and the peak shifted to 390 mμ and possessed about the same relative intensity. Furthermore, when the basic solution was acidified with alcoholic acetic acid, the spectrum obtained was identical with that of the initial alcoholic solution of (XVI). Although there is the possibility of phenoxide ion formation, the very large bathochromic shift of 55 mμ along with development of color, in base, and the lack of chemical reactivity tend to favor the existence of a quinoid structure and to indicate an existing tautomerization.

Conversely, when the hydroxyl group is located in a meta position on the aniline portion of the Schiff base, or in any position on the benzaldehyde portion of the molecule, there is no opportunity for such a quinoid structure to exist. A methoxyl group, in the ortho or para position of the aniline portion of the Schiff base would likewise prevent the formation of a quinoid structure. Hence reduction would be expected in such cases. This latter condition has been substantiated, though not rigorously, by the successful reduction of *N*-(*m*-hydroxybenzyliden)-aniline (XV) and *N*-benzylidene-*p*-anisidine (XVI).

EXPERIMENTAL

Reduction technique A. A 5–10% solution of the Schiff base, dissolved in absolute methanol, was placed in a 3-necked flask fitted with a mechanical stirrer, a dropping funnel, and a reflux condenser. A 2–10% solution of sodium borohydride, double the molar amount of Schiff base, was dissolved in absolute methanol. When the dropwise addition of the sodium borohydride was complete, the reaction solution was refluxed an additional 15 min. and then cooled. To this solution was added an equal volume of cold tap water whereby a precipitate of the secondary amine formed. In some earlier experiments, the secondary amine was liberated by the addition of a molar amount of sodium hydroxide which was twice that of the sodium borohydride used. In these cases, the sodium hydroxide was added as a 6*N* solution; this being followed by the addition of cold tap water which was equal in volume to that of the total solution. The precipitate of secondary amine was then collected by suction filtration, washed with water, and dried. In many cases the product was of sufficient purity that no recrystallization was necessary.

Reduction technique B. A 5–10% solution of the Schiff base, dissolved in absolute methanol, was placed in a 3-necked flask fitted with two glass stoppers and a reflux condenser. This solution was warmed or left at room temperature. To this was added an equimolar amount of solid sodium borohydride. The portion-wise addition was made through one of the necks of the flask. If the reduction reaction became too vigorous, the flask was momentarily placed in cold water. When the initial reaction had subsided, the contents of the flask were refluxed for 15 min. and then cooled. The secondary amine was liberated by means of water or sodium hydroxide plus water as in technique A. The precipitate of secondary amine thus formed was collected, washed with water, and dried. In many cases no recrystallization was necessary.

Preparation of benzoyl derivatives. The benzoyl derivatives were prepared from benzoyl chloride by the usual method and recrystallized from 95% ethanol.

Ultraviolet absorption analysis. *N*-Benzylidene-*p*-aminophenol of concentration 5.0 mg./l. was placed in a silica cell and the ultraviolet absorption curve obtained. A Beckman DK double beam instrument with matched cells was used. The reference cell was filled with 95% ethanol, the solvent from which the spectrum was obtained. After securing this absorption curve, two drops of a 1% solution potassium hydroxide solution in 95% ethanol was added to each cell. The color of the sample solution turned pale yellow. After obtaining this spectrum, 4 drops of a 2% acetic acid solution in 95% ethanol was added to each cell and a reading again taken.

Acknowledgment. The authors wish to thank Stephen Osborn for his help in connection with the ultraviolet part of this work.

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[CONTRIBUTION FROM THE WILLIAM H. NICHOLS CHEMICAL LABORATORY, NEW YORK UNIVERSITY]

Arylation of Aromatic Compounds by the Meerwein Reaction. Evidence for Aryl Radicals from Orientation Studies[1]

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Benzene, nitrobenzene, and chlorobenzene have been arylated under homogeneous Meerwein reaction conditions. Isomer distributions have been determined and have been found to correspond to radical orientation. This information supports the conclusion that the Meerwein reaction involves aryl radicals.

