sation. A significantly greater yield of mellitic acid was obtained by oxidation of the high temperature pitch. Both ultimate composition and mode of formation of this pitch indicate a condensed aromatic structure.

The actual recovery of mellitic acid from the triphenylene is 44.8% of theory, which becomes 47.5% if corrected for the solubility of ammonium mellitate. In the oxidation of hexaethylbenzene carbon dioxide was formed almost exclusively and no mellitic acid was recovered.[8]

In addition to mellitic acid, in many cases significant amounts of other acids were formed. The amounts can be found in each case by adding 4 g. to the mellitic acid recovered and subtracting the sum from the total acids in the third column of the table. These acids have not yet been characterized completely, but aliphatic acids such as oxalic are absent and it appears probable that they contain significant amounts of the simpler benzene carboxylic acids. It will be observed that relatively large amounts of these acids are formed in the oxidation of the coals, the low temperature pitch and the petroleum coke, and almost none from the natural graphite or any coke which has been formed at 1000°. An interesting difference between anthracite and graphite lies in the formation of significant amounts of acids other than mellitic by oxidation of the former.

Large variations are found in the weight of the residue remaining after the nitric acid oxidation. Triphenylene, the high temperature pitch and the petroleum coke yielded large residues following the nitric acid stage, indicating a similarity of structure.

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Summary

The yield of mellitic acid from coals increases with increasing rank. The yields of mellitic acid obtained from all carbonaceous materials which have been heated to 1000° are of the same order as from the graphite. A carbon black from natural gas gave the highest yield of any carbonaceous material. Triphenylene was oxidized to mellitic acid with a yield of 44.8%. Hexaethylbenzene yielded chiefly carbon dioxide and no mellitic acid was recovered. Commercial high temperature coke is a convenient starting material since it reacts at a controllable rate with fuming nitric acid and requires relatively small amounts of permanganate to complete the oxidation.

PITTSBURGH, PENNA. RECEIVED APRIL 24, 1937

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[8] No perceptible oxidation took place when alkaline permanganate alone was employed.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, FISK UNIVERSITY]

Reactions in the Presence of Metallic Halides. II. The Behavior of Fluorides and the Reactivity of the Halogens[1]

BY N. O. CALLOWAY

Introduction

Many papers have appeared dealing with the various types[2] of organic reactions which occur in the presence of metallic halides. Yet, little attention has been paid to the fluorides with exception of the use of boron fluoride in alkylations.[3] As a part of a general study on the Friedel–Crafts and related syntheses a report is made here on the fluorides as compared with the other halides.

We have found that the organic fluorides behave normally, acyl and alkyl halides yielding with benzene and aluminum chloride the typical ketone and hydrocarbon, respectively, in accordance with the following general schemes.

$$C_6H_6 \xrightarrow[AlCl_3]{CH_3COF} C_6H_5COCH_3$$

$$C_6H_6 \underset{AlCl_3}{\overset{n\text{-}C_4H_9F}{\rightleftarrows}} C_6H_5C_4H_9$$

It was found that aluminum fluoride would not catalyze the reaction in either acylation or alkylation using either organic fluorides or chlorides.

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[1] For the first paper see Calloway and Green, THIS JOURNAL, **59**, 809 (1937).

[2] Calloway, *Chem. Rev.*, **17**, 327 (1935).

[3] McKenna and Sowa, THIS JOURNAL, **59**, 470 (1937). See preceding papers also.

