increased entropy of desolvation corresponds to greater freedom for solvent molecules, which in turn means decreased interaction energy or increased enthalpy, thus qualitatively accounting for the compensation observed between the external parameters and demonstrated by Figure 4. Those substituents which tend to localize or accentuate the positive charge should give negative values of $\delta\Delta S^*_B$ and $\delta\Delta H^*_{ext}$. With the exception of *m*-methyl-N,N-dimethylaniline and the *ortho*-substituted compounds, all the results follow these predictions.

The significant divergence of the *o*-fluoro and -chloro compounds from the line in Figure 4 may be accounted for in terms of partial steric inhibition of resonance, so that in these circumstances the assumption that $\delta\Delta S^*_{int} = 0$ would be untrue, and the measured $\delta\Delta S^*_B$ represents the sum of activation structural changes, both internal and external to the molecule.

Amination of Haloaromatics with Trichloramine–Aluminum Chloride. σ Substitution and Nucleophilic σ Substitution[1,2]

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Abstract: Amination of halobenzenes (fluoro, chloro, and bromo) and halotoluenes (*o*-, *m*-, and *p*-fluoro, *o*-, *m*-, and *p*-chloro, and *m*-bromo) with trichloramine under Friedel–Crafts conditions was found to proceed by two main competing processes in yields of 20–41%. For example, the system, trichloramine–aluminum chloride–fluorobenzene, gave predominantly *m*-fluoroaniline and *p*-chloroaniline. We propose that the former is produced by a σ-substitution route while the latter is formed by a pathway involving nucleophilic displacement of halide in an intermediate chlorarenonium ion by a nitrogen-containing species (nucleophilic σ substitution). Analogous products were obtained from the other haloaromatics. The ratio of nucleophilic σ substitution/σ substitution was found to vary depending upon the nature of the aromatic substrate, with fluorobenzene and *m*-fluorotoluene providing the highest values. The pathway involving halide displacement represents a new method of aromatic substitution. In certain cases minor amounts of basic materials were isolated, arising from side reactions such as rearrangement and disproportionation. Several other reaction variables were also investigated: time, temperature, and additives. By means of a competitive technique the relative rate of amination, $k_{C_6H_5Cl}/k_{C_6H_6}$, was found to be 0.26–0.44.

Recent reports from this laboratory revealed that direct amination of alkylbenzenes with N-halamines in the presence of a Lewis acid catalyst represents a new method of aromatic substitution (σ substitution) resulting in unusual orientation.[4–6] For example, the predominant basic product from toluene–trichloramine–aluminum chloride consisted of *m*-toluidine. Biphenyl and naphthalene were also investigated in this system.[6] Relative rate studies provided evidence for the crucial involvement of an intermediate arenonium ion.[7] The purpose of the present study was to investigate the behavior of halogen-containing aromatic compounds, specifically the halobenzenes and halotoluenes, toward trichloramine–aluminum chloride.

Results and Discussion

Amination of the haloaromatics was generally carried out by addition of a solution of trichloramine to a heterogeneous mixture of catalyst and aromatic component. In earlier studies with toluene, optimum yields of *m*-toluidine were observed at low temperatures and short reaction times.[4,5,7] However, our investigations with bromobenzene revealed a marked variation in yield with time (Table I), *i.e.*, use of longer reaction periods resulted in greatly improved yields. Temperature was found to have a similar, profound influence (Table II). An increase from 5 to 25° tripled the amount of basic product formed from chlorobenzene (Table II). A further beneficial effect was noted when the reaction was carried out at 50°. At 25°, extending the reaction time beyond 2 hr evoked no change. A temperature of 25° and a reaction period of 2 hr were chosen for the standardized procedure. Higher temperatures were generally avoided due to the volatility, toxicity, and explosive nature of the halamine, and in

Table I. Yield *vs.* Time in Amination of Bromobenzene[a,b]

	Basic product, % yield			
Time, hr	Aniline	Chloroanilines	Bromoanilines[c]	Total
1.5	0.3	0.8	5.8	6.9
2	0.2	2.4[d]	12.3	14.9[e]
3	0.4	1.8	18.2	20.4

[a] *o*-Dichlorobenzene solvent, 5 ± 5°. [b] Analyzed on column A, 180°. [c] Typical isomer distribution, *o*/*m*/*p*/ ≃ 5/90/5. [d] *o*/*m*/*p*/ ≃ 30/0/70. [e] About 6% of the product was a higher boiling amine whose infrared spectrum indicated a 1,2,4-trisubstitution pattern.

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(1) Paper VI: Chemistry of N-Halamines.

(2) For preliminary reports, see P. Kovacic, J. J. Hiller, Jr., J. F. Gormish, and J. A. Levisky, *Chem. Commun.*, No. 22, 580 (1965); P. Kovacic, R. M. Lange, J. L. Foote, C. T. Goralski, J. J. Hiller, Jr., and J. A. Levisky, *J. Am. Chem. Soc.*, **86**, 1650 (1964).

(3) National Defense Education Act Fellow, 1964–1966.

(4) P. Kovacic, C. T. Goralski, J. J. Hiller, Jr., J. A. Levisky, and R. M. Lange, *J. Am. Chem. Soc.*, **87**, 1262 (1965).

(5) P. Kovacic, J. A. Levisky, and C. T. Goralski, *ibid.*, **88**, 100 (1966).

