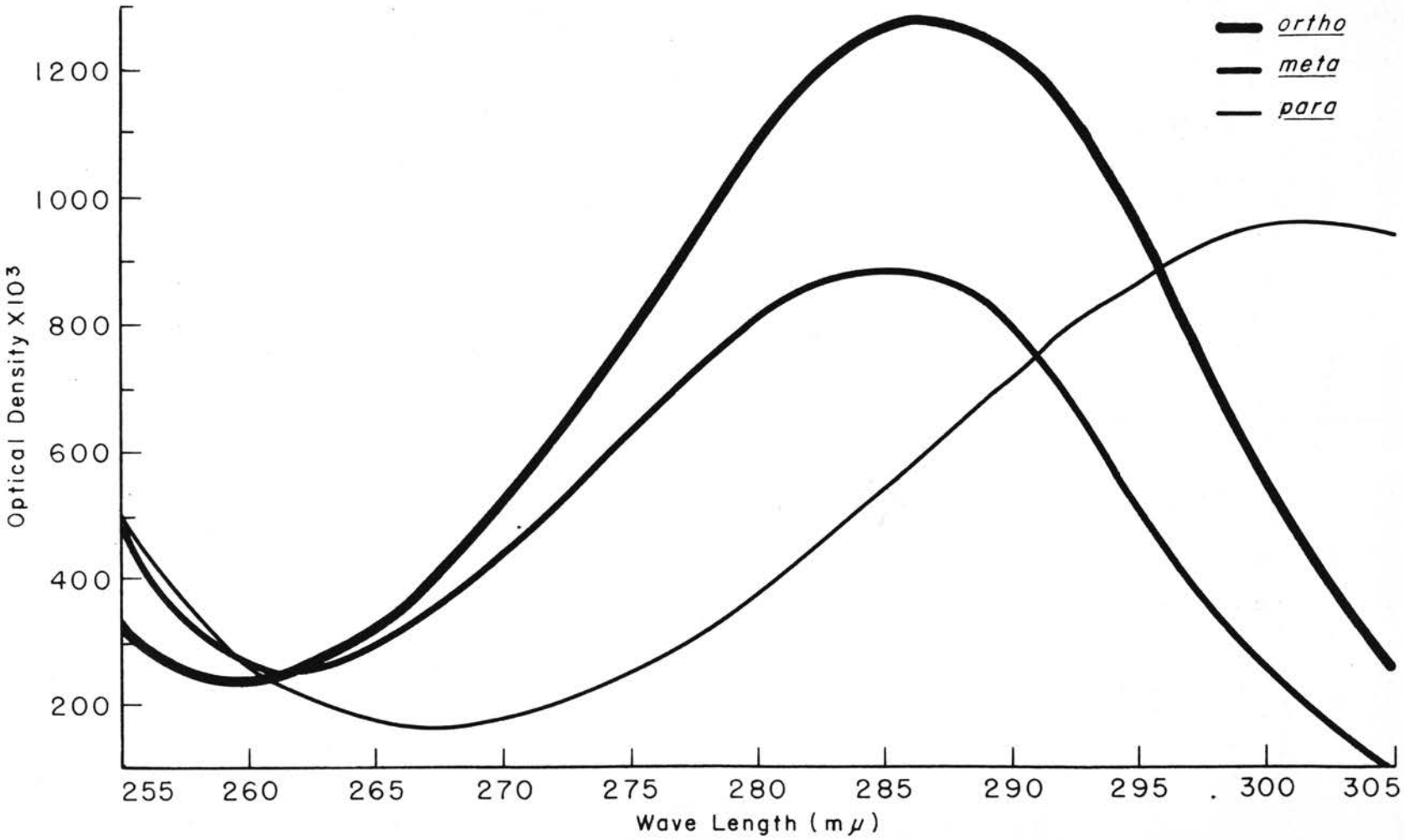


Figure 9. Optical Density Curves of the Isomeric Aminophenols

Table XV

DIFFERENCES IN OPTICAL DENSITIES AT SELECTED WAVE LENGTHS: AMINOPHENOLS (X 10^3)

Experimental results and matching solutions are designated by lettered columns:

A Values for solutions obtained from experimental procedures

B Values for matching solutions

Wave length mμ	Isomer o	Isomer m	Isomer p	Control Mixture A(a)	Control Mixture B(a)	Exp. No. 9 A	Exp. No. 9 B(a)
286 minus 258	1013	553	237	739	742	734	738
299 minus 264	298	18	757	401	399	328	330

(a) For compositions of control mixture and matching solutions, see footnotes to Table XIV.