Although the mechanism of the Meerwein reaction has been the subject of several recent investigations[2–4] the question of free aryl radical intermediates remains unanswered. This omission is primarily a result of the inapplicability of standard tests for free radicals in such complex systems. A new approach to this problem was provided by the observation that benzene was arylated under Meerwein reaction conditions.[2] Consequently, nitrobenzene and chlorobenzene have been arylated in the

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(1) Presented in part at the Meeting-In-Miniature of the New York Section of the AMERICAN CHEMICAL SOCIETY, March 16, 1956.

(2) A part of the present paper has appeared in preliminary form: S. C. Dickerman, K. Weiss, and A. K. Ingberman, *J. Org. Chem.*, **21**, 380 (1956).

(3) J. K. Kochi, *J. Am. Chem. Soc.*, **78**, 1228 (1956).

(4) O. Vogl and C. S. Rondestvedt, Jr., *J. Am. Chem. Soc.*, **78**, 3799 (1956).

same manner; the mixtures of isomeric biphenyls have been analyzed and the results compared with those reported for recognized radical attack on these substances.[5]

A homogeneous solution of nitrobenzene ($0.5M$), p-nitrobenzenediazonium chloride ($0.1M$), and cupric chloride ($0.1M$) in 70% aqueous acetone gave 13% of the isomeric dinitrobiphenyls. The composition of this mixture is shown in Table I together with the values which have been observed by others using accepted sources of aryl radicals. These mixtures of dinitrobiphenyls are not easily analyzed and the good agreement between the results of the Meerwein reaction and arylation *via* p-nitrobenzoyl peroxide might have been obscured had we not used a similar isolation procedure and an identical method of analysis.[6] The discrepancy between the p-nitrobenzoyl peroxide decomposition and the Gomberg-Bachmann reaction is disturbing since this represents the first instance known to us of a major difference between these well-known methods of generating aryl radicals.[8]

TABLE I

p-NITROPHENYLATION OF NITROBENZENE

Source of p-Nitrophenyl Group	Isomer Content (%) 2,4′	3,4′	4,4′
Meerwein reaction	65	14	21
p-Nitrobenzoyl peroxide[6]	58	13	29
Gomberg-Bachmann reaction[7]	34	23	43

A second arylation, the phenylation of chlorobenzene, was carried out in the same manner. The product, a mixture of chlorobiphenyls, gave an infrared tracing, Fig. 1, virtually identical with that of a mixture of chlorobiphenyl prepared by a Gomberg-Bachmann reaction. Hey and coworkers[9] have demonstrated the reliability of this method of comparison. The minor deviations between the two infrared curves represent differences in isomer content which are within experimental error.

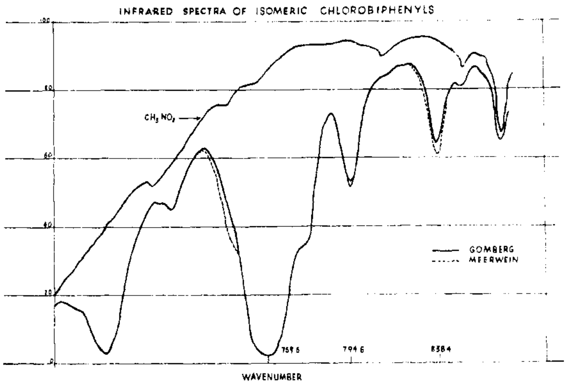

FIGURE 1.

The original example of Meerwein arylation, the 2,4-dichlorophenylation of benzene, has been investigated in some detail and results are summarized in Table II. The yield of 2,4-dichlorobiphenyl appears to be proportional to the concentration of benzene and inversely proportional to that of cupric chloride. It is significant that the addition of sodium acetate did not increase the yield of biphenyl.

