results are not. While the calculations correctly indicate that cyclooctatetraene will have alternating long and short bonds, II is predicted to be more stable than III, while the reverse is unquestionably true. The dianion, on the other hand, is definitely predicted to be planar and symmetrical, while the radical ion is predicted to be planar, but with bonds of alternating length.

For benzene the alternating bond length structure is predicted to be of lower energy than the symmetrical structure, but only by 2.7 kcal./mole. If configuration interaction of the singly excited configurations were to be included in the calculation, the alternating bond-form would be stabilized somewhat, but the symmetrical form, since the orbitals are already self-consistent, would not be. Hence, agreement with experiment would not be improved. In the present approximation, therefore, it would seem that the best that can be done is to say errors of perhaps 5–10 kcal./mole are to be expected, and in order to make a prediction as to whether or not a certain system has one configuration or another, the safest way is to compare with other known cases. Thus, the planar alternating bond structure of cyclooctatetraene is calculated to be more favorable than the symmetrical one by 44.0 kcal./mole, which shows the correct trend relative to benzene where the difference is only 2.7 kcal./mole.

There are various adjustments that might be made to improve the agreement between calculation and experiment, but any arbitrary adjustments would not lead to anything useful unless it was reasonably certain that such adjustments would carry over from one molecule to another. To raise the energy of the alternating bond structure of benzene above that calculated for the regular structure, one might try to have β fall off more slowly with distance. This would also lead to a lessening of the importance of resonance in the alternating bond structures of cyclooctatetraene and would tend to destabilize the planar form relative to the nonplanar, which would also be consistent with experiment. The inclusion of non-adjacent resonance integrals in III, although it causes some shifting about of energy levels, does not affect significantly the energy of the ground state. In any case, one can now see a possible reason for the fact previously considered anomalous,[24,31] namely that the long bonds in cyclooctatetraene are shorter than the long bond in butadiene (1.462 *vs.* 1.483 Å). The amount of resonance energy in cyclooctatetraene, while small compared to benzene, is still large compared to butadiene. Since very little compression energy is involved in going from 1.483 to 1.462 Å (0.4 kcal./bond) it is not too surprising that such a contraction occurs here, but not in butadiene. The fact that the C=C—C angle is 126.5° in cyclooctatetraene, compared to 121.5° in ethylene, can be attributed to a similar cause. The bond angle widens with increasing strain, but also increasing overlap across the long bond and increasing resonance. These two effects find a balance with the observed bond angle.

Since the method used seems in principle to be theoretically adequate, the discrepancy between theory and experiment is blamed on inaccurate empirically evaluated numerical quantities, and improvements in this direction will be considered in a subsequent paper.

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[31] B. Bak and L. Hansen-Nygaard, *J. Chem. Phys.*, **33**, 418 (1960).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, VANDERBILT UNIVERSITY]

The Swamping Catalyst Effect. IV. The Halogenation of Anilines[1]

B. R. SUTHERS,[2] P. H. RIGGINS,[2] AND D. E. PEARSON

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The halogenation of the aluminum chloride–hydrogen chloride complex of aniline and dimethylaniline gave monohalogenated products in the ratio 50–60% *meta* to 25–30% *para*. Without hydrogen halide, other than that from substitution, less *meta* substitution (*ca.* 25%) was obtained. The halogenation of the aluminum chloride–hydrogen chloride complexes of *p*-alkyl- and *p*-haloanilines gave good yields of 3-halo-4-alkyl- (or halo)-anilines and is the method of choice for preparation of these compounds.

The objective of this work was to investigate means of changing the orientation of the powerfully *o*- and *p*-directing amino group in anilines so that preparative amounts of *meta*-haloanilines could be obtained by direct substitution. The most successful previous effort in this regard was the work of Gorvin[3] in which he found that bromination of dimethylaniline in concentrated sulfuric acid containing silver sulfate gave a mixture of *ca.* 60% 3-bromo- and 20% 4-bromodimethylaniline

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[1] Paper III, D. E. Pearson, W. W. Hargrove, J. K. T. Chow, and B. R. Suthers, *J. Org. Chem.*, **26**, 789 (1961).