This is not surprising when the general inertness of aluminum fluoride is considered. In order to find what influence a larger and heavier central metallic atom would have in the metallic fluoride, zinc fluoride was used. Acetyl chloride and zinc fluoride produced the expected ketone with anisole. This result may be from one of two factors. First, this behavior may be ascribed to the greater activity of chlorine as compared to fluorine in the acetyl halide. Second, it may be the result of a prior reaction between the acetyl chloride and zinc fluoride. Thus, the acylation may actually have taken place between acetyl fluoride and zinc chloride which resulted from the interaction of the acid chloride and zinc fluoride. This latter view appears more plausible, since acetyl fluoride is known to result from the reaction of zinc fluoride and acetyl chloride.[4]

At first it would appear that the two possible mechanisms for the reaction might be differentiated by the hydrogen halide evolved, but in all cases where two halides entered a reaction both hydrogen halides were evolved. For example acetyl fluoride and aluminum chloride gave both hydrogen chloride and hydrogen fluoride in a reaction with benzene.

In alkylation, also, zinc fluoride was satisfactory as a condensing agent with *t*-butyl chloride and anisole. Here again both hydrogen chloride and hydrogen fluoride were evolved. However, *n*-butyl chloride and *n*-butyl bromide were inert in attempts to alkylate anisole in the presence of zinc fluoride. This is not surprising in view of the greater reactivity of the halogen attached to the highly branched *t*-butyl group.

Since the reactions of zinc fluoride appeared to be mild rather than vigorous, it was thought that this condensing agent might well be applied to the acylation and alkylation of unsubstituted furan. The alkylation of unsubstituted furan has not been realized.[5] However, when attempts were made to acylate furan using acetyl chloride and zinc fluoride a reaction occurred which was accompanied by vigorous decomposition and charring. Although there was copious evolution of hydrogen halide only a trace of ketone was found. This is to be contrasted with the good yields of ketone obtained using aluminum chloride.[5] In attempts to alkylate furan using zinc fluoride and butyl halides no perceptible reaction occurred.

The Relative Reactivities of the Acyl and Alkyl Halides.—The studies generally made to determine the reactivity of a series of halides containing the same R group but different halogen atoms consist in measuring the velocity of reaction with some type of substance that results in a reaction of the two molecules in a more or less direct manner. Such substances have been used as inorganic[6] and organic bases,[7] metals[8] or alcohols.[9]

Such studies have given series of "orders of reactivity" for a given R group connected to various halogens. In practically every case where R is acyl, aryl or alkyl the order found has been I > Br > Cl > F. Although variations have been observed in this series, unusual orders of reactivity have generally been explained by side reactions[10] or steric influences.[11,12] For example, in one case the reactivity of the acid halides with RMgX has been observed to be in the order F > Cl > Br. This was explained on the basis of steric influences of the halogens by assuming addition at the carbonyl double linkage rather than by reaction directly with the halogen.[12]

In the present study it was impossible to observe a reaction in which two substances take part by a more or less simple collision of two molecules.[7] In the simplest form, catalysis by metallic halides is complex. The rate determining factor is undoubtedly the decomposition of a complex molecule resulting from the permanent or temporary interaction of metallic halide, organic halide and hydrocarbon[2] (p. 380). Thus the measurement of the reactivity of a series of halides in the Friedel–Crafts or related syntheses is in reality the measurement of the decomposition rate of the complex. At present there are not data available on the relationship of the rate of formation of the complex to its rate of decomposition. The measurement of the rate of reaction, as an indication of the relative reactivities of the organic halides, must be accomplished by measuring the formation of some product of the reaction. The actual isolation or capture and measurement of any one product is generally tedi-

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[4] Meslans, *Compt. rend.*, **114**, 1022 (1891).

[5] Gilman and Calloway, THIS JOURNAL, **55**, 4202 (1933).

[6] Kryuger and Bednova, *J. Gen. Chem.* (*U. S. S. R.*), **3**, 67 (1933); [*C. A.*, **28**, 1593 (1934)].

[7] Baker, *J. Chem. Soc.*, 1448 (1936).

[8] Gilman and Vanderwal, *Bull. soc. chim.*, [4] **45**, 344 (1929); Wilson, *Chem. Rev.*, **16**, 149 (1935).

[9] Palomaa and Leimu, *Ber.*, **66**, 813 (1933).