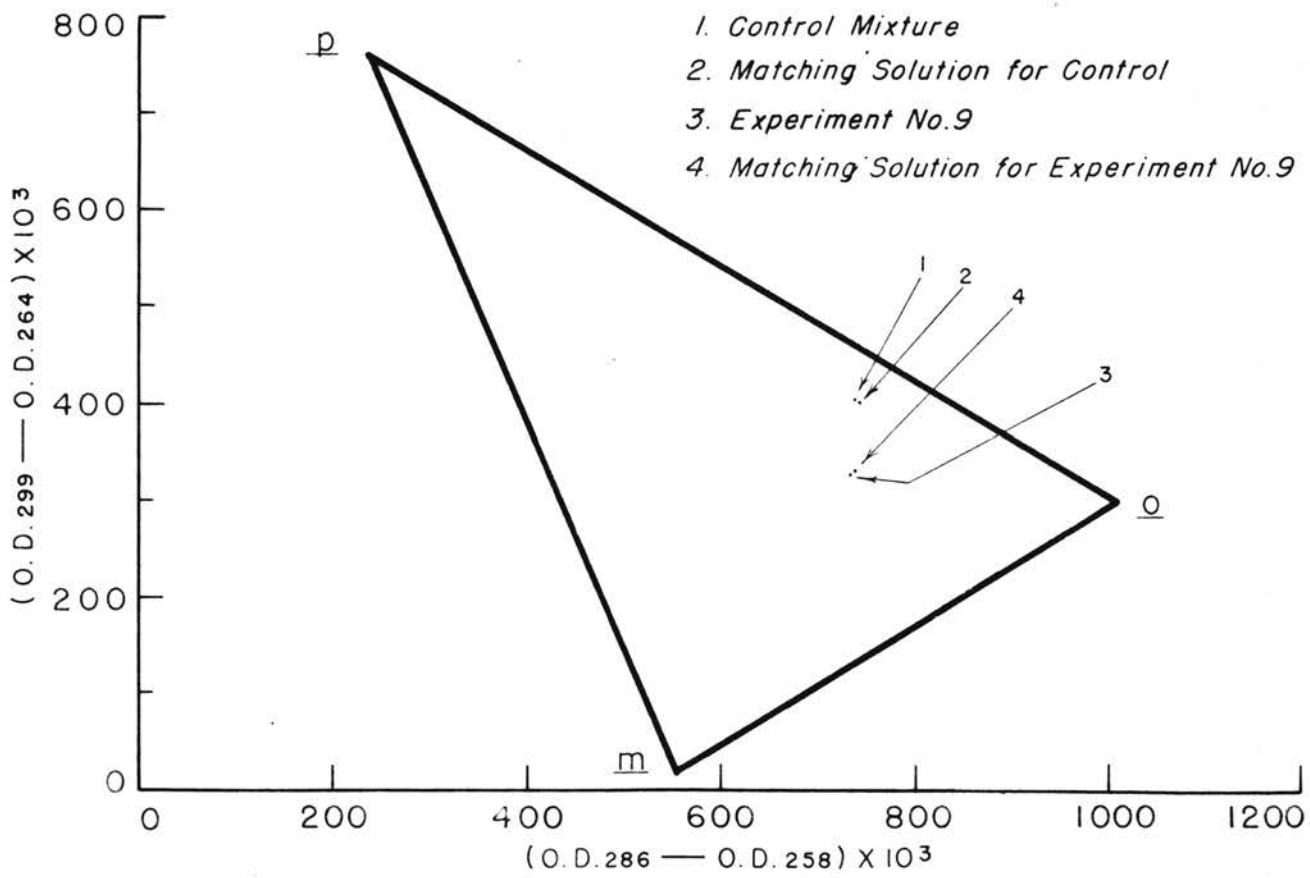


Figure 10. Differences in Optical Density at Selected Wave Lengths: Aminophenols

Table XVI

OPTICAL DENSITIES OF AMINOBENZOIC ACIDS (X 10^3)

Experimental results and matching solutions are designated by lettered columns:

A Values for solutions obtained from experimental procedures

B Values for matching solutions

Wave length mμ	Isomer			Control Mixture		Experiment		
	o	m	p	A[a]	B[b]	A	B	No.
240	1360	1720	292					
241	1380	1700	308					
242	1420	1680	324					
243	1440	1670	351					
244	1470	1660	384	1530	1520	810	804[e]	12
245	1490	1640	425			746	742[d]	13
246	1510	1610	469			752	750[e]	14
247	1530	1580	522			806	602[f]	15
248	1520	1495	574					
249	1510	1440	632					
250	1480	1370	694					
251	1460	1340	773					
252	1425	1220	854					
253	1375	1140	939					
254	1320	1040	1030					
255	1190	939	1120	1120	1120	1165	1165[e]	12
256	1080	854	1225			1145	1145[d]	13
						1150	1150[e]	14
						1135	1135[f]	15