[2] Taken in part from Ph.D. theses, Vanderbilt University, 1961.

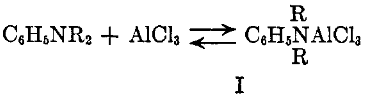
[3] J. H. Gorvin, *J. Chem. Soc.*, 1237 (1953).

separated by chemical means. He obtained 28% 3-chlorodimethylaniline isolated as a nitroso derivative, 46% 3,4-dibromo- from 4-bromodimethylaniline and 61% 3,4-dichloro- from 4-chlorodimethylaniline. At first, we thought it curious that the above work, together with two others,[3-5] were the only reports found on changing orientation in the halogenation of anilines or mono-substituted anilines.[6] But further study suggested a number of reasons for the paucity of reports. Aniline, converted to aniline sulfate in concentrated sulfuric acid, is very sluggish toward halogenation at room temperature.[5] At elevated temperatures it tends to form either tribromoaniline or sulfonated anilines. Second, the *meta*- and *para*-haloanilines obtained as products are difficult to separate, much more difficult than *m*- and *p*-nitroanilines. And last, the method so far exploited, concentrated sulfuric acid, halogen, and molecular quantities of silver sulfate, seems suitable only for small scale preparation (2–5 g.).[3] De La Mare and Ridd[4] summarize this status by saying that "change in over-all substitution-type by protonation of a powerfully electron-releasing group has been noticed much more seldom in halogenation than in nitration."

The essential problem is to bring to bear as much electron-withdrawal on the amino group of aniline as possible and to maintain this electron-withdrawal throughout the reaction. Protonation in sulfuric acid does serve to give the positive anilinium ion:

$$C_6H_5NR_2 + H_2SO_4 \rightleftarrows C_6H_5\overset{\oplus}{N}R_2H\overset{\ominus}{H}SO_4 \rightleftarrows C_6H_5\overset{\oplus}{N}R_2H + H\overset{\ominus}{S}O_4$$

but the incursion of *para*-substituted along with *meta*-substituted products suggests a partial dissociation to the free base or to an ion-pair which substitutes *para*.[7] Since the rate of substitution of the base or ion-pair is so much faster than the salt, only a small amount need be present for the formation of appreciable quantities of *p*-substituted products. We were convinced from our earlier work[1] that aluminum chloride, acting as a Lewis acid, would not only serve to create strong electron-withdrawal about the nitrogen atom, but the complex would have less tendency to dissociate, if at all:

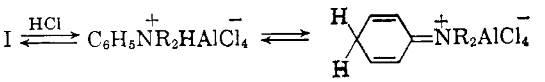


$$C_6H_5NR_2 + AlCl_3 \rightleftarrows C_6H_5\overset{R}{\underset{R}{N}}AlCl_3$$

I

All of the results in Table V of the Experimental were run under these conditions using aluminum chloride alone: the maximum *meta*-substitution obtained was 25% which probably originates from the reaction of generated hydrogen halide with complex I to form II. As a result of this rationalization it was discovered that a combination of aluminum chloride and hydrogen chloride was more effective in changing orientation than aluminum chloride itself.[8]

One equivalent of hydrogen chloride was absorbed by the complex I, and a change of color was noted. The course of the reaction may be as follows:



The yields of *meta*-substitution on halogenation of the complex II (III) were roughly 50% and of *para*-substitution 25%. The yields of *meta*-substitution in bromination of the dimethylaniline complex similar to II were 60% and of *para*-substitution 30%. These results possibly may be the best that can be obtained in the direct *meta*-substitution of aniline or dimethylaniline. The strongest possible Lewis or Brönsted acid has been

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(4) P. B. D. De La Mare and J. H. Ridd, *Aromatic Substitution*, Buttersworth Scientific Publications, 1959, p. 112. The bromination of *p*-dimethylaminoacetanilide in strong acid gave bromine substitution *ortho* to the acetamido grouping quoted from Reference 3.

