linked polyacrylic acid. There was an immediate reaction with the formation of a precipitate. It was separated by centrifuging. The resulting product is a solid, which does not fuse. Thus, the partially cross-linked polymer can be further cross-linked by dissolving in alcohol and adding the bis-diazoalkane to it with stirring.

Polymethacrylic acid reacted similarly with 1,6-bis-diazohexane.

BOSTON, MASSACHUSETTS

[CONTRIBUTION FROM THE MORLEY CHEMICAL LABORATORY, WESTERN RESERVE UNIVERSITY]

Free Radical Aromatic Substitution. II. The Relative Reactivities of the Phenyl Halides toward Phenyl Radical Attack[1,2]

BY RALPH L. DANNLEY, EARL C. GREGG, JR., ROBERT E. PHELPS[3] AND CURTIS B. COLEMAN

RECEIVED JUNE 24, 1953

Benzoyl peroxide has been thermally decomposed in equimolecular binary mixtures of pyridine with chlorobenzene, bromobenzene and iodobenzene. The relative reactivities of these solvents toward phenyl radical attack (determined by comparing the ratios of halobiphenyls to phenylpyridines formed in the competitive reactions) have been found to be iodobenzene 1.1, pyridine 1.0, chlorobenzene 0.9 and bromobenzene 0.9. The mixtures of isomeric biaryls formed are predominantly ortho with the meta and para isomers in approximately statistical ratio to each other. The percentages of the ortho, meta and para isomers in the isolated biaryl are significant despite the concomitant formation of large quantities of high molecular weight products, for when one of these isolated biaryls is partially converted to tarry substances by means of additional benzoyl peroxide, the residual binuclear fraction is found to consist of the original percentages of isomers. Some evidence of the mechanism of formation of the high molecular weight products has also been obtained.

A complete understanding of the mechanism of substitution of aromatic nuclei by free radicals (*e.g.*, the Hey and Gomberg reactions) will require knowledge of the influences of substituents initially present in the parent nuclei. For example, the relative activating or deactivating effects of such substituents must be determined. Several types of competitive reactions are available for determining these effects.[4] It was decided in the present work to decompose a free radical reagent (benzoyl peroxide) in equimolecular binary mixtures of pyridine with various phenyl halides and compare the ratios of yields of phenylpyridines to halobiphenyls as a measure of the reactivities of the parent solvents. This general method has been previously applied by Grieve and Hey.[5] Pyridine was selected as the reference solvent to which the reactivities of the phenyl halides would be related because the solubility of the pyridine derivatives in aqueous acid facilitates their purification.

When the phenyl radical reacts with such aromatic compounds, isomeric biaryls result from attack upon the various positions in the ring relative to the substituent initially present. It was decided in the present work to determine these ratios of isomers for several reasons.

1. Such substitution has been described as invariably ortho–para although only recently[6–8] have many accurate quantitative data been reported upon which to base such a conclusion. Additional data could be readily obtained in the present work.

2. The products of free radical aromatic substitution are usually quite complex. Only by determining the isomers present in the biaryls produced can the purity of the fractions be established.

3. In using competitive reactions of this type, there is always a possibility that the two mononuclear solvents may associate with each other so that the measured reactivities are not those of the discrete mononuclear species but of larger aggregates. If a single solvent is used as a reference material throughout a series of reactions, association with the competitive reagents would probably (although not necessarily) affect the ratios of isomeric products formed from the reference material. In other words, in the present work if the phenylpyridine fractions obtained are always of the same isomer composition regardless of the nature of the competitive halobenzene reagent, an absence of association of pyridine with the competitive solvent would be indicated.