[10] Gilman, Zoellner, Dickey and Selby, THIS JOURNAL, **57**, 1061 (1935).

[11] Sandin and Liskear, *ibid.*, **57**, 1304 (1935); Drake and McElvain, *ibid.*, **55**, 1155 (1933).

[12] Entemann and Johnson, *ibid.*, **55**, 2900 (1933).

ous and time consuming. Therefore, we turned to the measurement of the temperature when the rate of reaction was approximately constant for the various halides. That is, we measured the temperature when the rate of evolution of hydrogen halide was the same in similar reactions for the various alkyl and acyl halides. This is a simple method and gives concordant and reproducible results.

We have found that for the acyl halides the order of activity for the halogens is as might be expected, I > Br > Cl > F. The extreme sensitiveness of acetyl iodide to aluminum chloride caused a marked decomposition but did not materially interfere with the determination.

For the alkyl halides the surprising order found was F > Cl > Br > I. In fact, the iodine was so inert that *n*-butyl iodide did not react with benzene in eighteen hours in the presence of aluminum chloride at 29°, though the other halides reacted at rapid rates at lower temperatures. It is also of interest to note that the *n*-butyl iodide was stable in the reaction and was recovered unchanged.

Experimental

A. Studies on the Fluorides

The Preparation of Acetyl Fluoride.—A modification of the method of Nesmeyanov and Kahn[13] was used. Instead of using the disagreeable potassium fluoride we found that sodium acid fluoride worked equally well. Besides not being hygroscopic, sodium acid fluoride was prepared easily by adding a concentrated solution of the calculated quantity of sodium hydroxide to a slight excess of 48% hydrofluoric acid in a copper vessel in a cold (0°) water-bath. The acid salt was filtered from the cold reaction mixture washed with two small portions of cold water, two of methyl alcohol and one of ether. The salt was dried in an oven at 80–90°. *Anal.* Calcd. for $NaFH_2$: H, 1.61. Found: H, 1.48, 1.48.

The synthesis of acetyl fluoride was carried out in glass apparatus using rubber stoppers. The yields were not affected nor was the apparatus seriously etched. Because of the low molecular weight of acetyl fluoride 0.3 mole runs were found quite convenient. To a 1-liter 3-necked round-bottomed flask equipped with a dropping funnel and a mechanical stirrer there was connected a vertical condenser with a meter long jacket. To the top of the condenser there was attached a 5-mm. bore delivery tube with two right angle bends and with such length that a vertical spiral condenser cooled by ice and salt mixture could be attached to its end. The receiving flask in ice and salt mixture was attached to the delivery tube of the spiral condenser and vented through a tube of calcium chloride. One hundred cc. of acetic anhydride was placed in the flask and 18.6 g. (0.3 mole) of sodium acid fluoride was added with stirring. The salt did not dissolve appreciably. A water-bath at 30° was then placed around the flask and 23.6 g. (0.3 mole) of acetyl chloride was added dropwise. A slow evolution of acetyl fluoride occurred. When all the acetyl chloride had been added, the temperature of the water-bath was raised gradually to 90° and maintained at this temperature until no more condensate formed in the receiver. The temperature of the water in the vertical Liebig condenser was 18°. This allowed the acetyl fluoride to pass over but not the chloride or anhydride.

The yield of crude product was 28 g. Redistillation at 20–23° yielded 24 g., 132% based on acetyl chloride. This is evidence that the acetic anhydride takes part in the reaction. Based on $NaHF_2$, the yield was 66%.

The General Method.—The procedure was as follows. In a 500-cc., 3-necked round-bottomed flask fitted with a dropping funnel, mercury-sealed mechanical stirrer and a spiral reflux condenser closed by a tube of calcium chloride and vented to a suitable trap there was placed 100 cc. of carbon disulfide. In every case 0.1 mole of acyl or alkyl halide, 0.1 mole of metallic halide and 0.1 mole of hydrocarbon or its analog (*i. e.*, anisole or furan) were used.