(5) R. Hafner, *Ber.*, **22**, 2524, 2902 (1889). Aniline in concentrated sulfuric acid was attacked very slowly by chlorine or bromine to give very low yields of *p*-chloroaniline. *p*-Toluidine was chlorinated in the same medium to give a mixture of products from which 25% 3-chloro-4-toluidine was isolated. Under similar conditions using bromine a lower yield of 3-bromo-4-toluidine was isolated.

(6) Reports on change of orientation in nitration are more common. H. M. Fitch in *Org. Syntheses*, **Coll. Vol. III**, 658 (1955): Nitration of dimethylaniline in concentrated sulfuric acid gave 63% *m*-nitrodimethylaniline. H. A. Lubs, *The Chemistry of Synthetic Dyes and Pigments*, Reinhold Publishing Co., New York, 1955, p. 14: nitration of *N*-ethyl-*N*-acetyl-*p*-toluidide gave 88% substitution *ortho* to the methyl group but of *N*-acetyl-*p*-toluidide gave 68% substitution *ortho* to the acetamino group. H. E. Fierz-David and L. E. Blangey, *Fundamental Processes of Dye Chemistry*, Interscience Publishers, New York, 1949, p. 165: Nitration of *p*-toluidine in concentrated sulfuric acid gave 80% substitution *ortho* to methyl group. A. H. Blatt and N. Gross, *J. Am. Chem. Soc.*, **75**, 1245 (1953): nitration of *N*-acetyl-*p*-anisidide gave substitution *ortho* to the methoxyl group in sulfuric acid and *ortho* to the acetamino group in acetic acid.

(7) Nitration of diethylbenzylammonium sulfate in a 1*N* solution in concentrated sulfuric acid gave 44% *m*-nitro derivative and in a 0.5*N* solution gave 52% *m*-nitro derivative. The increase in *meta*-substitution in the more dilute solution suggests the more complete dissociation of an ion-pair, the more dissociated ion giving more *meta* substitution. B. Flürscheim and E. L. Holmes, *J. Chem. Soc.*, 1562 (1926).

(8) The effect is reminiscent of the reaction of aromatic hydrocarbons with aluminum chloride and hydrogen chloride. H. C. Brown and H. W. Pearsall, *J. Am. Chem. Soc.*, **74**, 191 (1952).

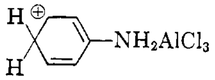
used,[9] and its complex with aniline (II or III) probably does not dissociate to the free base under conditions of the substitution because of its strong acidity. Thus, the *para*-substituted aniline, consisting of about 25% of the product, must be formed by attack on one of the complexes formed. Perhaps II dissociates in part to the complex I which gives rise to *para*-substitution because of its partially covalent nature. The structure of II (or III) is unknown at the present time, but it must have interesting features to give rise to a material which is colored and relatively low-melting, and which directs mostly *meta* but partly *para* in substitution reactions. If it is a single substance, the *para*-substitution in our opinion is extraordinary. Alternate suggestions for its structure are that it is a diprotonated salt or protonated complex such as  which is *meta*-directing itself[12] but dissociates to less positive complexes which give some *para*-substitution or that it is simply II which is *meta*-directing but gives rise to ion-pairs which are weaker *meta*-directors and are less selective toward the attacking agent. More study on these complexes is planned. Whatever the structure of the complex, the practical results were such that we have only partially accomplished the original objective of changing orientation in monohalogenation of aniline or dimethylaniline. However, one other important feature of the complex led to gratifying results in controlling orientation in substituted anilines. The complex seems to be of such a structure and in such an electronic state that a second substituent on the ring controlled the position of substitution. Table I illustrates this point, and the method of choice for making these compounds is *via* the aluminum chloride–hydrogen chloride complexes. Without complexing, all of the substitution would have been in the 2-position of the anilines. The conditions are such that no limit need be placed on the amount synthesized.