Wave length mμ	Isomer o	Isomer m	Isomer p	Control Mixture A[a]	Control Mixture B[b]	Experiment A	Experiment B	Experiment No.
257	939	764	1350					
258	771	673	1450					
259	608	594	1570					
260	459	513	1680					
						630	635[c]	12
						650	657[d]	13
310	578	486	1680	550	545	696	691[e]	14
311	607	493	1470			540	548[f]	15
312	636	501	1320					
313	669	510	1110					
314	699	517	945					
315	731	522	796					
316	759	523	677					
317	792	528	560					
318	819	527	458					
319	849	526	381					
320	875	525	310					
321	898	521	244					
322	935	519	194					
323	954	516	156					
						810	804[c]	12
324	978	506	121			746	742[d]	13
325	1001	498	94	768	763	752	750[e]	14
						806	802[f]	15

(a) Control mixture contained, before treatment, 50% o-, 30% m-, 20% p-.

(b) Matching solution for control mixture contained 53% o-, 49% m-, 0% p-.

(c) Matching solution for Exp. No. 12 contained 68% o-, 25% m-, 7% p-.

(d) Matching solution for Exp. No. 13 contained 55% o-, 36% m-, 9% p-.

(e) Matching solution for Exp. No. 14 contained 60% o-, 28% m-, 12% p-.

(f) Matching solution for Exp. No. 15 contained 60% o-, 40% m-, 0% p-.