In all free radical aromatic substitutions, large quantities of high molecular weight tars are obtained. These tars may be formed by polysubstitution of the initial biaryl products but this mechanism has not been proved. If polysubstitution is the principal cause of formation of the high molecular weight products, then the following two effects might result: (a) The composition of the isomeric biaryl mixtures initially produced (*e.g.*, *o*-, *m*- and *p*-chlorobiphenyls) might be altered by polysubstitution, for one of the isomers (*e.g.*, *p*-chlorobiphenyl) might be more reactive than the others. Therefore the yields of isomeric biaryls isolated as products would not be representative of the reactivities of the corresponding positions in the parent benzene compounds. In the present work it was decided to measure directly the effect of polysubstitution on the isomeric biaryl mixtures. (b) The ratios of phenylpyridines to halobiphenyls formed in the competitive reactions might not be a true measure of the relative reactivities of the two mononuclear solvents, for the biaryls produced from one might be more susceptible to polysubstitution than the biaryls produced from the other. Therefore the ratios of phenylpyridines to halobiphenyls would be altered by polysubstitution. In

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(1) This paper is partially based upon a thesis submitted by Earl C. Gregg, Jr., to the Graduate School, Western Reserve University, in partial fulfillment of the requirements for the doctor's degree.

(2) Presented at the Buffalo meeting of the American Chemical Society, March, 1952.

(3) Research Corporation Predoctoral Fellow, 1952–1953.

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the present work the use of mixtures of pyridine with phenyl halides in competitive reactions permits the determination of the solvent nuclei incorporated in the tars by nitrogen and halogen analyses of the materials. If polysubstitution is the only mechanism of tar formation, a simple relationship of solvent nuclei converted to biaryls and to tars would be expected. A correction factor might then be applied to the yields of biaryls produced to permit a more accurate determination of relative reactivities of parent solvents. It was therefore decided to perform nitrogen and halogen analyses of the tars in the present work.

Experimental

All infrared spectra were measured as films of *ca.* 0.001 in. thickness with a Perkin-Elmer Model 12A spectrometer.[9] The composition of isomeric mixtures was determined by comparison of the spectra of unknown mixtures to the spectra of known artificial mixtures of pure isomers until duplication was obtained. Comparison measurements were taken from samples contained in the same cell of fixed thickness. In the spectra of each of the isomeric mixtures, absorption peaks of measurable intensity characteristic of at least two of the three components were obtained.

Chlorobiphenyls.—*o*-, *m*- and *p*-chlorobiphenyls were prepared according to the method of Gomberg[10] from the corresponding chloroanilines obtained from the Eastman Kodak Company.

Bromobiphenyls.—*o*- and *p*-bromobiphenyls were obtained from the Eastman Kodak Company. *m*-Bromobiphenyl was prepared from *o*-aminobiphenyl by acetylation, bromination and deamination according to the method of Huber.[11]

Iodobiphenyls.—*o*-Iodobiphenyl was obtained from Eastman Kodak Company; *m*- and *p*-iodobiphenyl were prepared from the corresponding amines by the method of Campaigne and Reid.[12]

Methyl Phenylbenzoates.—Methyl *o*-, *m*- and *p*-phenylbenzoates were prepared from the corresponding methyl aminobenzoates by the Gomberg[10] reaction. The identification of the esters was checked by saponifying them to the corresponding free acids, the melting points of which are known.

Phenylpyridines.—A mixture of isomeric phenylpyridines was prepared from aniline according to the method of Haworth.[13] A total of 150 g. of isomeric phenylpyridines was converted to the picrates which were extracted with hot acetone to dissolve the *o*- and *m*-phenylpyridine picrates and leave crude *p*-phenylpyridine picrate. The mixture of *o*- and *m*-phenylpyridine picrates was converted efficiently to the free amines according to the method of Kaye.[14] The pure isomers were obtained by fractional crystallization of the oxalate salts. The oxalate salts served admirably for this purpose of purification, providing crystals of sharp melting point, although analysis of these salts, even after numerous recrystallizations, showed that the simple salts expected were not always obtained.