TABLE I

HALOGENATION OF SUBSTITUTED ANILINES COMPLEXED WITH ALUMINUM CHLORIDE AND HYDROGEN CHLORIDE

Reactants	Halogen	Products	Yield, %
p-Bromoaniline	Br_2	3,4-Dibromoaniline	77
p-Chloroaniline	Cl_2	3,4-Dichloroaniline	71
p-Toluidine	Br_2	3-Bromo-4-toluidine	45
p-Toluidine	Cl_2	3-Chloro-4-toluidine	71
p-Chloroaniline	Br_2	3-Bromo-4-chloroaniline	82
p-Bromoaniline	Cl_2	3-Chloro-4-bromoaniline	71
o-Chloroaniline	Br_2	2-Chloro-5-bromoaniline	73
3,4-Dibromodimethylaniline	Br_2	3,4,5-Tribromodimethylaniline	33

The results of Table I suggest that dihalogenation of aniline should lead directly to good yields of 3,4-dibromoaniline. It is not so. The 50% *m*-bromoaniline formed in the first step of the dibromination leads to a mixture of 2,5- and 3,4-dibromoanilines which are difficult to separate. However, the dibromination of dimethylaniline was successful; yields of 57% 3,4-dibromo-*N*,*N*-dimethylaniline were obtained. A steric effect probably prevented the formation of the 2,5-dibromo product which ordinarily is formed from the *meta*-bromodimethylaniline intermediate. To summarize the advances towards the original objective, we have been able partially but not completely to alter orientation in the monohalogenation of aniline and dimethylaniline. We have been able to alter orientation more successfully in *p*-alkyl or *p*-haloanilines to obtain good yields of 3-halo-4-alkyl- or haloanilines. All products could be separated by gas chromatography except the *meta*- and *para*-haloanilines. Their percentages were estimated by means of infrared analysis as described in the Experimental. Toward the end of the work, a substrate for gas chromatography was found that did separate *m*- and *p*-bromodimethylanilines. Although the substrate was satisfactory for this work and shows promise of surpassing most of the polar resins in separation of *meta*- and *para*-substituted aromatic compounds, it had the disadvantage of losing its activity over a period of days. Work is under way to improve the stability of this resin.

EXPERIMENTAL

Typical procedure for halogenation of anilines. In a three-necked, round-bottomed flask equipped with a stirrer of good torque, a dropping funnel, and a condenser (all entrances protected from moisture with calcium chloride tubes), aniline (37 g., 0.4 mole) was added dropwise but rapidly to stirred, anhydrous aluminum chloride (111 g., 0.83 mole, Baker and

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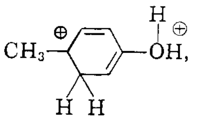
[9] Although many strong acid sequences have been proposed,[10] we suggest that the sequence: $HAlCl_4$[11] > $AlCl_3$ > H_2SO_4 should stand very high on the list if not at the top. The acid $HAlBr_4$, may be stronger than $HAlCl_4$, but we have not studied its complexes fully. $SO_3^{\oplus}H$ is a very powerful acid but tends to substitute so readily that it defeats the objectives of this paper.

[10] R. A. Coleman, M. S. Newman, and A. B. Garrett, *J. Am. Chem. Soc.*, **76**, 4534 (1954); H. C. Brown and R. R. Holmes, *J. Am. Chem. Soc.*, **78**, 2173 (1956); D. Bethell, V. Gold, and D. P. N. Satchell, *J. Chem. Soc.*, 1918 (1958). The latter propose that H_2ZnCl_4 is the strongest acid studied.

[11] The free acid is not known, but its salts are well characterized. H. C. Brown and H. W. Pearsall, *J. Am. Chem. Soc.*, **73**, 4681 (1951).

[12] The suggestion has been made that a double-charged cation of *p*-cresol, $CH_3C_6H_4OH_3^{++}$, possibly better described as



nitrates *meta* to the hydroxyl group. H. J. Lucas and Y. Liu, *J. Am. Chem. Soc.*, **55**, 1271 (1933).