(6) P. Kovacic and A. K. Harrison, unpublished work.

(7) P. Kovacic and J. A. Levisky, *J. Am. Chem. Soc.*, **88**, 1000 (1966).

Table II. Yield *vs.* Temperature, Solvent, and Time in Amination of Chlorobenzene[a–c]

Temp, °C	Basic product, % yield
5	6.2[d,e]
25	20.3[e]
50	29.6[e]
25[f]	33.3[g]
25[h]	32.7[g]

[a] *o*-Dichlorobenzene solvent, 2 hr. [b] The *ortho* isomer was determined by glpc and *para* was estimated by infrared analysis. [c] Column A, 180°, or column B, 150°. [d] Triple size run: chlorobenzene (3 moles total), and trichloramine (0.3 mole) in chlorobenzene. [e] Average isomer distribution: *o*/*m*/*p* ≅ 3/91/6. [f] 1,2-Dichloroethane solvent, 2 hr. [g] *o*/*m*/*p* = 2/93/5. [h] 1,2-Dichloroethane solvent, 3 hr.

order to minimize side reactions, such as rearrangement and disproportionation. The necessity for large amounts of aluminum chloride was demonstrated by the striking decrease in yield from the fluorobenzene reaction when the molar ratio of catalyst to trichloramine was reduced to 1 (2% yield) from the usual ratio of 2 (34% yield) (Table III). In general, 1,2-dichloroethane and *o*-dichlorobenzene as solvent gave similar results, except for chlorobenzene in which case the former was preferred (Table III).

Table III. Amination of Halobenzenes[a]

X in C_6H_5X	Substituted aniline product, % yield *p*-Cl	 *o*-Cl	 *m*-X[b]
F[c,d]	13.5	1.4	19.4
F[d,e]	12.8	1.5	21.9
Cl[c,f]	0.1[g]	0.7	32.5
Cl[e,f]	0.7[g]	1.0	18.6
Br[c,f]	<0.1	0.4	32.7[h]
Br[e,f]	0.3	1.1	30.4[i,j,k]
I[e,f]	. . .	. . .	<1
F[c,d,l]	14.1	0.3	9.0
F[c,d,m]	16.2	1.0	8.3
F[c,n]		2% total yield	

[a] 25 ± 5°, 2 hr. [b] >99% isomerically pure unless otherwise indicated. [c] 1,2-Dichloroethane solvent. [d] Column A, 180°, and column C, 150°. [e] *o*-Dichlorobenzene solvent. [f] Column A, 180°. [g] Estimated from the infrared spectrum since the *para* and *meta* isomers could not be separated by glpc. [h] Plus aniline, 1.5% yield. [i] Plus aniline, 1.2% yield. [j] *p*-Dibromobenzene was detected (glpc retention time and infrared spectrum) in the neutral product. [k] *o*/*m*/*p* = 1.6/>96/<2.4. [l] LiCl added, $NCl_3/AlCl_3/LiCl$ = 1/2/1. [m] LiCl added, $NCl_3/AlCl_3/LiCl$ = 1/2/2. [n] $AlCl_3/NCl_3$ = 1.

In contrast to the monoalkylbenzenes which usually afforded a single basic product, the haloaromatics generally produced a mixture. The results for amination of the halobenzenes are shown in Table III. Fluorobenzene gave *m*-fluoroaniline (19%) and chloroanilines (15%) possessing *ortho–para* orientation. In the case of chlorobenzene we obtained a mixture of chloroanilines (33%) containing mainly the *meta* isomer. Bromobenzene yielded predominantly *m*-bromoaniline (33%) with traces of the other isomers, plus small amounts of aniline and *o*- and *p*-chloroanilines. Iodobenzene gave rise to a negligible amount of basic product which was not characterized.

Amination of the *o*-halotoluenes (Table IV) resulted in substitution at the four open positions (26–31%). In addition, with *o*-fluorotoluene a major reaction product was 4-chloro-2-methylaniline (15%). The basic material (41%) from *m*-fluorotoluene (Table V) consisted primarily of chloro-*m*-toluidines along with 3-fluoro-5-methylaniline. Similarly with *m*-chlorotoluene, chloro-*m*-toluidines and 3-chloro-5-methylaniline were obtained in a combined yield of 26%. The amination of *m*-bromotoluene provided 3-bromo-5-methylaniline (14%) accompanied by smaller quantities of chlorotoluidines, *m*-toluidine, 2-bromo-5-methylaniline, and 5-bromo-2-methylaniline. In the case of the *p*-halotoluenes (Table VI) (24–30% yield of basic product) substitution at the two open sites predominated over formation of *p*-toluidine and 2-chloro-4-methylaniline. Furthermore, *p*-fluorotoluene gave 3-chloro-4-methylaniline.

Table IV. Amination of *o*-Halotoluenes[a–c]

X in *o*-CH_3C_6-H_4X	Substituted aniline product, % yield 2-X-3-CH_3	 3-X-2-CH_3	 3-X-4-CH_3	 4-X-3-CH_3
F	0.6[d]	8.6	16.1	0.3[d,e]
Cl	3.4	12.4	12.2	3.3[f]

[a] 1,2-Dichloroethane solvent, 0 ± 5°. [b] Identification was based on comparison with authentic materials, except as noted. [c] Column E, 140°. [d] Identification was based on the infrared substitution pattern and relative order of retention times by analogy with the corresponding products from *o*-chlorotoluene. [e] Plus 4-chloro-2-methylaniline, 14.8% yield. [f] No 4-chloro-2-methylaniline was detected.