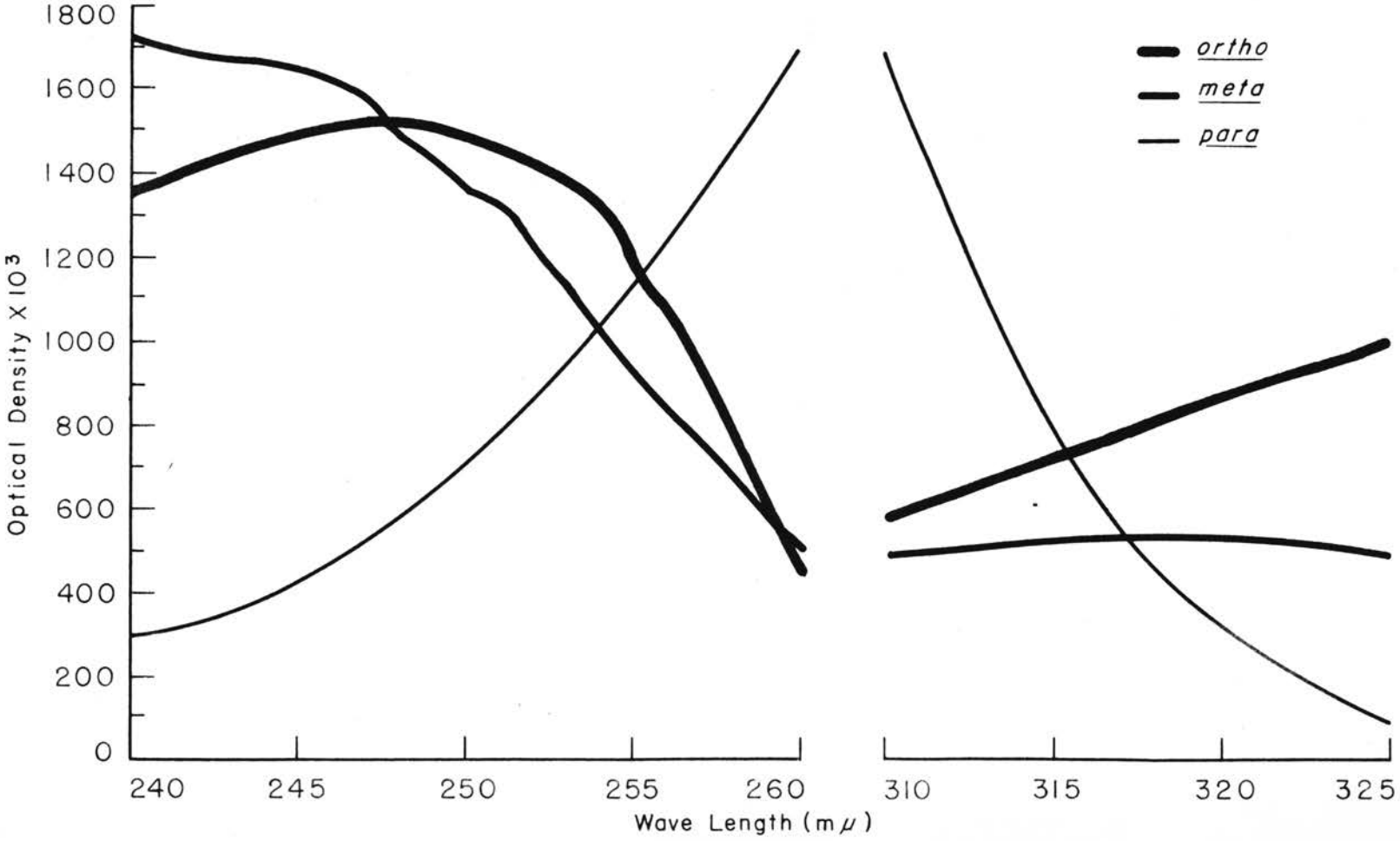


Figure II. Optical Density Curves of the Isomeric Aminobenzoic Acids

Table XVII

DIFFERENCES IN OPTICAL DENSITIES AT SELECTED WAVE LENGTHS: AMINOBENZOIC ACIDS (X 10^3)

Experimental results and matching solutions are designated by lettered columns:

A Values for solutions obtained from experimental procedures

B Values for matching solutions

Wave length mμ	Isomer			Control Mixture		Experiment		
	o	m	p	A(a)	B(a)	A	B	No.
255 minus 310	612	453	-560	570	575	535	530(a)	12
						495	488(a)	13
						454	459(a)	14
						595	587(a)	15
244 minus 325	469	1162	290	762	757	635	643(a)	12
						754	768(a)	13
						688	695(a)	14
						769	778(a)	15

(a) For compositions of control mixture and matching solutions, see footnotes to Table XVII.