Adamson, resublimed). Heat was evolved, and a green liquid complex formed. The dropping funnel was replaced with a tube to introduce dry hydrogen chloride under the surface of the complex. The weight of the hydrogen chloride absorbed was 15 g., calculated for 0.4 mole, 1 equivalent, 14.6 g. Bromine (64 g., 0.4 mole) was added dropwise from the reinserted dropping funnel over a period of approximately 2 hr. while the more muddy-colored complex was maintained at as low a temperature as possible without causing solidification—usually 60–80°. After the addition and observation that the bromine had been consumed, the mixture was allowed to cool either to room temperature or to the point where solidification began and poured onto 500 ml. of ice with vigorous stirring. The aqueous solution was then made alkaline with 120 g. of sodium hydroxide dissolved in 500 ml. of water. The amines were steam-distilled vigorously at this point.[13] Weight of steam-distilled amines was 60 g., 87% based on a monobrominated aniline. The crude product was subjected to analysis by infrared means or by gas chromatography when it was inseparable (in the case of the monobrominated aniline) and to isolation by fractional distillation or crystallization in all other cases.

Chlorination was carried out in a similar manner with provision for introducing chlorine.[1]

Identification by gas chromatography.[14] Five microliters of mixed bromoanilines was passed through a 3-ft. column of 20% silicon grease on Columnpak (60 mesh) at 160° and a flow-rate of 105 ml./min. The following compounds and their percentages are shown in Table II.

TABLE II

MONOBROMINATION OF ANILINE–ALUMINUM CHLORIDE–HYDROGEN CHLORIDE COMPLEX (II,III)

	%	Retention Volume, Ml.
Aniline	7	87
o-Bromoaniline	11	192
m- and *p*-Bromoaniline	74	270
2,4-Dibromoanilines	*ca.* 3	607
3,4-Dibromoanilines	*ca.* 3	987

The percentages of the monobrominated anilines and aniline were estimated by making up known mixtures and comparing areas under each curve. Breakdown of the *m*- and *p*-bromoanilines percentage is shown in the section on infrared analysis.

The mixed chloroanilines (5 λ) were analyzed under similar conditions with column at 156° and 54 ml./min. flow-rate, and the results shown in Table III.

TABLE III

MONOCHLORINATION OF II(III)

	%	Retention Volume, Ml.
Aniline	6	104
o-Chloroaniline	13	162
m- and *p*-Chloroaniline	75	246
2,5-Dichloroaniline	*ca.* 3	435
3,4-Dichloroaniline	*ca.* 3	738

Breakdown of the mixture of *m*- and *p*-chloroaniline percentage is given in the Infrared Section.

The *m*- and *p*-bromo-*N*,*N*-dimethylanilines, in contrast to the bromoanilines, were separated by gas chromatography. The 7-ft. column was filled with Celite impregnated with 15% by weight of a resin made from the alkylation of methyl benzoate with trimethylene dibromide under swamping conditions followed by saponification and acidification. The carboxylic resin was more efficient than any other substrate tested but unfortunately lost its efficiency in about 3 days at the temperature of separation. It is noteworthy that primary aromatic amines did not even emerge from this acid resin column. The column was held at 227° with a flow-rate of 32 ml. of helium per minute. The crude bromo-*N*,*N*-dimethylanilines were isolated in 80% yield by use of the general procedure. Analysis of the crude mixture was obtained by matching the Gaussian curves with those from known samples, and the results are shown in Table IV.

TABLE IV

MONOBROMINATION OF II(III), R = CH_3

Compound	Retention Vol., Ml.	%
N,*N*-Dimethylaniline	144	3
o-Bromodimethylaniline[a]	230	3
m-Bromodimethylaniline	487	59
p-Bromodimethylaniline	553	31
Unknown[a]	608	3

[a] Not matched with known samples. % is estimated by assuming area relationship to concentration being the same as for the other compounds.