The mixture of *o*- and *m*-phenylpyridines was dissolved in boiling acetone and added to a boiling acetone solution of an equivalent amount of oxalic acid based on the binoxalate salt. Crystals formed almost immediately, and the mixture was filtered while hot. Two crystallizations of the precipitate from ethanol yielded large, stout, colorless needles; m.p. 164–165°. *Anal.* Calcd. for $C_{11}H_9N \cdot H_2C_2O_4$: C, 63.6; H, 4.50; N, 5.72; $H_2C_2O_4$, 36.7. Found: C, 63.6; H, 4.56; N, 5.58; $H_2C_2O_4$, 36.5. This binoxalate was decomposed with excess aqueous potassium hydroxide to liberate the free amine; b.p. 102–103° (3 mm.), yield 7 g.; picrate, m.p. 161–163°, which corresponds to the picrate of *m*-phenylpyridine.[13]

The filtrate from the mixed amines–oxalic acid reaction was allowed to cool and crystals formed. Recrystallization from acetone gave fluffy needles; m.p. 120–122°. *Anal.* Calcd. for $2C_{11}H_9N \cdot 3H_2C_2O_4$: C, 57.9; H, 4.14; N, 4.83; $H_2C_2O_4$, 46.5. Found: C, 58.5; H, 4.20; N, 4.98; $H_2C_2O_4$, 45.7. The binoxalate was decomposed with excess aqueous potassium hydroxide to the free amine; b.p. 102–103° (3 mm.), m.p. 11–12°; picrate, m.p. 178–180°, which corresponds to the picrate of *o*-phenylpyridine[13]; yield 15 g.

The crude *p*-phenylpyridine picrate was converted through the free amine to the binoxalate, m.p. 147–149°, from acetone. *Anal.* Calcd. for $C_{11}H_9N \cdot H_2C_2O_4$: C, 63.6; H, 4.50; N, 5.72; $H_2C_2O_4$, 36.7. Found: C, 62.0; H, 4.42; N, 5.66; $H_2C_2O_4$, 39.2. The binoxalate was decomposed to the solid free amine; m.p. 67–69°, platelets from petroleum ether; yield 7 g.; picrate, m.p. 196–197°, which corresponds to the picrate of *p*-phenylpyridine.[13]

Reaction of Benzoyl Peroxide with Bromobenzene and Pyridine.—A slurry of 123 g. (0.496 mole) of 97.8%[15] pure benzoyl peroxide (Lucidol) in 300 ml. of a mixture of 316 g. (4.0 mole) of pyridine and 658 g. (4.0 mole) of bromobenzene was added to the balance of the solvent mixture maintained at 70 ± 2°. The addition required 2.5 hours following which the reaction mixture was maintained at 70 ± 2° for 50 hours. The yield of carbon dioxide collected in an ascarite train was 15.23 g. (0.346 mole).

The unreacted solvents were removed by distillation at reduced pressure. The distilland was dissolved in benzene and extracted with four 250-ml. portions of aqueous sodium hydroxide and two 200-ml. portions of water which removed 78.2 g. of benzoic acid which contained some isomeric phenylbenzoic acids.

The benzene raffinate was extracted with three 200-ml. portions of 10% aqueous sulfuric acid and two 200-ml. portions of water which removed 14.7 g. (0.095 mole) of phenylpyridines, b.p. 100–120° (3 mm.), and 2.1 g. of unidentified tar. Analysis by infrared methods showed the composition of the phenylpyridine fraction to be 58% *o*-, 28% *m*- and 14% *p*-phenylpyridine.

The benzene raffinate from the extraction of phenylpyridines was distilled at atmospheric pressure to remove the benzene. The distilland was distilled at reduced pressure to yield a fraction of impure bromobiphenyls, b.p. 110–145° (1.5 mm.) and 26.8 g. of unidentified residual tar. The bromobiphenyls were contaminated with some benzoic acid which was removed with cold concentrated sulfuric acid to yield 2.60 g. (0.021 mole) of benzoic acid. An infrared spectrum of the extracted bromobiphenyls showed them to be pure. The yield was 20.6 g. (0.088 mole). Analysis of the mixture by infrared methods showed the composition to be 48.5% *o*-, 33% *m*- and 18.5% *p*-bromobiphenyl.