After reaction the mixture was hydrolyzed by pouring upon cracked ice. The aqueous layer was washed with two 25-cc. portions of carbon disulfide. The combined carbon disulfide layers were washed with two 50-cc. portions of water and one of 10% sodium bicarbonate solution, then dried over sodium sulfate. The solvent was distilled off on a water-bath and the residual material was distilled under the appropriate conditions.

Acylation by Fluorides.—In these runs the acetyl halides were added to the metallic halide in carbon disulfide cooled to 0°. This mixture was stirred for fifteen minutes and the hydrocarbon was added rapidly. The reaction mixture was then allowed to come to room temperature after which it was heated at a gentle reflux for twenty minutes. The products were worked up as described in the foregoing section. The results are summarized in Table I. The ketones were identified through their semicarbazones.

Alkylation by Fluorides.—The same set-up was used in these runs. The hydrocarbon or its analog was added together with a butyl halide to the metallic halide in carbon disulfide. The reaction mixture was refluxed for two hours and then hydrolyzed by pouring upon cracked ice. The alkylated products were converted into the corresponding benzoic acids by oxidation with chromic anhydride (see Table II).

B. The Relative Reactivity of the Halides

The set-up was as already described. One-tenth mole runs were used. For acylation the metallic halide and acetyl halide complex was cooled to −5° and stirred for fifteen minutes. After the benzene had been run in rapidly, the cooling bath was removed and the contents of the flask allowed to warm slowly in an air-bath at 30°. The stirring was continued. The dropping funnel was replaced with a low-temperature thermometer, the bulb of which was submerged in the reaction mixture. As the temperature gradually rose, the stirring was stopped for twelve seconds (stop watch) after each degree rise. The supernatant solvent was observed closely for bubbles by means of transmitted light. If no bubbles were observed,

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(13) Nesmeyanov and Kahn, *Ber.*, **67**, 370 (1934).

TABLE I

ACYLATION BY FLUORIDES

Condensing agent	Acid halide	Hydrocarbon[a]	Product	B. p., °C.	Yield, %
$AlCl_3$	CH_3COF	Benzene	$C_6H_5COCH_3$	199–201	41.6
AlF_3	CH_3COF	Benzene	None[c]		
AlF_3	CH_3COCl	Anisole[d,b]	None		
ZnF_2	CH_3COCl	Anisole	p-CH_3O-$C_6H_4COCH_3$	251–259	1.3
ZnF_2	CH_3COF	Anisole	None		
ZnF_2	CH_3COCl	Furan	2-$C_4H_3OCOCH_3$		0.06

[a] Or analog. [b] Also run in 100 cc. of benzene. Stood overnight. [c] No product and no evidence of reaction. [d] Refluxed three hours.

TABLE II

ALKYLATION BY FLUORIDES

Condensing agent	Alkyl halide	Hydrocarbon[a]	Product	B. p., °C.	Yield, %
AlF_3	*t*-Butyl chloride	Anisole	None[b]		
$AlCl_3$	*n*-Butyl fluoride	Benzene	*t*-Butylbenzene	165–180	10
ZnF_2	*t*-Butyl chloride	Anisole	*p*-*t*-Butylanisole	217–223	30.6
ZnF_2	*n*-Butyl chloride	Anisole	None		
ZnF_2	*t*-Butyl chloride	Furan	None		
ZnF_2	*n*-Butyl bromide	Anisole	None		

[a] Or analog. [b] No product and no evidence of reaction.

the stirring was continued until the temperature had advanced another degree, stopped for twelve seconds, and observed for bubbles. This process was continued until the first minute bubbles were seen to rise through the solvent. The temperature was taken as the temperature of incipient reaction, when the velocity of reaction became sufficient to cause visible bubbles to be evolved.