Infrared analysis of the monohalogenated anilines. The absorption peaks utilized in the analysis were as follows:

820 cm.$^{-1}$	2 adjacent hydrogens	*p*-haloaniline
775 cm.$^{-1}$	3 adjacent hydrogens	*m*-haloaniline
725 cm.$^{-1}$	4 adjacent hydrogens	*o*-haloaniline

The extinction coefficient of each absorption curve was found to be approximately equal within percentage ranges pertinent to this study. The percentage of each monohalogenated aniline could then be calculated by obtaining the ratio of the area of each peak over the total area of the three peaks and multiplying by 100. The breakdown of the percentage of *m*- and *p*-haloaniline from gas chromatography are shown:

m-Bromoaniline	50 ± 5%	*p*-Bromoaniline	25 ± 5%
m-Chloroaniline	50 ± 5%	*p*-Chloroaniline	25 ± 5%

These percentages refer to the amount present in the original crude mixture.

Variation on the procedure for halogenation. Considerable work was done on the halogenation of aniline using aluminum chloride without hydrogen chloride. The yields of *meta*-substituted haloanilines shown in Table V were markedly less and the products were accompanied by considerably more tar.

The halogenation of aniline was also carried out without any catalyst at all under conditions closely matching those of the general procedure. The results are shown in Table VI.

Technique for isolation of substantial quantities of dihaloanilines. For relatively large scale runs, the dihaloanilines were isolated from tars by steam distillation when necessary. The crude solid was then washed with four portions (50 ml. each) of cold pentane. The pentane extract in all cases was an oil which resisted further purification. The solid remaining was extracted with consecutive 50-ml. portions of boiling hexane until it was all dissolved. Each portion was allowed to crystallize, and those crystals of identical m.p. were combined. Treatment with Norit was carried out when necessary. The washing with cold pentane was essential to the success of the isolations.

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(13) Benzene or ether extraction or filtration (if product was a solid) were alternate methods of isolation.

(14) We are indebted to Dr. D. C. Bardwell, Vanderbilt University, and to Mr. Dwight Kinzer for advice and technical help in building a series of gas chromatography columns using thermal conductivity detectors.

TABLE V

PER CENT HALOANILINE FROM HALOGENATION OF ANILINE–ALUMINUM CHLORIDE COMPLEX WITHOUT HYDROGEN CHLORIDE[a]

	Ratio of Aluminum Chloride–Aniline–Bromine			
Products	2-1-0.5	1-1-1	2-1-1	2-1-2
Aniline	52	4	7 (11)[b]	1 (2)
o-Bromoaniline	5	13	12 (13)	1 (3)
m-Bromoaniline	—	22	22 (25)	4 (2)
p-Bromoaniline	41	57	52 (46)	4 (2)
2,5- and 2,4-Dibromoaniline				30 (30)
3,4-Dibromoaniline	2[c]	4[c]	7 (5)[c]	50 (50)
2,4,6-Tribromoaniline				10 (10)

[a] Without added hydrogen chloride but it is generated in the substitution reaction. [b] Figures in parentheses relate to the corresponding chloro compounds. [c] Yields for combined di- and tribrominated products.

TABLE VI

HALOGENATION OF ANILINE IN THE ABSENCE OF ALUMINUM CHLORIDE

	Ratio of Aniline to Bromine		
Products	1-0.5	1-1	1-2
Aniline	65	52	10
o-Bromoaniline	5	1	1
p-Bromoaniline	20	15	12
2,4-Dibromoaniline	5	12	45
2,4,6-Tribromoaniline	5	20	32

3,4-Dibromoaniline. The complex between the reactants, p-bromoaniline and aluminum chloride–hydrogen chloride, was blue-purple in color. The yield from 0.2 mole using the crystallization technique just described was 77%, m.p. 80–81°; N-acetyl m.p. 128–130°, reported[15] m.p. 128°; picrate m.p. 149–150°, reported[16] m.p. 149°.

3,4-Dichloroaniline. The complex was blue-green in color. The chlorine entrained by the hydrogen chloride was trapped in Dry Ice and recycled as described previously.[1] The yield from 0.4 mole of p-chloroaniline was 71%, m.p. 71–72°; N-acetyl derivative m.p. 122–123°, reported[15] m.p. 121°; N-benzoyl m.p. 146–147°.