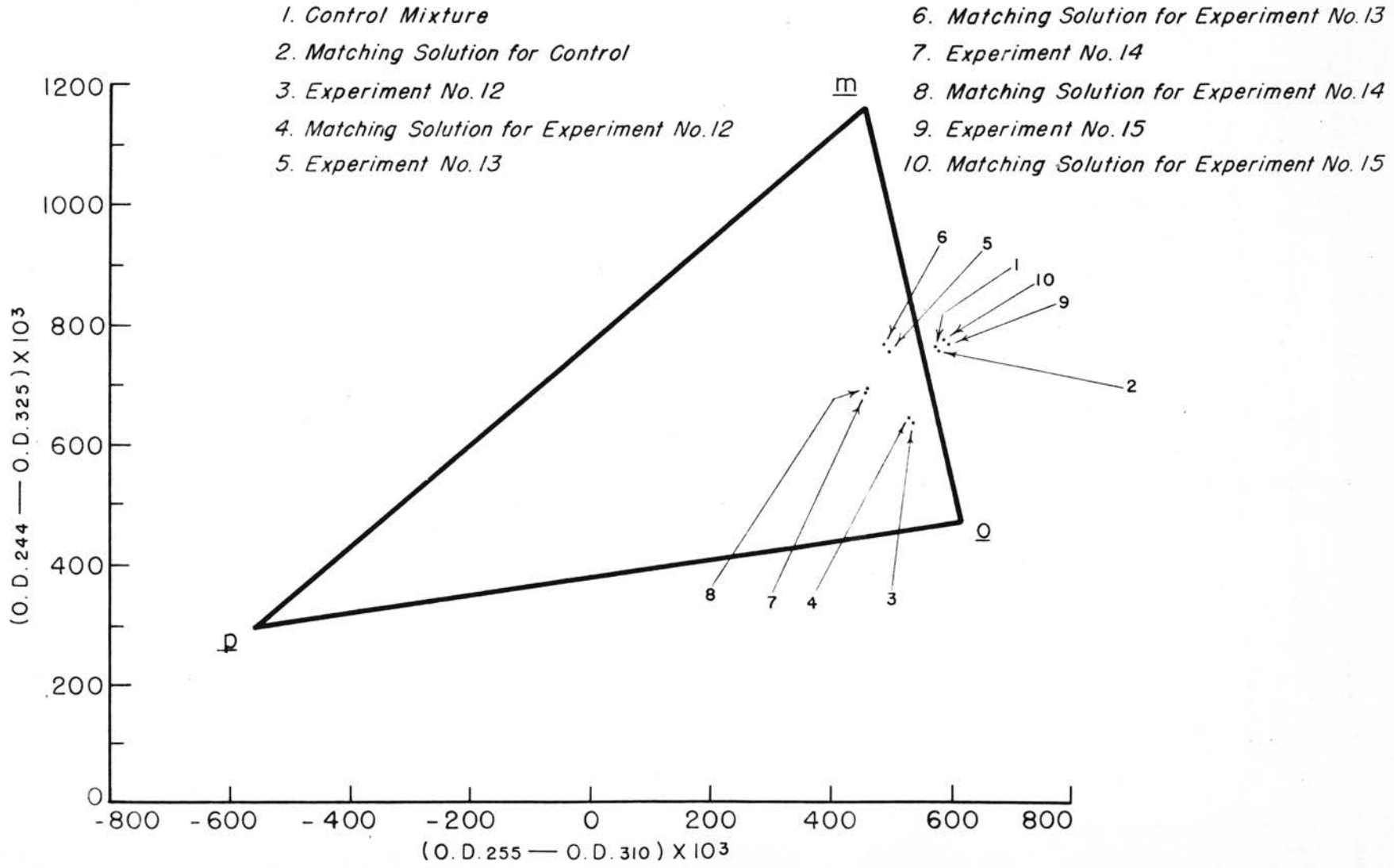


Figure 12. Differences in Optical Density at Selected Wave Lengths: Aminobenzoic Acids

However, the similarity of the results obtained from Experiments 12, 13, 14, and 16 to those from a known mixture containing a large proportion of the ortho-isomer leads to the conclusion that the o-aminobenzoic acid does predominate.

Although crystalline products were isolated from Experiment 11 with benzonitrile and Experiment 15 with benzoyl chloride (Table V), no meaningful results were obtained from these experiments in subsequent procedures.

The desired products from heating benzenesulfonyl azide in nitrobenzene were not identifiable but it was noticed during the course of the reaction that a brown gas was given off. The yield of the gas was not determined, but a considerable amount was produced. When this gas was passed through a solution of potassium iodide in water, iodine was liberated rapidly in sufficient quantity to cause a very dark coloration of the solution within a short time. It is evident therefore that the gas liberated was nitrogen dioxide, but since the object of this work was to study orientation the course of the reaction was not followed further. The impossibility of obtaining crystalline sulfonanilides from the tar produced is in agreement with the observation of Curtius (49).

It appeared probable that chloramine-T might decompose and react like benzenesulfonyl azide. Accordingly chloramine-T was heated in nitrobenzene in approximately 7% solution. At 140° there was evolution of a brown gas, as was the case with benzenesulfonyl azide in nitrobenzene, but examination of the reaction mixture gave no evidence of nitroanilides of p-toluenesulfonic acid. Owing to the comparatively high decomposition point of chloramine-T, the reaction was not attempted in lower boiling aromatic liquids.

Before concluding the experimental portion of this thesis, mention should be made of the attempted decomposition of benzenesulfonyl azide by ultrasonic vibration instead of by heat. Seven grams of benzenesulfonyl azide was added to 100 g. of chlorobenzene in a 32 x 200 mm. test tube and the solution was subjected to ultrasonic vibrations from a quartz crystal (2000 volts and 250 milliamperes) for thirty minutes. There was no evidence of decomposition of the azide nor was there any evidence of change in the mixture as a whole.

DISCUSSION

Chlorination of Aromatic Nuclei with Carbon Tetrachloride and Benzoyl Peroxide

Chlorine atoms (radicals) are not active enough to displace hydrogen from aromatic nuclei in general under the conditions used. Fieser and co-workers (77, 78) found the same to be true of methyl radicals. They did find that methyl radicals would attack nuclei of aromatic molecules that were highly activated for radical attack, such as trinitrotoluene, for example. Wibaut and his co-workers (118, 192, 215, 216, 217, 218) found that halogenations of aromatic nuclei follow the usual orientation rules at ordinary temperatures but that they fail to follow these rules at high temperature, and they postulated an attack by atomic halogen at elevated temperatures. It would seem probable therefore that chlorine atoms would replace hydrogen on aromatic nuclei which are properly activated by substituents already present or that they would attack less highly activated compounds at elevated temperatures in sealed-tube reactions.

Substitutions of Aromatic Nuclei by the Benzenesulfonimido Radical

Isomer ratios. The observed ratios of isomers obtained from the decomposition of benzenesulfonyl azide in various aromatic liquids are summarized in Table XVIII.