Table V. Amination of *m*-Halotoluenes[a]

X in *m*-CH_3-C_6H_4X,	Substituted aniline product, % yield 3-X-5-CH_3	 4-Cl-3-CH_3	 2-Cl-5-CH_3	 2-Cl-3-CH_3
F[b,c]	5.4[d]	34.4	0.6	0.6
Cl[e,f]	17.2	8.1	0.6	0.5
Br[b,g]	13.8	2.6	0.3	0.2[h]

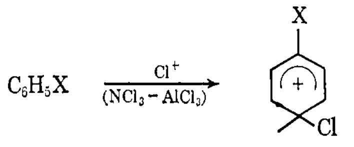
[a] In 1,2-dichloroethane, 0°. [b] Yields were determined by glpc (*o*-chloroaniline internal standard). [c] Column C, 160°, and column D, 150°. [d] *Anal.* Calcd for C_7H_8NF: C, 67.18; H, 6.44; N, 11.19; F, 15.18. Found: C, 67.25; H, 6.44; N, 11.33; F, 15.32. [e] Yields were determined by glpc (*m*-toluidine internal standard). [f] Column C, 140°. [g] Column F, 150; column G, 180°. [h] Plus *m*-toluidine, 1.6%, 2-bromo-5-methylaniline, 1.9%, and 5-bromo-2-methylaniline, 0.9%.

Table VI. Amination of *p*-Halotoluenes[a]

X in *p*-CH_3-C_6H_4X,	Substituted aniline product, yield % 4-CH_3	 2-X-5-CH_3	 5-X-2-CH_3	 2-Cl-4-CH_3
F[b]	2.9	3.6	13.8	3.5[c,d]
Cl[e–g]	2.2	6.8	14.5	0.8[h]

[a] 1,2-Dichloroethane, 0 ± 5°. [b] Column F, 150°. [c] Plus 3-chloro-4-methylaniline, 7% yield. [d] 5.8% of the volatile basic product was unidentified; distillation residue, 32% of the crude product, was found to possess a molecular weight of 802 (vapor pressure osmometer, benzene solution), and the empirical formula $C_{21}H_{16-17}NX_2$ from elemental analyses. *Anal.* Found: C, 76.37; H, 5.86; N, 4.17; Cl, 4.05; F, 7.89. [e] Either at 0 or 25°. [f] Column D, 150°, and column E, 140°. [g] The only neutral products detected were 2,4- and 3,4-dichlorotoluenes in the ratio 70/30. [h] Distillation residue comprised 20% of the crude basic product.

With product information in hand, we are now in a position to discuss reaction pathways in terms of a simple mechanistic picture. Formation of the *meta*-substituted products from the monohalobenzenes is expected by analogy with the previous studies involving alkylbenzenes.[4,5] The route leading to this unusual orientation has been discussed previously,[4,7] and is outlined in eq 1 and 2. Relative rate studies with aromatic hydrocarbons provided evidence for involvement of an intermediate σ complex.[7] Nucleophilic attack by a nitrogen-containing species followed by rearomatization through loss of hydrogen chloride completes the reaction sequence. This unique transformation has been designated σ substitution.[4] Since the actual nucleophile which participates is at present unknown,[5] amide ion is used for the sake of simplicity (X = halogen).



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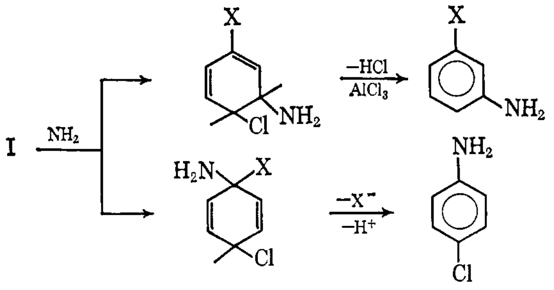

(2)

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At this point we wish to interject some of our thoughts concerning the significance of the demonstrated need for large amounts of catalyst. As mentioned previously,[4] this requirement may result from complexing of the aluminum chloride with trichloramine and aniline-type product. Alternatively, the aromatic amine may be in the form $ArN(AlCl_2)_2$ at the end of the reaction. By analogy with the recent discussion[5] on possible modes of interaction between aluminum chloride and halamines, the indicated transformation is set forth. Of course a prerequisite is the presence

$$ArNCl_2 + 2AlCl_3 + 2ArH \longrightarrow ArN(AlCl_2)_2 + 2ArCl + 2HCl \quad (4)$$

of the aminated product in the halamine form during the reaction course. Further evidence is available which indicates that the product generated in amination does not possess the NH_2 group. Only a little basic material was recovered when *p*-toluidine was treated with trichloramine–aluminum chloride.