TABLE II

2,4-DICHLOROPHENYLATION OF BENZENE

	Reactants (Molarity)[a]			Products (%)[b]		
Run	$ArN_2^+Cl^-$[c]	$CuCl_2$	C_6H_6	$C_{12}H_8Cl_2$	$C_6H_4Cl_2$	$C_6H_3Cl_3$
1	0.046[d]	0.051	0.80	29	18	5
2	0.10	0.050	0.50	19	37	14
3	0.10	0.050	0.50	21	36	14

[a] In 70% aqueous acetone. Homogeneous except for Run 3 to which was added sodium acetate. [b] 2,4-Dichlorobiphenyl, 1,3-dichlorobenzene, 1,2,4-trichlorobenzene. [c] 2,4-Dichlorobenzenediazonium chloride. [d] Solid diazonium salt was used.

Discussion. It is generally accepted that arylations of aromatic compounds, *via* benzoyl peroxides or Gomberg-Bachmann reactions, involve aryl radicals. The results of our isomer distribution studies clearly indicate that the same species, p-nitrophenyl and phenyl radicals, are produced in Meerwein reactions involving the corresponding diazonium salts. The conclusion that the Meerwein reaction proceeds by a radical mechanism is in agreement with the early suggestion of Koelsch and Boekelheide[10] and with the more comprehensive mechanism recently presented.[2] In terms of the latter mechanism the yield of biphenyl is determined by the efficiency with which arylation competes with hydrogen abstraction from acetone and halogen abstraction from cupric chloride. In addition the rate of reaction of the diazonium cation with the dichlorocuprate (I) ion is important. If this reaction is slow, solvolysis can compete with Meerwein reaction. An example of this situation is the slow reaction which gave chlorobiphenyls in low yield accompanied by phenol formation. The limited data at hand permit only the general conclusion that electron-attracting substituents favor arylation. The kinetics of the reaction of 2,4-dichlorobenzenediazonium chloride

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(5) This method of detecting aryl radicals was developed and has been used extensively by Hey and coworkers; see, for example, D. H. Hey, C. J. M. Stirling, and G. H. Williams, *J. Chem. Soc.* 3963 (1955).

(6) R. T. Morrison and R. F. Sweeney, Abstracts, 130th Meeting AMERICAN CHEMICAL SOCIETY, Sept. 1956, p. 74-O. R. F. Sweeney, Ph.D. thesis, New York University, June 1956.

(7) D. F. DeTar and A. A. Kazimi, *J. Am. Chem. Soc.*, **77**, 3842 (1955).

(8) This difference may be rationalized in part by postulating that some of the 4,4′-isomer isolated from the Gomberg-Bachmann reaction arises by a coupling.

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

(10) C. F. Koelsch and V. Boekelheide, *J. Am. Chem. Soc.*, **66**, 412 (1944).

with benzene as well as other Meerwein reactions have been studied in the presence and absence of air and a detailed discussion of the mechanism of the Meerwein reaction will appear in that article.

EXPERIMENTAL

All melting and boiling points are uncorrected. Microanalyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside 77, New York, N. Y. Spectra were determined on Beckman Model DK-2 and Perkin-Elmer Model 112 spectrophotometers.[11]

All arylation reactions were performed in a three-necked flask, fitted with a gas-tight stirrer, connected through a condenser to a simple eudiometer, and immersed in a constant temperature bath at 35°.

p-Nitrophenylation of nitrobenzene. *p*-Nitroaniline hydrochloride (17.45 g.) was suspended in a mixture of 21 ml. of concentrated hydrochloric acid and 80 ml. of water. After heating to effect solution the mixture was cooled to 0° and diazotized in the presence of 30 g. of ice by rapid addition of a solution of 7.0 g. of sodium nitrite in 40 ml. of water. After 30 min. the turbid solution was filtered and diluted to a volume of 200 ml. with water.