A duplicate reaction was run using 124 g. (0.500 mole) of 97.8% pure benzoyl peroxide and the reaction mixture was heated for 26 hours. Otherwise, the conditions were identical and the reaction products were isolated in the same manner. From this second reaction was isolated 88.6 g. of benzoic acid which contained some isomeric phenylbenzoic acids. The benzoic acid was distilled at reduced pressure to leave 8.5 g. (0.043 mole) of phenylbenzoic acids as distilland. For identification and analysis of the phenylbenzoic acids, see the experimental section of the chlorobenzene–pyridine reaction with benzoyl peroxide. There was isolated 14.1 g. (0.091 mole) of isomeric phenylpyridines and 19.3 g. (0.083 mole) of isomeric bromobiphenyls. The isomer percentages in the phenylpyridine and bromobiphenyl fractions were the same as in the preceding experiment. An unidentified residual tar weighing 28.5 g. was obtained and analyzed for bromine and nitrogen content: Found: Br, 18.16, 18.06; N, 1.77, 1.95.

A portion of this residual tar was dissolved in dry benzene and treated with anhydrous hydrogen chloride. The material which precipitated was washed with benzene and sub-

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[9] These spectra have been deposited as Document number 4070 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and by remitting $1.25 for photoprints, or $1.25 for 35 mm. microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

[10] M. Gomberg and W. E. Bachmann, THIS JOURNAL, **46**, 2339 (1924).

[11] W. F. Huber, M. Renoll, A. G. Rossow and D. T. Mowry, *ibid.*, **68**, 1105 (1946).

[12] E. Campaigne and W. B. Reid, Jr., *ibid.*, **68**, 1663 (1946).

[13] J. W. Haworth, I. M. Heilbron and D. H. Hey, *J. Chem. Soc.*, 349 (1940).

[14] I. A. Kaye, I. C. Kogon and W. Burlant, THIS JOURNAL, **72**, 5752 (1950).

[15] V. R. Kokatnur and M. Jelling, *ibid.*, **63**, 1432 (1941).

jected to elemental analysis. Both bromine and nitrogen were found to be present.

Reaction of Benzoyl Peroxide with Chlorobenzene and Pyridine.—This reaction was conducted in a manner identical with the bromobenzene reaction. From 124 g. (0.500 mole) of 97.8% pure benzoyl peroxide acting on a mixture of 450 g. (4.0 moles) of chlorobenzene and 316 g. (4.0 moles) of pyridine was obtained 15.59 g. (0.354 mole) of carbon dioxide and 86.0 g. (0.640 mole) of benzoic acid which contained some phenylbenzoic acids. The mixture of acids was dissolved in 500 ml. of ether. A 100-ml. aliquot was reacted with excess diazomethane. The resulting methyl benzoate was distilled at reduced pressure and the distilland was extracted with petroleum ether to remove the methyl phenylbenzoates. These esters were further purified by chromatographic adsorption on alumina from petroleum ether solution. The infrared spectrum of the mixture showed it to be isomeric methyl phenylbenzoates. The yield was 1.7 g. (0.008 mole). Analysis of the mixture by infrared methods showed the composition to be 49% *o*-, 20% *m*- and 31% *p*-isomers. These isomer percentages may not be significant, for chromatographic adsorption may have altered the ratio of isomers.

There was obtained 14.7 g. (0.095 mole) of a phenylpyridine fraction, the isomer percentages of which were the same as those from previous runs, and 16.3 g. (0.086 mole) of isomeric chlorobiphenyls. The chlorobiphenyls were purified in the same manner as the bromobiphenyls. Analysis by infrared methods showed the composition of the chlorobiphenyls to be 54% *o*-, 31% *m*- and 15% *p*-isomers.

An unidentified residual tar was obtained, weight 24.6 g. It was analyzed for chlorine and nitrogen. Found: Cl, 7.92, 7.96; N, 1.71, 1.75.