The existence of *o*- and *p*-chloroanilines among the products from the halobenzenes can be accommodated mechanistically by use of the same intermediate chlorarenonium ion. According to this route (eq 3), nucleophilic attack occurs at the carbon bearing the halogen substituent with resulting displacement of halide ion and loss of a proton. Alternatively, elimination of hydrogen halide might be a concerted process. In either case, since the net result is nucleophilic displacement of halide, an appropriate designation for this pathway would be nucleophilic σ substitution. It is significant that when such a replacement occurs, a chlorine atom is introduced *ortho* or *para* to the amine functionality. This novel reaction represents a new method of aromatic substitution in the benzenoid series. The classical analog entails displacement by a nucleophile of an atom or group, *e.g.*, halogen or alkoxyl, on a nucleus containing an appropriately situated substituent such as NO_2 or SO_2R.[8] In our case a similar over-all transformation occurs involving the benzene nucleus which, however, bears no activating group in the usual sense. In fact, the reaction proceeds with aromatic compounds considered to be deactivated in the context of the familiar nucleophilic substitution procedure. In addition to the examples to be presented from the halotoluene series, one can visualize potentially wide generality for nucleophilic σ substitution on the basis of variation in the electrophile, nucleophile, and leaving group. Further evidence in support of our mechanism is provided by the decreasing ease of halogen replacement in the indicated order: F/Cl/Br = 40/15/7 (Table VII). This same arrangement (F $\gg$ Cl $\geq$ Br) was observed in substitution of halogen by methoxide ion in the 1-halo-2,4-dinitrobenzene series.[9]

Table VII. Variation of Nucleophilic σ Substitution/σ Substitution with Substrate[a]

Substrate	Nucleophilic σ substitution/ σ substitution
C_6H_5F	40/60
C_6H_5Cl	15/85
C_6H_5Br	7/93
m-$CH_3C_6H_4F$	87/13
m-$CH_3C_6H_4Cl$	35/65
m-$CH_3C_6H_4Br$	18/82
o-$CH_3C_6H_4F$	36/64
o-$CH_3C_6H_4Cl$	1/99
p-$CH_3C_6H_4F$	44/56
p-$CH_3C_6H_4Cl$	12/88
C_6H_5F[b]	68/32
C_6H_5F[c]	40/60
C_6H_5Cl[c]	8/92
C_6H_5Br[c]	4/96
C_6H_5F[d]	43/57
C_6H_5Cl[d]	2/98
C_6H_5Br[d]	1.5/98.5

[a] 1,2-Dichloroethane solvent, 0°. [b] LiCl added, $LiCl/NCl_3 = 2$. [c] *o*-Dichlorobenzene solvent, 25°. [d] 1,2-Dichloroethane solvent, 25°.

Similarly, the bulk of the basic products from the halotoluene reactions can be explained in terms of these same competing processes. For example, with *m*-fluorotoluene the 3-fluoro-5-methylaniline is apparently produced by σ substitution, and the chloro-*m*-toluidines by nucleophilic σ substitution. The *meta* isomers elicited a higher ratio of nucleophilic σ substitution/σ substitution than in the case of the halobenzenes (Table VII). With both types of substrates, however, the preferred site for electrophilic attack is

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[8] J. F. Bunnett and R. E. Zahler, *Chem. Rev.*, **49**, 273 (1951); J. F. Bunnett, *Quart. Rev.* (London), **12**, 1 (1958).

[9] J. F. Bunnett and W. D. Merritt, Jr., *J. Am. Chem, Soc.*, **79**, 5967 (1957); A. L. Beckwith, J. Miller, and G. D. Leahy, *J. Chem. Soc.*, 3552 (1952); C. W. L. Bevan and G. C. Bye, *ibid.*, 3091 (1954).

ortho or *para* to the halogen atom.[10] Obviously, presence of the *meta* substituent decreases the statistical probability of σ substitution. The influence of the inductive and resonance effects of the alkyl moiety on the competing reactions is not well understood.

With *o*-halotoluenes the ratio of products derived from substituent displacement to those from σ substitution is smaller than in the case of the halobenzenes or the *m*-halotoluenes. For example, the ratio for *o*-fluorotoluene is 36/64 compared to 87/13 for *m*-fluorotoluene. Of the base arising from *o*-fluorotoluene more than 97% is derived from initial electrophilic attack *ortho* or *para* to the halo substituent, whereas the corresponding figure for the *o*-chloro isomer is 79%. There is ample evidence indicating that fluorine is better able than chlorine to participate in delocalization of a positive charge. It is pertinent that in the nitration of *o*-chlorotoluene only 62% of the reaction occurs *ortho* or *para* to the halogen.[10b]

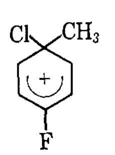
A number of underlying factors might be expected to play important roles in determining the composition of the amine product, *e.g.*, relative rate of proton loss and relative rate of nucleophilic attack in the isomeric chlorarenonium ions. Other effects are no doubt operating. Since the problem is exceedingly complex, a more detailed discussion would be inappropriate at this time.

A similar situation exists with the *p*-halotoluenes (Table VI). However, in this case some doubt is cast on the validity of the observed orientation data inasmuch as tar constituted a significant fraction of the basic material. Analysis of the volatile product from amination of *p*-chlorotoluene revealed that 69% was formed through initial interaction *ortho* to the halogen, although this is not the preferred site for electrophilic attack.[10b] From examination of the neutral products, 2,4- and 3,4-dichlorotoluene were found to be the principal components, in the ratio 70:30. For comparison, the literature reveals a ratio of 58:42 in the nitration reaction.[10b] It therefore appears that the predominant product from amination is not derived from the preferred σ complex in the *o*- and *p*-halotoluene reactions.