This solution of the diazonium salt was mixed at 35° with 700 ml. of C.P. acetone, 75 ml. of water, 51.5 ml. of purified nitrobenzene, and 25 ml. of 2*M* cupric chloride. Gas evolution began at once and 99% of the theoretical volume of nitrogen was evolved in 9 min. The addition of solid sodium chloride produced two phases. The organic phase was extracted with saturated ammonium chloride solution and the extracts were added to the aqueous phase. The latter was exhaustively extracted with ether and the extracts were added to the original organic phase. The combined extracts were concentrated to a volume of 100 ml., dried over magnesium sulfate, and fractionated. All of the nitrobenzene and most of the *p*-nitrochlorobenzene were removed at a maximum head temperature of 81° at 2 mm. The brown, semisolid residue was dissolved in purified methylene chloride and diluted to exactly 250 ml.

The isomeric dinitrobiphenyls were isolated by a procedure similar to that of Morrison and Sweeney.[6] The residue, 208 mg., from a 10 ml. aliquot of the crude dinitrobiphenyl solution was dissolved in a 1:1 mixture of purified petroleum ether and purified methylene chloride and chromatographed on a column of Alcoa Alumina XF-21 which had been activated by heating at 450° for 5 hr. The column was prepared, developed and eluted with 5700 ml. of the 1:1 solvent mixture. A total of 37 fractions were collected after which the eluant left no residue on evaporation. The first 9 fractions contained *p*-nitrochlorobenzene which was removed by evaporation at room temperatures and 0.06 mm. for 16.5 hr. The residue which amounted to 7.5 mg. was combined with the remaining fractions to give an almost colorless, crystalline residue having a faint camphor-like odor. The unknown impurity responsible for this odor was removed by rechromatographing on a fresh column, prepared from the same sample of alumina, using 1200 ml. of methylene chloride as the eluant. Fractions 1–7 gave 120 mg. (12%) of almost colorless, odorless crystalline residue. The ultraviolet spectrum of fraction 7 identified it as 2,4′-dinitrobiphenyl. Fractions 8 and 9 gave 3.4 mg. of a yellow oil with a strong, camphor-like odor having an ultraviolet spectrum very different from that of the biphenyl.

The mixture of dinitrobiphenyls was analyzed using the procedure and the extinction coefficients of the individual dinitrobiphenyls reported by Morrison and Sweeney.[6] The mixture was dissolved in methylene chloride and diluted with "isooctane" to give a solution containing 0.8% methylene chloride and a solid content of 13 mg. per liter. The ultraviolet absorption spectrum of this solution was determined and the isomer content was calculated by the method of least squares from the optical densities at ten regularly spaced wave lengths from 230 mμ to 320 mμ. The composition was found to be 65% 2,4′, 14% 3,4′, and 21% 4,4′.

Phenylation of chlorobenzene. Freshly distilled aniline (8.9 g.) was diazotized using 17.5 ml. of concd. hydrochloric acid, 25 ml. of water, 25 g. of ice, and a solution of 6.7 g. of sodium nitrite in 20 ml. of water. The solution of diazonium salt was filtered and diluted to a volume of 100 ml. with water. This solution was mixed with 1400 ml. of C.P. acetone, 300 ml. of water, 130 ml. of chlorobenzene, and 200 ml. of 0.535*M* cupric chloride solution. Evolution of nitrogen began at once and 99% of the theoretical amount was given off in 70 min. The reaction mixture was diluted with water and exhaustively extracted with ether. The combined extracts were concentrated, dried, and fractionated at atmospheric pressure until most of the chlorobenzene had been removed. The residual oil was steam-distilled and the 5 l. of distillate was extracted with ether. The extracts were washed with 1*N* sodium hydroxide solution and then with water until neutral. The ether solution was dried, concentrated, and distilled. After a fore-run of chlorobenzene the crude chlorobiphenyls (0.35 g., 2%) were collected from 74–155° at 0.08–0.60 mm. The alkaline extracts yielded phenol which was brominated to give 4.4 g. of 2,4,6-tribromophenol. This represents a minimum yield of 14% of phenol.