3-Bromo-4-toluidine. It was obtained by fractional distillation in 45% yield, b.p. 72–73° at 0.1 mm., n^{25}_{D} 1.6110, m.p. and reported[17] m.p. 25–26°, N-acetyl derivative m.p. and reported[15] m.p. 113–114°, N-benzoyl derivative m.p. 132–133° and reported[18] m.p. 132°, picrate m.p. 197–198°. The residue from the distillation gave 6% 3,5-dibromo-4-toluidine, m.p. and reported[19] m.p. 90–91°. Attempts to dibrominate p-toluidine gave a mixture of products.

3-Chloro-4-toluidine. It was obtained in 71% yield, b.p. 62–63° at 0.5 mm., n^{25}_{D} 1.5828, m.p. 21–22°, reported[15,20] m.p. 25° and 18°, N-acetyl derivative m.p. and reported[21] m.p. 104–104.5° from pentane and m.p. 85–86° from ethanol, N-benzoyl derivative m.p. 119–120°, reported[15] m.p. 122°. A small amount of 3,5-dichloro-4-toluidine, m.p. 57–59°, reported[22] m.p. 57° was isolated from the residue.

3-Bromo-4-chloroaniline. From 0.1 mole of p-chloroaniline, the bromination procedure gave the titled compound in 82% yield, m.p. 81–82°, reported[21] m.p. 82°, N-acetyl derivative m.p. 127–128°, reported[21,23] m.p. 127–128° and 130°, picrate m.p. 148.5–149.5°.

3-Chloro-4-bromoaniline. From 0.1 mole of p-bromoaniline, the chlorination procedure gave the titled compound in 71% yield, m.p. 66–67°, reported[23,16] m.p. 67–68°, N-acetyl derivative m.p. and reported[16] m.p. 124–125°, hydrochloride m.p. 228–229°, reported[21] m.p. 227°, picrate m.p. 140.5–142°, reported[16] m.p. 141°.

2-Chloro-5-bromoaniline. From 0.2 mole of o-chloroaniline, the bromination procedure gave the titled compound in 73% yield, m.p. 48.5–49.5°, reported[23] m.p. 45°; N-acetyl derivative m.p. 143.5–145°, reported m.p. 141°.

3,4-Dibromo-N,N-dimethylaniline. From 0.24 mole of dimethylaniline, the yield of titled compound was 57%, m.p. 66.5–67.5°; mixed m.p. with an authentic sample made by the method of Gorvin[3] from p-bromodimethylaniline was the same. The green complex of dimethylaniline–aluminum chloride changed to a yellow-tan color at about 90°.

3,4,5-Tribromodimethylaniline. From 0.09 mole of 3,4-dibromodimethylaniline, the bromination procedure gave the titled compound in 33% yield, m.p. 138–140°.

Anal. Calcd. for $C_8H_8Br_3N$: C, 26.84; H, 2.26; N, 3.91; Br, 66.98. Found: C, 26.83; H, 2.38; N, 3.86; Br, 67.14.

The mother liquors from hexane recrystallization yielded an oil (5.3 g.), b.p. 123° at 1 mm., which was not identified further. Tribromination of dimethylaniline itself gave only a 14% yield of the titled compound. The structure of the titled compound, relative to its isomers, is based on the high melting point and no indication of steric inhibition of resonance in the absorption spectrum.

Attempted monobromination of aniline in sulfuric acid. Aniline (0.1 mole) was dissolved in 60 ml. of concentrated sulfuric acid. Bromine (0.2 mole) was added to the stirred solution. The bromine did not seem to react over a period of three days whereupon the temperature was raised slowly to 130°. After 24 hr. the bromine had been consumed. The mixture was cooled, poured onto cracked ice, and neutralized with aqueous sodium hydroxide (1.5 mole). After the precipitate was filtered, washed, dried, and recrystallized from ethanol, it was identified as 2,4,6-tribromoaniline, 17 g., 81% based on bromine, m.p. and mixed m.p. 122°.

Acknowledgment. We are indebted to the National Science Foundation for support of part of this program of research.

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