Examination of other reaction variables proved interesting (Table VII). Variations of solvent and temperature caused some change in the ratio nucleophilic σ substitution/σ substitution. On replacing *o*-dichlorobenzene with 1,2-dichloroethane, or raising the temperature from 0 to 25°, the ratio was reduced when chloro- or bromobenzene was used as substrate, but increased slightly with fluorobenzene. Introduction of lithium chloride into the fluorobenzene system produced a striking change in product distribution. The ratio of nucleophilic σ substitution to σ substitution increased from 42/58 to 68/32. The salt may produce a change in polarity, solvation, or the nature of the catalyst (compare $LiAlCl_4$ with $NaAlCl_4$ and $LiAlH_4$).[11] Admittedly the underlying influences are little understood.

In a few instances the principal processes were accompanied by competing side reactions, notably isomerization and disproportionation. For example, bromobenzene produced small amounts of aniline. The result is quite expected since this halobenzene is known to disproportionate more readily than fluoro- or chlorobenzene,[12] forming benzene and dibromobenzene. The aniline can thus be easily accounted for by amination of the generated benzene. Similarly, 2-bromo-5-methylaniline and 5-bromo-2-methylaniline (from *m*-bromotoluene) apparently arise by amination of *p*-bromotoluene formed *via* rearrangement of the *meta* isomer.[13] However, once generated, the amines are stable toward isomerization. The various bromoanilines were recovered unchanged on exposure to simulated reaction conditions.

The formation of *p*-toluidine from *p*-fluorotoluene is somewhat more difficult to visualize. One possibility entails intervention of the intermediate II. Nucleophilic displacement of fluoride followed by loss of Cl^+ would then complete the sequence. The same arenonium ion also can account for 3-chloro-4-methylaniline. Following nucleophilic displacement of fluoride, a 1,2 shift involving the chlorine, and then proton loss, would lead to the indicated structure. A similar type of σ complex has been proposed as a prerequisite for intramolecular isomerization of *p*-fluorotoluene.[13]



II

The origin of the polymeric material in the *p*-halotoluene reactions is puzzling. The basic tar from amination of the fluoro isomer contained carbon, hydrogen, nitrogen, chlorine, and fluorine with a C/N atomic ratio of 21 which corresponds to three aromatic units per amine functionality. The average molecular weight of 802 indicates approximately seven aromatic nuclei per molecule.

A brief investigation was carried out with bromodurene. We surmised that nucleophilic σ substitution might be the sole pathway since there was no position available for σ amination. However, a gross mixture of products was obtained with none of the desired 1-amino-4-chlorodurene in evidence. Apparently isomerization and disproportionation occur to such an extent that nucleophilic σ substitution cannot compete favorably.

Relative rate investigations were carried out with chlorobenzene since this aromatic substrate participated mainly in the σ amination pathway. The experimental values for $k_{C_6H_5Cl}/k_{C_6H_6}$ (0.44 in 1,2-dichloroethane and 0.26 in *o*-dichlorobenzene) (Table VIII) are to be compared with corresponding literature figures for halogenation in Table IX. The data for amination indicate an electrophile possessing appreciable activity. In a recent publication the significance of the relative rates in terms of the σ-substitution mechanism has been discussed in detail.[7] Variation in relative rate with solvent is analogous to the situation observed with benzene–toluene in competitive amination studies.[7]

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(10) P. B. D. de la Mare and J. H. Ridd, "Aromatic Substitution. Nitration and Halogenation," Academic Press Inc., New York, N. Y., 1959: (a) p 85; (b) p 90.

(11) G. A. Olah, "Friedel-Crafts and Related Reactions," Vol. I, G. A. Olah, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, p 248.

(12) G. A. Olah, W. S. Tolgyesi, and R. E. A. Dear, *J. Org. Chem.*, 27, 3441 (1962).

(13) G. A. Olah and M. W. Meyer, *ibid.*, 27, 3464 (1962).

Table VIII. Relative Rates of Amination[a,b]

C_6H_5Cl/C_6H_6, M	$k_{C_6H_5Cl}/k_{C_6H_6}$ Obsd	Calcd
2/1[c]	0.88	0.44
5/1[c]	2.20	0.44
2/1[d]	0.52	0.26

[a] $NCl_3/AlBr_3/ArH$/solvent = 1/3/*ca.* 50/*ca.* 50; 0°; 15 min. [b] Column D, 130°. [c] 1,2-Dichloroethane solvent. [d] *o*-Dichlorobenzene solvent.

Table IX. $k_{C_6H_5Cl}/k_{C_6H_6}$

Reaction	Conditions	$k_{C_6H_5Cl}/k_{C_6H_6}$	Ref
Bromination	Br_2, $FeCl_3$, CH_3NO_2	0.12–0.35	*a*
Chlorination	Cl_2, $FeCl_3$, CH_3NO_2	0.17	*b*
Chlorination	Cl_2, $AlCl_3$, CH_3NO_2	0.19	*b*
Chlorination	Cl_2, HOAc	0.10	*c*

[a] G. A. Olah, S. J. Kuhn, S. H. Flood, and B. A. Hardie, *J. Am. Chem. Soc.*, **86**, 1044 (1964). [b] G. A. Olah, S. J. Kuhn, and B. A. Hardie, *ibid.*, **86**, 1055 (1964). [c] L. M. Stock and F. W. Baker, *ibid.*, **84**, 1661 (1962).