The crude mixture of isomeric chlorobiphenyls contained colored impurities which were removed by chromatography on alumina with petroleum ether as eluant. A colorless sample of the chlorobiphenyls of b.p. 91–99° at 0.65–0.85 mm. was isolated. The infrared spectrum of this material in nitromethane solution[9] is compared in Fig. 1 with an authentic sample of mixed chlorobiphenyls prepared by a Gomberg-Bachmann reaction and purified as described above.

2,4-Dichlorobiphenyl. (*a*) *Using solid diazonium salt.* 2,4-Dichlorobenzenediazonium chloride (6.00 g.), prepared by the method of Knoevenagel, was dissolved in a mixture of 420 ml. of C.P. acetone, 120 ml. of water, 45 ml. C.P. benzene, and 60 ml. of 0.535*M* cupric chloride solution. Nitrogen evolution began immediately and a total of 95% of the theoretical amount was evolved in 24 min. Addition of solid sodium chloride to the homogeneous solution caused separation of two phases. The acetone-rich phase was washed with saturated ammonium chloride solution and the washings were added to the aqueous layer. This solution was exhaustively extracted with benzene and the extracts were combined with the acetone-rich phase. The resulting solution was dried with magnesium sulfate and concentrated by distillation through a short, packed column. The residue was steam-distilled up to a bath temperature of 185° and the distillate was extracted with ether. The combined and dried ether extracts were concentrated and distilled to yield 0.74 g. (18%) of 1,3-dichlorobenzene of b.p. 171–172°, 0.26 g. (5%) of 1,2,4-trichlorobenzene of b.p. 90–101° at 12.0–13.5 mm., and 1.85 g. (29%) of 2,4-dichlorobiphenyl of b.p. 90–92° at 0.13–0.14 mm., Table II.

Colored impurities in this sample of 2,4-dichlorobiphenyl were removed by chromatographing on alumina using purified petroleum ether as solvent and eluant. The colorless biphenyl was redistilled before analysis.

Anal. Calcd. for $C_{12}H_8Cl_2$: C, 64.6; H, 3.61; Cl, 31.8. Found: C, 64.8; H, 3.64; Cl, 31.6. The ultraviolet absorption spectrum of this material was identical with that of a sample of 2,4-dichlorobiphenyl prepared by the Gomberg-Bachmann reaction.

(*b*) *Using aqueous diazotization.* 2,4-Dichloroaniline hydrochloride (20.0 g.) was diazotized at 0° using 21 ml. of concd. hydrochloric acid, 80 ml. of water, 30 g. of ice, and 7.0 g. of sodium nitrite in 40 ml. of water. The solution of diazonium salt was filtered and diluted with water to a volume of 200 ml.

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[11] The authors wish to thank Mr. Yugi Tajima of the Dept. of Chemical Engineering of New York University for making the infrared tracings.

The diluted solution of the diazonium salt was mixed with 700 ml. of C.P. acetone, 45 ml. of C.P. benzene, and 100 ml. of 0.50*M* cupric chloride solution. A total of 99% of the theoretical volume of nitrogen was evolved in 10 min. The procedure described above was followed with minor variations to give 5.53 g. (37%) of 1,3-dichlorobenzene, 2.63 g. (14%) of 1,2,4-trichlorobenzene, and 4.26 g. (19%) of 2,4-dichlorobiphenyl.

(*c*) *Using sodium acetate.* The quantities of reagents and procedure were identical with (b) except for the addition of an amount (12.8 g.) of anhydrous sodium acetate equivalent to the excess hydrochloric acid. A two phase reaction mixture resulted which evolved the theoretical volume of nitrogen in 17 min., yield 5.35 g. (36%) of 1,3-dichlorobenzene, 2.63 g. (14%) of 1,2,4-trichlorobenzene, and 4.74 g. (21%) of 2,4-dichlorobiphenyl.