For alkylation exactly the same procedure was followed except that a mixture of 0.1 mole benzene and 0.1 mole alkyl halide was added to the stirred aluminum chloride in carbon disulfide cooled to 10° below the temperature of incipient reaction (found by preliminary experiments). In all cases the reaction mixture was allowed to react for two hours after the initiation of hydrogen halide evolution. The described method of working up the products was used.

All results were checked in at least two separate experiments over a period of several months.

In all alkylations the yields were substantially the same. This resulted from the fact that with the large excess of aluminum chloride the velocity of reaction was very rapid. Attempts to reduce the quantity of metallic halide to the point where the reactions were appreciably slow led to serious mechanical difficulties. On the other hand, under the conditions of experimentation, attempts to reduce the time to a point where a difference in the yields for the various halides might be observed at a fixed temperature, 30°, led to such short time intervals (less than one minute) that it was not possible to duplicate the results.

In the alkylation of benzene the following fractions were obtained from individual comparative runs with both *n*- and *t*-butylbenzenes: 160–180°, 1.5 g., largely monobutylbenzenes; 180–200°, 1 g., mixture of mono- and dibutylbenzenes; 200–260°, 3 g., polyalkylbenzenes; residue, 2.5 g. consisting of saponifiable sulfur-containing substances and polyalkylbenzenes. The identification of the fractions was made by repeatedly fractionating cumulative fractions from a large number of runs.

It is to be noted that *n*-butyl iodide gave no alkylated products. It is singular that *t*-butyl iodide gave one fraction, b. p. 163–170°. This was practically pure *t*-butylbenzene.

Results and Discussion

The first visible evolution of hydrogen halide was taken as the temperature at which measurable reaction began. This has been termed the temperature of incipient reaction. The inverse order of these temperatures was taken as the order of activity for acyl and alkyl halides. Thus the temperatures given in Table III represent the temperatures at which the first visible evolution of hydrogen halide occurred for the reaction between the acetyl halides, aluminum chloride and benzene.

TABLE III

REACTION TEMPERATURES FOR ACETYL HALIDES

Acetyl halide	B. p., 0°C./749 mm.	Temp.[a] of start °C.		Highest temp. reached	Time of reaction, hours	Yield of ketone[a] G.		Av., %
Fluoride	20–24	24	26	29	2	2.5	2.6	21.2
Chloride	50–52	19	20	29	2	6.4	6.5	53.8
Bromide	75–76	15	15	29	2	8.5	8.4	70.4
Iodide	102–105	3	3	30	2	0.2	0.3	2.1

[a] Two observations on separate runs.

In the runs with *n*-butyl halides, aluminum chloride and benzene the data given in Table IV were found.

The order of reactivity obtained by this method represents reactivity at the instant of initiation of reaction. This means that the reactivity is

TABLE IV

REACTION TEMPERATURES FOR *n*-BUTYL HALIDES

n-Butyl halide	B. p., °C.	Temp., °C. Start[a]		Highest temperature reached	Time reaction, hours
Fluoride[14]	32–35	−10	− 9	29	2
Chloride	77	− 3.5	− 4	29	2
Bromide	100.5–102	15	16	29	2
Iodide	128–130	27	28	29	18[b]

[a] Two observations on separate runs. [b] 13.1 g. of *n*-butyl iodide, b. p. 128–131°, recovered unchanged.

measured at a time when the concentrations are known and not after the reaction has proceeded for a time interval and the concentration of reactants changed so that they are no longer definite. This leaves the possibility, however, that the reactivity after a given reaction period may not be the same as at the instant of initiation of reaction. This point is being examined further and will be communicated in a later paper.