The literature is scant of reports which bear analogy to our nucleophilic σ substitution reaction. Oae and Kiritani[14] found that the hydroxyl group of phenol can be replaced by mercaptan under acidic conditions to produce the corresponding sulfide. The authors invoked nucleophilic attack on the protonated σ complex derived from phenol. Additional examples may be cited which are somewhat further removed in similarity. Conversion of *o*- and *p*-alkoxyphenols to the corresponding quinones by ceric sulfate or sodium periodate apparently involves nucleophilic attack by water on an intermediate carbonium ion.[15,16] Finally, 1,2-dichlorotetraphenylethane is transformed to *p*-alkoxytetraphenylethylene by solvolysis in the presence of alkoxide ion.[17]

Experimental Section[18]

Materials. 1,2-Dichloroethane, *o*-dichlorobenzene (containing about 10% of the *para* isomer), benzene, and the halobenzenes were fractionally distilled from calcium hydride. The other reagents were high-purity commercial materials which were used as obtained. Gas chromatographic and infrared examination indicated a purity for the organic reagents of >99% generally. Unless otherwise specified, authentic samples were commercial materials, purified when necessary by glpc before use.

Analytical Procedures. Infrared spectra were obtained with Beckman IR-5A or IR-8 infrared spectrophotometers on neat samples or dilute solutions in carbon disulfide or carbon tetrachloride. The spectra of reaction products and authentic substances were taken with samples purified by glpc. Gas chromatographic work was carried out on a homemade unit with the indicated columns: (A) 12 ft × 0.25 in., Apiezon L (14%) on Chromosorb P (40–60 mesh) (5% NaOH); (B) 6 ft × 0.25 in., Ucon Polar 50 HB 2000 (2.5%) on Chromosorb W (40–60 mesh) (5% NaOH); (C) 8 ft × 0.25 in., Carbowax 6000 (14%) on Chromosorb P (40–60 mesh) (5% NaOH); (D) 6 ft × 0.25 in., Apiezon L (14%) on Chromosorb P (30–60 mesh) (5% NaOH); (E) 12 ft × 0.25 in., sodium dodecyl benzenesulfonate (10%) Ucon Polar 50 HB 2000 (7%) on Chromosorb W (35–60 mesh) (5% NaOH); (F) 5 ft × 0.25 in., Carbowax 6000 (20%) on Chromosorb P (30–60 mesh) (5% NaOH); (G) 5 ft × 0.25 in., Carbowax 20M (20%) on Chromosorb P (30–60 mesh) (5% NaOH).

Molecular weight data were obtained by vapor pressure osmometry with a benzene solution.

Preparation of Trichloramine Solutions. A published procedure[4] (Method B) was used with either *o*-dichlorobenzene or 1,2-dichloroethane as solvent. Analysis for positive halogen was accomplished according to a published procedure[4] (iodometric method in acetic acid).

Amination of Aromatics with Trichloramine. A previously published procedure[4] was followed except that addition of the trichloramine solution was made over a period of 1 hr. The reagents were used in the molar ratio, $NCl_3/AlCl_3$/aromatic/*o*-$C_6H_4Cl_2$ = 1/2/*ca.* 12/*ca.* 17, and $NCl_3/AlCl_3$/aromatic/$ClCH_2CH_2Cl$ = 1/2/10/25, unless otherwise indicated. Yields are based on an equimolar relationship between trichloramine and basic product. For determination of individual yields, the mixture of bases resulting from distillation was subjected to glpc analysis. When distillation was not feasible, as in the case of high-melting solids, analysis was accomplished with an internal standard. Reference curves were made up with known mixtures of authentic materials.

Product identification generally is based on comparison of glpc retention time and infrared spectrum with those of the authentic material. In certain cases, elemental analyses, nmr spectrum, and refractive index were also used to aid in characterization.

In order to effect glpc analysis of neutral products the organic phase from the reaction mixture after acid extraction was washed with dilute caustic, then with water, and dried over anhydrous sodium sulfate. Major components, *e.g.*, chlorinated aromatic substrates, were determined directly. For minor components, *e.g.*, dibromobenzene from disproportionation of bromobenzene, the solvent and substrate were first removed by distillation through a 1-ft column packed with glass helices, followed by examination of the fractions and residue.

Competitive Amination. The technique is described elsewhere.[7]

Amination of Bromodurene. Addition of aluminum chloride (26.6 g, 0.2 mole) to a solution of bromodurene (200 g, 0.94 mole) in 1,2-dichloroethane (255 ml) produced an orange-brown sludge. Amination with a solution (200 ml) of trichloramine (0.1 mole) in 1,2-dichloroethane according to the general procedure provided 2.9 g of crude basic product. Glpc examination (column D, 200°) revealed a gross mixture with no detectable amounts of 1-amino-4-chlorodurene.