(*d*) *By Gomberg-Bachmann reaction.* 2,4-Dichloroaniline hydrochloride (20.0 g.) was diazotized in the usual manner in a total volume of 146 ml. Excess nitrous acid was destroyed with urea and 400 ml. of C.P. benzene was added The mixture was cooled to 10°, vigorous agitation was begun, and 50 ml. of 5*N* sodium hydroxide was added over a period of 45 min. The isolation procedure previously described was followed and yielded 12.3 g. (55%) of 2,4-dichlorobiphenyl, b.p. 95–102° at 0.10–0.15 mm. A 1.49 g. sample of the biphenyl was purified by chromatography, yield 1.47 g. of colorless oil, b.p. 94–97° at 0.06–0.08 mm.

Anal. Calcd. for $C_{12}H_8Cl_2$: C, 64.6; H, 3.61; Cl, 31.8. Found: C, 64.7; H, 3.51; Cl, 31.9.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF TENNESSEE]

Competitive Metalation of Diphenyl Sulfone and 4,4'-Dimethyldiphenyl Sulfone by *n*-Butyllithium

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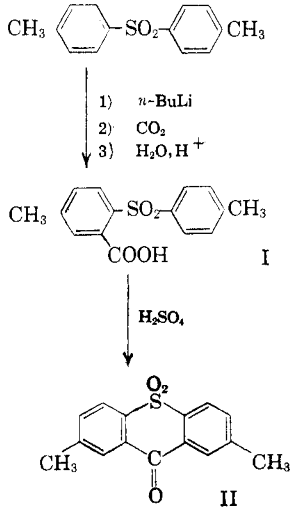
Competition between diphenyl sulfone and 4,4'-dimethyldiphenyl sulfone for an insufficient amount of *n*-butyllithium resulted in 47% metalation of diphenyl sulfone and 53% metalation of the dimethyldiphenyl sulfone. This unexpected preferential metalation of the rings supposedly deactivated by methyl groups may be due to the rapid and reversible formation of a larger concentration of the sulfone-*n*-butyllithium complex of the more basic dimethyldiphenyl sulfone. Determination of van't Hoff *i* factors in sulfuric acid for the two sulfones indicated the dimethyldiphenyl sulfone to be the more basic.

We have been studying the effect of simple alkyl substituents on the metalation of aromatic rings by *n*-butyllithium. An earlier paper[2] from this laboratory on the metalation of 4-*tert*-butyldiphenyl sulfone showed that the *tert*-butyl group caused deactivation of the ring to which it is attached, since metalation occurred predominantly in the unsubstituted ring. This result was in accord with some earlier observations by Truce[3] and Bryce-Smith[4] and the "protophilic" nature[4] of the metalation reaction. Thus, 4-methyldiphenyl sulfone was metalated[3] with *n*-butyllithium and 59% of the metalation was reported to occur in the unsubstituted phenyl ring and 41% in the ring containing the methyl group. Our work[2] with 4-*tert*-butyldiphenyl sulfone indicated an expected greater deactivating effect by the *tert*-butyl group as compared with a methyl group. These experiments were based on the intramolecular competititon of the two reactive positions adjacent to the sulfone group for the *n*-butyllithium. Intermolecular competitive metalation experiments have been used[4,5] by several workers to show relative activating and deactivating effects of functional groups toward the metalation reaction. We decided to study the intermolecular competitive metalation of diphenyl sulfone and 4,4'-dimethyldiphenyl sulfone to see how the results compared with the intramolecular competititon experiments of Truce and Norman[3] on 4-methyldiphenyl sulfone.



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[1] Present address: The Koppers Co., Monaca, Pa.

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[3] W. E. Truce and O. L. Norman, *J. Am. Chem. Soc.*, **75**, 6023 (1953).

[4] D. Bryce-Smith, *J. Chem. Soc.*, 1079 (1954).

[5] (a) H. Gilman and C. G. Stuckwisch, *J. Am. Chem. Soc.*, **67**, 877 (1945). (b) H. Gilman, M. Van Ess, H. B. Willis, and C. G. Stuckwisch, *J. Am. Chem. Soc.*, **62**, 2606 (1940). (c) H. Gilman and F. Breuer, *J. Am. Chem. Soc.*, **56**, 1123 (1934).