The general validity of the method is supported by the following facts. First, the velocity of reaction for the catalysis by metallic halides varies with the temperature.[15] Thus at the temperature of incipient reaction, the velocity constants for two reactions must be the same. Therefore, the reactivities are inversely related to the temperatures. Second, the order found for the acid halides is the same as that given earlier for acid chlorides and bromides.[16] Third, the yields of ketones were in good agreement with the reactivity observations. Fourth, while the yields of alkylated products were generally small and uniformly close to one another, the fact remains that the chlorides reacted at temperatures at which the bromides were completely inert, and the bromides in turn reacted at temperatures at which the iodides were unreactive. In these latter comparative runs, no alkylated product was found when there was no evolution of hydrogen halide.

This was ascertained in the alkylation experiments by allowing a run to rise just to the temperature of incipient reaction and to remain until there was a distinct evolution of hydrogen halide. On working up runs made in this manner, no alkylated products were found. This is evidence that negligible reaction occurs below the temperature of incipient reaction. The fact that in these runs 71.0% of the *n*-butyl iodide and 51% of *n*-butyl bromide were recovered indicates that whatever the nature of the complex formed during the process of reaction there must be at least two phases in its life: the first when it is formed, and the second when it becomes sufficiently activated to react. These latter observations also indicate that the evolution of hydrogen halide is primarily coincident with the formation of alkylated products. This fact is of value since it was possible that the complex might have undergone rearrangement at the instant of its formation prior to evolution of hydrogen halide so that actually the alkylation preceded the evolution of gas by an appreciable time interval. Thus we may have been measuring the temperature at which the second phase of the complex liberated the hydrogen halide rather than the temperature of actual alkylation (Reaction A).

$$\text{A.}\quad \mathrm{RX{\cdot}AlCl_3{\cdot}C_6H_6} \xrightarrow{\text{Rearrange}} \mathrm{R-C_6H_5{\cdot}AlCl_3{\cdot}HX} \longrightarrow \mathrm{R-C_6H_5{\cdot}AlCl_3 + HX}$$

However, the above observations indicate that the hydrogen halide is evolved at the instant that the complex becomes sufficiently reactive to rearrange to alkylhydrocarbon, aluminum halide and hydrogen halide.

Since it is virtually impossible to introduce the *n*-butyl group directly, it was possible that the tendency of the alkyl group to isomerize[2] (pp. 332, 342) was being measured rather than the tendency to alkylate benzene. This possibility was eliminated by observing the order of reactivity for the *t*-butyl halides. Again the same order of reactivity was observed, namely, Cl > Br > I. It is also to be noted that the highly branched *t*-butyl group markedly activated the halogens (see Table V).

TABLE V

REACTION TEMPERATURES FOR *t*-BUTYL HALIDES

t-Butyl halide	B. p., °C.	Temp., start, °C.		Highest temp. reached	Time of reaction, hours
Chloride	51	−36	−38	30	2
Bromide	73	−13		30	2
Iodide	98	+14		30	4

It seems from the foregoing evidence that here is a case in which the effective reactivity of the halogens attached to alkyl groups is actually the reverse of the commonly accepted "order of reactivity." There is no readily apparent reason for this anomalous series although there are several possible explanations that are receiving experimental attention and will be reported later.

It need not be considered surprising that the series for acylation is the opposite to alkylation. This situation is no more unusual than the general

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(14) Desreux, *Bull. sci. acad. roy. Belg.*, **20**, 457 (1934) [*C. A.*, **28**, 5805 (1934)]; Henne and Midgley, THIS JOURNAL, **58**, 884 (1936).

(15) Olivier, *Rec. trav. chim.*, **33**, 91 (1914).

(16) Olivier, *ibid.*, **37**, 205 (1918).

marked difference between acylation and alkylation in regard to mechanism, yields, conditions and velocity of reaction.[2]

Summary

1. The alkyl and acyl fluorides undergo the typical reactions with benzene in the presence of aluminum chloride.
2. Aluminum fluoride is inert in acylation and alkylation.
3. Zinc fluoride may be used to acylate and alkylate under selected conditions.
4. The order of reactivity for acyl halides in the Friedel–Crafts ketone synthesis is I > Br > Cl > F.
5. The order of reactivity of alkyl halides in the Friedel–Crafts alkylations is F > Cl > Br > I.
6. Alkylation may be primarily dependent on the formation of hydrogen halide.