Isomerization Studies. A solution of *o*-bromoaniline (6.6 g, 0.038 mole) in *o*-dichlorobenzene (100 ml) was stirred with a suspension of aluminum chloride (25 g, 0.187 mole) in *o*-dichlorobenzene (200 ml). A steady stream of hydrogen chloride was passed through the reaction mixture for 2 hr at 25°. The mixture was then stirred with ice–dilute hydrochloric acid and worked up according to the general procedure. Distillation gave *o*-bromoaniline, 6 g (91% recovery), with no evidence (glpc column D, 170°, infrared spectrum) for the presence of the other isomers. The residue weighed 0.06 g.

By the same procedure *p*-bromoaniline and *m*-bromoaniline were recovered unchanged (94.8 and 95.2%, respectively).

Aniline and Trichloramine. A solution of aniline (10 g, 0.11 mole) in 200 ml of *o*-dichlorobenzene was added to a suspension of aluminum chloride (25 g, 0.187 mole) in *o*-dichlorobenzene (50 ml). Then a solution of trichloramine (0.048 mole) in *o*-dichlorobenzene (100 ml) was introduced during 30 min at 25°. Next, hydrogen chloride gas was passed through the reaction mixture for 90 min. Treatment with ice–dilute hydrochloric acid and work-up according to the general procedure resulted in a 74.3% recovery of aniline in addition to an 8.7% yield (based on aniline) of *p*-chloroaniline and trace amounts of *o*-chloroaniline (<0.5%). Thus, 83% of the initial aniline can be accounted for.

***p*-Toluidine and Trichloramine.** A solution of *p*-toluidine (10 g, 0.93 mole) in 100 ml of 1,2-dichloroethane was added to a suspension of aluminum chloride (26.6 g, 0.2 mole) in 50 ml of 1,2-dichloroethane at 0°. After the addition of trichloramine (0.1 mole) in 1,2-dichloroethane (200 ml) during 30 min, the mixture was stirred for an additional 90 min and worked up according to the general procedure. Large amounts of ether (1.5 l.) were used to extract the amine. Removal of the ether gave 2 g of black tar which on extraction with 10 ml of ether in small portions provided 0.4 g of soluble material. Analysis (glpc, column D, 150°) revealed the presence of aniline (1.8%), *p*-toluidine (4.6%), 2-chloro-4-methylaniline (22.7%), 3-chloro-4-methylaniline (17.9%), and unidentified higher

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boiling material (53%). The isolated bases accounted for only about 4% of the initial *p*-toluidine.

Bromodurene. This compound was synthesized by a reported procedure. The distilled product, after recrystallization from methanol, melted at 58.5–60° (lit.[19] mp 60–61°). Analysis (glpc, column D, 200°) indicated a purity of >99%.

Chlorodurene. The method of Töhl[20] gave a product, 19% yield, melting at 45–46° (lit. mp 48°,[20] 45.5–46.1° [21]). Glpc analysis revealed a purity of >99%.

1-Chloro-4-nitrodurene. Concentrated nitric acid (10.5 ml) was added dropwise over a period of 15 min at 50° to a stirred mixture of 16.8 g of chlorodurene and 20 ml of concentrated sulfuric acid. After an additional 5 min, the mixture was poured onto 200 g of crushed ice. The resulting solid was collected by filtration and recrystallized from 95% ethanol, mp 160–165°. After three crystallizations, 7.1 g (33%) of a light tan solid was obtained which melted at 169–170°.

Anal. Calcd for $C_{10}H_{12}ClNO_2$: C, 56.20; H, 5.67; N, 6.56; Cl, 16.60. Found: C, 56.09; H, 5.80; N, 6.40; Cl, 16.84.

1-Amino-4-chlorodurene. A mixture of 3 g of 1-chloro-3-nitrodurene, 50 ml of 50% ethanol, 4.2 g of tin metal (20 mesh), and 8 ml of concentrated hydrochloric acid was heated at reflux for 3 hr. After basification in the cold with 50% sodium hydroxide, the mixture was steam distilled. The dried ether extract of the distillate was treated with gaseous hydrogen bromide. The amine hydrobromide was filtered, washed with ether, (mp 254–255° dec), and treated with aqueous ammonia. After the amine was taken up in ether, removal of the solvent gave a light yellow solid, 1.4 g (45%), which was 90% pure by glpc analysis (column D, 200°). Preparative scale glpc provided a white solid, mp 129.5–130°.

Anal. Calcd for $C_{10}H_{14}ClN$: C, 65.39; H, 7.68; N, 7.62; Cl, 19.31. Found: C, 65.10; H, 7.46; N, 7.80; Cl, 19.13.

2-Chloro-4-methyl-6-nitroaniline. Treatment of a warm solution of 4-methyl-2-nitroaniline (105 g, 0.69 mole) in 1 l. of glacial acetic acid with a stream of chlorine for 1 hr with stirring caused formation of a dark brown mixture. After being stirred for 1 additional hr, the mixture was poured into 5 l. of water. The viscous material which separated was collected by filtration and steam distilled. After extraction of the distillate with ether, removal of solvent gave 40 g (31%) of an orange solid melting at 62–64° (lit.[22] mp 70.5°), which was used without further purification.

3-Chloro-5-nitrotoluene. To a solution of 35.6 g (0.193 mole) of 2-chloro-4-methyl-6-nitroaniline in 200 ml of absolute ethanol was added 30 ml of concentrated sulfuric acid. Sodium nitrite (30 g, 0.4 mole) was introduced (foaming) in small portions as quickly as possible at the reflux temperature. The dark mixture was refluxed for 30 min, cooled, and poured into 1.5 l. of water. Extraction with ether, followed by solvent removal, gave crude 3-chloro-5-nitrotoluene which was used in the next step without further purification.