A duplicate reaction was run under the same conditions and with the same amounts of reagents. There was obtained 15.49 g. (0.352 mole) of carbon dioxide, 85.7 g. of benzoic acid which contained some isomeric phenylbenzoic acids, 14.5 g. (0.094 mole) of phenylpyridines, 16.0 g. (0.085 mole) of chlorobiphenyls and 27.2 g. of an unidentified residual tar which was analyzed for chlorine and nitrogen. Found: Cl, 8.40, 8.37; N, 1.89, 1.89.

The isomer percentages in the chlorobiphenyl and phenylpyridine fractions were the same as those obtained in the first reaction.

Reaction of Benzoyl Peroxide with Iodobenzene and Pyridine.—This reaction was conducted in a manner identical with the bromobenzene reaction. From 123.1 g. (0.5 mole) of 98.4% pure benzoyl peroxide and a mixture of 326.4 g. (4.12 moles) of pyridine and 831 g. (4.08 moles) of iodobenzene was obtained 14.25 g. (0.323 mole) of carbon dioxide and 107.95 g. of benzoic acids. Analysis of the acid fraction with diazomethane, etc., as described in the chlorobenzene–pyridine reaction showed that 73.9 g. (0.606 mole) of benzoic acid, 9.04 g. (0.0456 mole) of phenylbenzoic acids and 26.86 g. of acid residue were present.

The phenylpyridine fraction, 11.66 g. (0.0751 mole), contained the same percentage of isomers as obtained in the preceding experiments. The residue from the phenylpyridine distillation weighed 2.0 g.

The iodobiphenyl fraction was isolated by distillation and purified by treatment with 10% sodium hydroxide and irradiating with ultrasonic waves. This gave excellent dispersion to permit extraction of 1.85 g. of benzoic acid and leave 22.7 g. (0.081 mole) of isomeric iodobiphenyls. Comparison of the infrared spectrum of this mixture to that of known mixtures showed the composition to be 55% *o*-, 28% *m*- and 16.5% *p*-iodobiphenyl. The residues were combined (28.7 g.) and found to contain 1.88% N and 15.58% I.

A duplicate run gave essentially the same results within the limits of error indicated in the previous experiments.

Reaction of Benzoyl Peroxide with the Isomeric Phenylpyridines.—A mixture of phenylpyridines was prepared which was composed of the same percentage of isomers as the phenylpyridine fraction isolated from the preceding reactions. To a stirred sample of 58.8 g. of these isomeric phenylpyridines, heated to 70 ± 2°, was added in portions of *ca.* 1 g. a total of 25 g. of 97.8% pure benzoyl peroxide over a period of one hour. The mixture was stirred and maintained at 70 ± 2° for 30 hours. The reaction mixture was dissolved in 100 ml. of benzene and extracted with three 150-ml. portions of 15% aqueous sodium hydroxide followed by two 150-ml. portions of water to remove benzoic acid. The benzene was removed by distillation at atmospheric pressure. The unreacted phenylpyridines were recovered by distillation at reduced pressure, b.p. 85–90° (1 mm.); yield 45.4 g. Thus, 22.8% of the original mixture reacted with benzoyl peroxide.

Infrared spectra of the isomeric phenylpyridines before and after reaction with benzoyl peroxide were identical.

Reaction of Benzoyl Peroxide with the Isomeric Iodobiphenyls.—To 56.3 g. (0.201 mole) of an iodobiphenyl mixture (identical in isomer percentages to the iodobiphenyl fraction obtained in the pyridine–iodobenzene reaction) was added 24.2 g. (0.1 mole) of benzoyl peroxide at 70° over a period of two days. After the reaction was complete, the benzoic acids were removed with alkali and the iodobiphenyls vacuum distilled, b.p. 95–135° (1 mm.), yield 10.6 g. Thus 20% of the original mixture of solvents was recovered. This deviation from the 77% recovery in the phenylpyridine experiment is partially explained by the greater molar ratio of benzoyl peroxide to biaryl used in the present experiment.