NASHVILLE, TENN. RECEIVED APRIL 8, 1937

[CONTRIBUTION FROM THE ORGANIC LABORATORIES, SCHOOL OF PHARMACY, UNIVERSITY OF MARYLAND]

Diazonium Borofluorides, II. Their Use in the Preparation of Nitro Compounds[1]

BY EDGAR B. STARKEY

During the course of an investigation under way in our Pharmaceutical Chemical Laboratories, certain aromatic nitro compounds which could not be obtained by nitration were desired as intermediates. Sandmeyer[2] and Hantzsch and Blagden[3] have reported the substitution of the nitro group for the amino group through the diazonium reaction. However, no reference could be found to the replacement of an amino group by the nitro group, when the amino group was para or ortho to a nitro, carbonyl or similar group, except the preparation of para dinitrobenzene in 23.7% yield from *p*-nitroaniline by Meisenheimer and Patzig.[4] Since the diazonium borofluorides of Balz and Schiemann[5] have been used in our Laboratories for the preparation of mercury compounds,[1] and since they are stable, easily purified and obtained in good yield, they were chosen for the preparation of the desired nitro intermediates. These will be reported elsewhere.

The method described below and represented by the equation $RN_2BF_4 + NaNO_2 \longrightarrow RNO_2 + N_2 + NaBF_4$, proved satisfactory. Other available amines were used in similar experiments to determine the effect of substituents in the ring on the ease of replacement, and on the yield. The results are summarized in Table I.

While the method is recommended in no case where the compound can be prepared readily either directly or indirectly by nitration, it has been found valuable in all cases tried where the compound could not be obtained conveniently by nitration, *e. g.*, *p*- and *o*-dinitrobenzenes.

Experimental

Amines of technical quality were used and from these the diazonium borofluorides were prepared by the procedure already described.[1]

Replacement of the Diazonium Group by the Nitro Group.—One-eighth of a mole of the diazonium salt as a thin aqueous paste, was added in small portions to a well-stirred suspension of 20 g. of copper metal, precipitated powder, in a solution of 80 g. of sodium nitrite in 160 cc. of water, contained in a one-liter beaker. The reaction was carried out at room temperature. In those cases where a fair yield of the nitro compound was obtained, the reaction was rapid and accompanied by copious frothing. The froth was broken by adding a few cc. of ether to the reaction mixture from time to time. In a few cases it was necessary to warm the reaction mixture slightly, or to add more copper powder in order to complete the reaction (alkaline β-naphthol test), but in all such cases the yield was

TABLE I

Amino compound	Yield of diazonium compd., %	Yield of pure nitro compd., %	M. p. of nitro compd., °C.
Aniline	92	20	210.0 (B. p.)
o-Nitroaniline	80	33	116.5
m-Nitroaniline	99	43	90.0
p-Nitroaniline	98	64	173.0
o-Chloroaniline	96	32	244.0 (B. p.)
m-Chloroaniline	97	15	44.5
p-Toluidine	74	10	51.5
Ethyl *p*-aminobenzoate	94	50	57.0
p-Aminophenetole	46	..	59.0
p-Aminoazobenzene	92	..	125.5
p-Aminodiphenyl	90	..	112.0
α-Naphthylamine	83	..	58.5

(1) Additional papers in this series are in prospect. The paper by Dunker, Starkey and Jenkins, THIS JOURNAL, **58**, 2308 (1936), will be considered number 1.

(2) Sandmeyer, *Ber.*, **20**, 1494 (1887).

(3) Hantzsch and Blagden, *ibid.*, **33**, 2544 (1900).

(4) Meisenheimer and Patzig, *ibid.*, **39**, 2526 (1906).

(5) Balz and Schiemann, *ibid.*, **60**, 1186 (1927).