3-Chloro-5-methylaniline. The crude 3-chloro-5-nitrotoluene was dissolved in 100 ml of 95% ethanol and treated with 45 g of tin metal (20 mesh) and 100 ml of concentrated hydrochloric acid. After 30 min on a steam bath, the mixture was poured into 1.5 l. of water, made basic with 50% sodium hydroxide, and extracted with ether. Removal of ether from the dried extract, followed by distillation of the residue, provided 11.3 g (41% over-all yield from 2-chloro-4-methyl-6-nitroaniline) of product, bp 90° (1.2 mm) (lit.[23] bp 242° (730 mm)).

3-Bromo-5-nitrotoluene. A published procedure[24] was used. The steam-distilled product was crystallized from 95% ethanol, mp 82–84° (lit.[24] mp 81–83°).

3-Bromo-5-methylaniline. A suspension of 3-bromo-5-nitrotoluene (39 g, 0.18 mole) in 100 ml of 95% ethanol was treated with 45 g of tin metal (20 mesh) and 100 ml of concentrated hydrochloric acid. The mixture was heated on the steam bath for 30 min, then distilled to half-volume. The resulting solution was cooled, made strongly basic with 50% sodium hydroxide, and filtered. The inorganic solid was washed with sodium hydroxide, then with ether, and the washings were combined with the filtrate. Extraction of the aqueous portion with ether and evaporation of the dried, combined ether solutions provided the crude amine. Distillation gave 26 g (78% yield) of product, bp 150–154° (4 mm) (lit.[25] bp 255–260°), mp 35.5–36.5° (lit. mp 35–36°,[26] 37–38° [27]).

3-Bromo-5-fluorotoluene. A. From 3-Fluoro-5-methylaniline. The crude amine product from amination of *m*-fluorotoluene was distilled under reduced pressure until the evolved material began to solidify. The distillate (0.2 g) predominantly 3-fluoro-5-methylaniline with some chlorotoluidines (glpc analysis, column D, 150°), was dissolved in 10 ml of absolute ether. After dry hydrogen bromide was passed through the solution for 10 min, the amine salt was filtered and washed with absolute ether (10 ml). Amyl nitrite (3 g) was added below 5° portionwise to a stirred solution of the salt in 10 ml of absolute ethanol. After 10 min, absolute ether (50 ml) was added to precipitate the diazonium salt which was filtered, washed with absolute ether, and dried in air at room temperature. A suspension in 10 ml of dry carbon tetrachloride was refluxed for 50 min, and then concentrated by distillation, yielding about 0.05 ml of a dark liquid. The major component from gas chromatography (column D, 120°) proved to be a clear liquid having a retention time and infrared spectrum identical with those of authentic 3-bromo-5-fluorotoluene.

B. From 3-Bromo-5-methylaniline. To 3-bromo-5-methylaniline (16 g, 0.086 mole) was added a solution of 16.6 ml of concentrated hydrochloric acid in 15 ml of water. The resulting suspension was treated with a solution of 7.5 g of sodium nitrite (0.1 mole) in 15 ml of water below 5°. Following an additional 20 min of stirring, a cold solution of 48% fluoroboric acid (22 g, 0.12 mole) was added below 0°. After 30 min the solid diazonium fluoroborate was collected by filtration, washed with 10 ml of water, and sucked dry. Washing was accomplished portionwise with 60 ml of methanol and 60 ml of absolute ether, accompanied by sucking to dryness after each wash. By increasing application of a direct flame, the dry solid was decomposed in a round-bottom flask equipped for distillation with two receivers connected in series and and immersed in Dry Ice–acetone. The ether wash of the complete apparatus was extracted first with 10% sodium hydroxide and then with water. Removal of the ether from the dried solution followed by distillation of the residue gave 8.5 g (52%) of 3-bromo-5-fluorotoluene, bp 63–66° (2 mm), n^{25}D 1.5247.

Anal. Calcd for C_7H_6BrF: C, 44.48; H, 3.20; Br, 42.27; F, 10.05. Found: C, 44.49; H, 3.30; Br, 42.21; F, 10.09.

3-Fluoro-2-methylbenzoic Acid. The material was obtained in 10% yield by the method of Newman and Wiseman,[28] mp 156–158° (lit.[28] mp 156–157°).

When, instead of filtration of the reaction mixture, the crude product was taken up in ether, extracted into dilute caustic, acidified, and extracted with ether, the solid obtained after solvent removal melted at 111–117°. Recrystallization from ethanol gave material melting at 122–125°, which on decarboxylation[28] yielded a mixture of *o*- and *m*-fluorotoluenes (identified by comparison of the infrared spectra with those of the authentic materials).

3-Fluoro-2-methylaniline. Treating a solution of 3-fluoro-2-methylbenzoic acid (1 g) in 20 ml of chloroform with 15 ml of concentrated sulfuric acid and sodium azide (0.65 g) at 50° provided the amine hydrochloride. Work-up gave 0.7 g (87%) of 3-fluoro-2-methylaniline of 98% purity. The glpc retention time and infrared spectrum of the glpc purified product were identical with those of the corresponding material isolated from amination of *o*-fluorotoluene.

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