Infrared spectra of this residual iodobiphenyl fraction showed the isomer percentages to be identical with the parent mixed solvent although contaminated with some biphenyl.

Discussion

The yields of products are listed in Table I. Direct comparison of the ratios of halobiphenyls to phenylpyridines establishes the following relative reactivities of the parent solvents toward phenyl radical attack: iodobenzene 1.1, pyridine 1.0, chlorobenzene 0.9 and bromobenzene 0.9. These values do not take into consideration the solvent nuclei incorporated in the tarry products. The quantities reported in the pyridine–chlorobenzene reaction differ somewhat from those recently reported.[16]

TABLE I

Product	Moles of products per mole of $(C_6H_5COO)_2$ in competitive reaction of pyridine and		
	C_6H_5Cl	C_6H_5Br	C_6H_5I
$C_5H_5NC_6H_5$	0.19(0.19)	0.18(0.19)	0.15(0.15)
$C_6H_5C_6H_4X^a$	.17(.17)	.17(.18)	.16(.16)
CO_2	.71(.70)	.73(.71)	.65(.71)
C_6H_5COOH	1.28(1.40)	1.31(1.32)	1.21(1.17)
$C_6H_5C_6H_4COOH$	0.08	0.09	0.09
X^a in residue	.11	.13	.09
N in residue	.06	.08	.08

[a] X refers to respective halogen. The figures in parentheses were obtained in a duplicate determination.

In the bromobenzene–pyridine competitive reaction, the tarry residue was found to include a basic fraction containing bromine. The most probable interpretation is that bromobenzene and pyridine nuclei are incorporated in a single molecule. Any other explanation would necessitate a rupture of the aromatic carbon to bromine bond and no such phenomenon has been observed in reactions of this type. Therefore a simple free radical polysubstitution of the biaryls cannot account for all of the tar formation as it would not produce a molecule containing both halobiphenyl and pyridine nuclei. The improbability of the polysubstitution mechanism can also be deduced from the elemental analysis of the residues. Inasmuch as elemental analysis accounts for about one-third of the residue as solvent nuclei, a polysubstitution mechanism would imply that the tar molecules average about three aromatic rings. Such molecules should be

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(16) D. R. Augood, D. H. Hey and G. H. Williams, *J. Chem. Soc.*, 2094 (1952).

completely volatile under the conditions of distillation. As the data prove that the high molecular weight products are not formed exclusively through simple polysubstitution of biaryls, the above calculation of relative reactivities based entirely upon the yields of binuclear products seems the most logical method available.

The percentages of isomers in the biaryl fractions are listed in Table II. The accuracy of the analytical technique is indicated by the deviations shown.

TABLE II

	Ortho	Meta	Para
Chlorobiphenyl	54 ± 3.0	31 ± 2.0	15 ± 1.0
Bromobiphenyl	48.5 ± 3.0	33 ± 2.0	18.5 ± 1.0
Iodobiphenyl	55 ± 3.0	28 ± 2.0	16.5 ± 1.0
Phenylpyridine	58 ± 3.5	28 ± 3.0	14 ± 1.5
Methyl phenylbenzoates	49 ± 2.0	20 ± 3.0	31 ± 1.0

Since the reaction of benzoyl peroxide with isomer mixtures of the above percentages has been found to leave biaryl fractions of unchanged composition, the percentages of isomers shown are significant despite the accompanying formation of large quantities of tar. In other words, subsequent reactions of biaryls initially formed would not alter the percentage of isomers. Conversely it has been shown that the orientation of a single substituent in a substituted biphenyl does not appreciably affect the reactivity of the nuclei toward free radical substitution.