Great care has been exercised in each step of the analytical procedure to avoid alterations of the isomer ratios. The products obtained

Table XVIII

SUMMARY OF RESULTS

Isomer Ratios in Substitution Products

From Decomposition of Benzenesulfonyl Azide

Exp. No.	Aromatic Liquid	Substitution Product	Hydrolysis Product	Isomer Ratios % o-	m-	p-
1	Toluene	Benzenesulfon-toluidides	Toluidines(a)	61.0	10.5	28.0
2	Toluene	Benzenesulfon-toluidides	Toluidines(a)	60.0	12.5	27.5
3	Chloro-benzene	Benzenesulfonamido-chlorobenzenes	Chloro-anilines	57	13	30
4	Chloro-benzene	Benzenesulfonamido-chlorobenzenes	Chloro-anilines	53	18	28
5	Bromo-benzene	Benzenesulfonamido-bromobenzenes	Bromoanilines	54	14	32
6	Bromo-benzene	Benzenesulfonamido-bromobenzenes	Bromoanilines	61	6	33
7	Anisole	Benzenesulfon-anisidides	Anisidines	48	26	26
8	Anisole	Benzenesulfon-anisidides	Anisidines	60	17	33
9	Phenol	Benzenesulfonamido-phenols	Aminophenols	58	20	22
10	Nitro-benzene	No product isolated	None	None		
11	Benzo-nitrile	Benzenesulfonamido-benzonitrile	Aminobenzoic acids	Not determinable		
12	Benzo-nitrile	Benzenesulfonamido-benzonitrile	Aminobenzoic acids	68	25	7
13	Methyl	Benzenesulfonamido-benzoic acids	Aminobenzoic acids	55	36	9

Exp. No.	Aromatic Liquid	Substitution Product	Hydrolysis Product	Isomer Ratios % o-	m-	p-
14	Methyl benzoate	Benzenesulfonamido-benzoic acids	Aminobenzoic acids	60	28	12
15	Benzoyl chloride	Benzenesulfonamido-benzoic acids	Aminobenzoic acids	Not determinable		
16	Benzoyl chloride	Benzenesulfonamido-benzoic acids	Aminobenzoic acids	60	40	0

(a) Only with the toluidines does the final analysis appear to justify reporting fractions of percent and these have been given only to the nearest half percent.

from the decomposition of benzenesulfonyl azide were isolated by extraction of the reaction mixtures with sodium hydroxide. This procedure isolated the desired alkali-soluble compounds, after volatile components had first been removed by distillation. No attempt was made at this stage to separate benzenesulfonamide from the N-substituted amides since such a separation would have been prejudicial to the maintenance of original isomer ratios. This separation was effected by the subsequent hydrolysis in hydrochloric acid, followed by steam distillation from alkaline solutions and extraction with organic solvents which would remove a negligible amount of ammonia from the dilute aqueous solutions. In each case distillation with steam was continued until no positive test could be obtained for aromatic amine in the distillate.

The procedure subsequent to hydrolysis effected a second purification. Steam was first passed through the acid reaction mixture to remove any volatile material which might still have been present and steam distillation after the solution had been made alkaline effected a further separation from any possible non-volatile components still present.

It should be remembered that the results reported for the reaction with phenol are based upon one experiment only and that isolation of the mixed aminophenols was accomplished by extraction rather than by steam distillation. Nevertheless, comparison of the results with those of the control procedure with the aminophenols leads to the conclusion that the results are substantially correct.

It appears that the pH chosen for precipitation of the aminobenzoic acids did not allow them to be isolated in the ratio of isomers which existed in the reaction products. It is extremely doubtful whether any suitable single pH value could be found for this precipitation. It is

probable that a chromatographic procedure could be developed which would effect a suitable separation of the benzenesulfonamidobenzoic acids before hydrolysis or the mixed aminobenzoic acids resulting from hydrolysis.

The analytical procedure (203) used in determining the isomer ratios of the various mixtures of isomeric substituted anilines is effective only when a maximum of three compounds is present in the mixture. This condition was met by the purification steps cited above which are inherent in the experimental procedure. That this is true is evident from the close agreement between the values of spectrophotometric readings for experimental mixtures and those of synthetic matching mixtures. In the course of the work it was noted that slight amounts of impurities caused patterns of readings which could not be matched by synthetic mixtures of the compounds even though they were within the desired limits. It should be emphasized that in each case the graphical analysis was supplemented by the preparation of known mixtures to verify the composition of the experimental product.