The isolation of phenylpyridine fractions of constant composition despite the variation of competitive phenyl halide solvent indicated that association of the phenyl halide and pyridine did not occur. However, since the completion of the major portion of this work, Hey[7] has reported that the reaction of benzoyl peroxide with chlorobenzene in the absence of a competitive solvent produces 62% *o*-, 24% *m*- and 14% *p*-chlorobiphenyl. This deviation from the values found in the present work indicates that association of the solvents in each competition reaction might have occurred but that the effect on the isomers produced from pyridine must be constant. Because of this possible association, the application of the relative reactivities determined in this paper to other systems of solvents may not be accurate.

The limited data available to date indicate that substitution by free radicals is properly described as invariably ortho, but that the ratio of meta to para substitution may be statistical with groups which are ortho para directing for the common ionic substitution reactions.

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CLEVELAND, OHIO

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WESTERN AUSTRALIA]

The S_N Mechanism in Aromatic Compounds. VI. Carbonyl and Nitrile Substituents

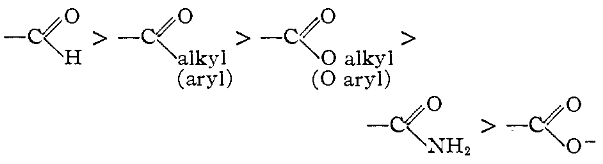
BY JOSEPH MILLER

RECEIVED MARCH 26, 1953

The activating power in aromatic S_N reactions of substituent groups containing C=O and C≡N bonds has been measured and discussed in terms of electronic effects. The Arrhenius parameters for the compounds containing the aldehyde and nitrile groups are abnormal and require either a special mechanism or the occurrence of side reactions which are reversible and do not affect the products.

In discussing a series of substituents of the general type $-\mathrm{C}\genfrac{}{}{0pt}{}{\diagup\!\!\diagup \mathrm{O}}{\diagdown \mathrm{X}}$ Ingold[1] pointed out that as the electron donating power of X increases so the external effect of the whole group decreases.

In aromatic S_N reactions it has already been pointed out by the author[2] that these substituents are activating and that, following Ingold, one should then have the sequence of activating power

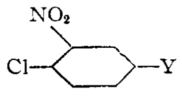


$$-\mathrm{C}\genfrac{}{}{0pt}{}{\diagup\!\!\diagup \mathrm{O}}{\diagdown \mathrm{H}} > -\mathrm{C}\genfrac{}{}{0pt}{}{\diagup\!\!\diagup \mathrm{O}}{\diagdown \text{alkyl (aryl)}} > -\mathrm{C}\genfrac{}{}{0pt}{}{\diagup\!\!\diagup \mathrm{O}}{\diagdown \text{O alkyl (O aryl)}} > -\mathrm{C}\genfrac{}{}{0pt}{}{\diagup\!\!\diagup \mathrm{O}}{\diagdown \mathrm{NH_2}} > -\mathrm{C}\genfrac{}{}{0pt}{}{\diagup\!\!\diagup \mathrm{O}}{\diagdown \mathrm{O^-}}$$

As is common, the C≡N group is to be included with this series.

It should be noted that only the permanent electron repulsion effects of X should operate.

These predictions have been tested by measuring the rate constants and Arrhenius parameters for the replacement of Cl by OMe^- in dry methanol, in the series



where Y = $-\mathrm{C}\genfrac{}{}{0pt}{}{\diagup\!\!\diagup \mathrm{O}}{\diagdown \mathrm{X}}$, —C≡N or H. The compounds actually investigated were: (i) *o*-chloronitrobenzene, (ii) sodium 4-chloro-3-nitrobenzoate, (iii) 4-chloro-3-nitrobenzamide, (iv) methyl 4-chloro-3-nitrobenzoate, (v) 4-chloro-3-nitroacetophenone, (vi) 4-chloro-3-nitrobenzophenone, (vii) 4-chloro-3-nitrobenzaldehyde and (viii) 4-chloro-3-nitrobenzonitrile.

The relevant results are given as Table I, which

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[1] C. K. Ingold, *Chem. Revs.*, **15**, 225 (1934).

[2] J. Miller, *Revs. Pure Appl. Chem.* (*Aust.*), **1**, 171 (1951).