Sulfonamide/sulfonanilide ratios. As previously explained, no attempt was made to separate benzenesulfonamide from the benzenesulfonanilides produced in a reaction because it was desirable to avoid possible alteration of the isomer ratio in the mixture of anilides. It is quite likely that a determination of the amount of benzenesulfonamide could be made by use of a chromatographic technique, by determination of ammonia in the alkaline hydrolyzate by aeration and titration, or by calculation based upon determination of total amount of benzenesulfonic acid formed by hydrolysis less the amount found to be equivalent to the total amount of aromatic amine. The information thus obtained would furnish an in-

sight into the nature of the benzenesulfonimido radical. It would show, for example, whether the radical preferentially extracts hydrogen from an aromatic nucleus or whether its action is predominantly an attack on the nucleus itself. A high proportion of benzenesulfonamide would indicate a preference for extraction of hydrogen and the formation of smaller amounts of the benzenesulfonanilides might then result from a small number of instances wherein the remainder of that molecule or a fragment of another, was able to attach itself to nitrogen before a second hydrogen could be made available. A small percentage of benzenesulfonamide might indicate a preferential initial attack on the nucleus of a molecule with subsequent migration of the hydrogen atom to nitrogen.

This might occur as envisioned by Huisgen and Horeld (137) by a "Kryptoradical" mechanism. It might also be possible that $:NSO_2Ar$ could first add to an aromatic nucleus much as :CHR from aliphatic azo compounds does with a subsequent rupture of one bond coincident with or subsequent to migration of hydrogen from carbon to nitrogen.

Curtius (49) stated that more benzenesulfonamide was formed at higher temperatures. This might indicate that extraction of hydrogen from different aromatic molecules is favored, at higher temperatures, over the formation of unstable addition complexes.

Abnormal behavior of nitrobenzene. The liberation of nitrogen dioxide by the thermal decomposition of benzenesulfonyl azide in nitrobenzene and the apparent absence of benzenesulfonamide and the benzenesulfonamidonitrobenzenes are not readily explainable. The nitro group is noted for its activation of this ring for radical attack and has itself

appeared quite stable in most instances. Curtius and co-workers (49) stated that the benzenesulfonimido radical did not attack the nucleus of such compounds as nitrobenzene and benzaldehyde to form benzenesulfonanilides. They did not, however, provide a detailed discussion of experimental results with these compounds nor did they attempt an explanation of the failure of the substitution reaction. These authors did state, however, that the attack was invariably on the nucleus which apparently is not wholly true, in the case of nitrobenzene at least.

Hammond and his co-investigators (103, 104, 105) have found, as was found in this investigation, that the nitro group is sometimes attacked by radicals. They found (103) that a polyallyl acetate radicals react with the nitro group of nitrobenzene and that triphenylmethyl also attacks the nitro group of nitrobenzene (104). In the latter case azobenzene, azoxybenzene, nitrosobenzene, biphenyl and some terphenyl were found in the reaction mixture. No attempt was made in the present work to determine whether similar compounds were produced but attempts to explain the production of nitrogen dioxide, or of nitric oxide with subsequent oxidation to nitrogen dioxide, on the basis of formation of such products does not appear feasible. If, however, the benzenesulfonimido radical is capable of removing an aromatic nucleus from hydrogen as it apparently does in the formation of benzenesulfonanilides, then it might well be capable of removing Ar from nitrobenzene. In this case, however, one should be able to isolate nitrogen dioxide and benzenesulfonamidonitrobenzene or N,N-bis(nitrophenyl)benzenesulfonamide in equivalent amounts which was not accomplished in the present investigation. The fact that nitrogen dioxide is evolved indicates that the benzenesulfonimido radical is very active. Elucidation of the course of the reaction will re-

quire careful measurement of the amount of gas liberated and very careful examination of the products present as liquids and solids.

Evidence for radical nature of the reaction. The question naturally arises as to whether the reaction under consideration is in fact a radical reaction. Evidence, both theoretical and experimental, leads to the conclusion that radicals are indeed involved in the reaction. The $C_6H_5SO_2N$: particle formed from the liberation of N_2 from $C_6H_5SO_2N_3$ has six electrons around the nitrogen atom. There are four orbitals each capable of containing two electrons. One orbital is engaged in bonding N to S, leaving four electrons in three orbitals. Two of these are paired and occupy one orbital. Thus there are two remaining electrons in two orbitals and since each orbital must have at least one electron before any orbital can have two, these two electrons must be unpaired.

Evidence for the radical nature of the reaction is also found in the extreme reactivity of the $C_6H_5SO_2N$: particles as shown by their attack on aromatic nuclei and by the formation of nitrogen dioxide during the thermal decomposition of benzenesulfonyl azide in nitrobenzene. Recent unpublished work by Dermer (63) gives further support for radical interpretation. The ability of a substance to initiate polymerization of vinyl monomers is accepted as a sensitive test for free radicals (228, 229). Accordingly, Dermer decomposed small amounts of benzenesulfonyl azide at 110° in various vinyl monomers which had been freshly distilled in an atmosphere of natural gas. The azide did in fact catalyze polymerization of acrylonitrile in a marked extent and caused a very noticeable amount of polymerization of methyl acrylate. He found that the polymerization of acrylonitrile in the presence of benzenesulfonyl azide was inhibited by the addition of very small amounts of hydroquinone or

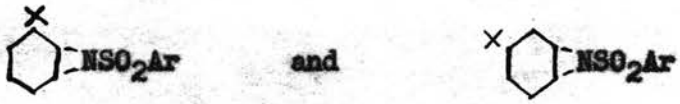
p-benzoquinone. This inhibition is still further proof of radical-catalyzed polymerization of the vinyl monomers. Thus the presence of neutral radicals formed by the thermal decomposition of benzenesulfonyl azide has been established.

The question also arises as discussed previously in the historical section, whether the radicals involved in this investigation are free radicals. This question cannot be answered on the basis of information presently available. Curtius (49) stated that free radicals are involved. However, one cannot say with certainty that they are actually present. The reaction may proceed, as previously discussed, by an azide-aromatic complex mechanism or possibly by an induced mechanism as suggested by De Tar (66) and discussed briefly in the historical section of this dissertation. As previously noted Hodgson (130, 131) and Huisgen (137) have discounted the free-radical mechanisms proposed for other reactions and an ionic mechanism has even been proposed for decomposition of acyl peroxides (75).

Theoretical consideration of isomer ratios. No completely satisfactory explanation of the predominance of the ortho substitution products can be given. Coulson (45, 46) states that quantum-mechanical calculations lead to the conclusion that free radicals should attack the ortho-position preferentially in the absence of steric or other factors which might interfere. Some purely steric hindrance in attack by a particle the size of $ArSO_2N$: is conceivable but that does not appear to have been a dominant factor.

If a cyclic intermediate addition complex involving a Kekule bond is formed, one would expect on a purely statistical basis that there would

be equal amounts of



If the bonds had equal probability of rupturing or remaining intact, this should lead to a predominance of the meta-isomer. If the bonds to the ortho and para positions are more stable, one would still expect equal amounts of the corresponding isomers. If this mechanism is involved it appears evident that the ortho-meta complex must predominate and that the bond to the ortho-position is the stronger of the two. One can only say that the distribution of isomers is the same as that obtained in a majority of radical reactions. It is hoped that more experimental work coupled with advancement in theoretical treatment will elucidate the mechanism of such reactions and offer an explanation for the orientation in radical substitutions.

Suggestions for future work. Future work with this reaction should include careful kinetic studies with a wide variation of conditions in order to give some insight as to mechanism of the process. The ratio of benzenesulfonamide to benzenesulfonanilides should be determined, and the effect of variations in conditions on this ratio. Studies on ring closures might well be included and the results should be considered in the light of similar studies, such as that of De Tar (66). It is of interest to note that Smith (193) working with azidobiphenyls found that when ring formation was favored it did occur, but that amines were formed when ring formation was not favored.

Careful investigation of the reaction products should be made also to determine the nature of those products which are not alkali-soluble. As pointed out by Curtius (53), when amide formation occurs one would

expect to find substituted biphenyls formed from the aryl radicals produced by extraction of hydrogen from the molecules. Likewise there may be some reaction of these compounds to give N,N-diaryl sulfonamides which would not be alkali-soluble.

$$RSO_2N: + 2C_6H_5R' \longrightarrow RSO_2NH_2 + 2R'C_6H_4\cdot$$

$$2R'C_6H_4\cdot \longrightarrow R'C_6H_4C_6H_4R'$$

$$RSO_2N: + 2R'C_6H_4\cdot \longrightarrow RSO_2N(C_6H_4R')_2$$

One might expect some formation of biphenyl itself along with benzenesulfonanilide and the N,N-diaryl amide when decomposition of the azide occurs in nitrobenzene with the production of nitrogen dioxide. The presence of compounds of this nature would be strong evidence for the formation of free radicals during the course of the reaction -- particularly the presence of biphenyls. Such a study carried out with compounds such as benzaldehyde and accompanied by a careful gas analysis might well give an insight to the failure of the reaction to occur in the expected manner.

Finally, more work should be done on the initiation of polymerization by the benzenesulfonimido radical. Particularly needed is such a study of copolymerization followed by analysis of the polymer (205) to determine whether the initiation is of a radical nature or acid-catalyzed.

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