Amination of Toluene with Trichloramine–Lewis Acid Catalyst[1]

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An unusual orientation is obtained in the amination of toluene with trichloramine under Friedel–Crafts conditions. The system toluene–trichloramine–aluminum chloride yielded a basic product (42% yield) which was predominantly m-toluidine. The toluidine isomers were stable to rearrangement under simulated reaction conditions. Several reaction variables were investigated: catalyst strength, temperature, $AlCl_3$:NCl_3 *ratio, and diluents. Best results were obtained with strong Friedel–Crafts catalysts, temperatures in the range of −35 to +10°, and* $AlCl_3$:NCl_3 *molar ratio of at least 2. No m-toluidine was found in the presence of additives, such as triethylamine, which coordinate strongly with the catalyst. The reaction (σ-substitution) is believed to proceed via nucleophilic attack of trichloramine upon the toluene σ-complex. The principal neutral reaction product is a mixture of chlorotoluenes (ortho:meta:para = 68:1:31).*

Introduction

There is only a meager amount of prior literature dealing with aromatic amination by N-halamines. The earliest work was apparently by Lellmann and Geller[5] who allowed N-chloropiperidine to intereact with benzene in the presence of aluminum chloride. The odor of N-phenylpiperidine was detected from the reaction product.

Later, Raschig[6] found that chloramine and phenol yielded small amounts of *p*-aminophenol, in addition to 4,4′-dihydroxydiphenylamine and the corresponding iminoquinone. With sodiophenoxides, deep-seated rearrangements occurred resulting in ring expansion.[7] Aniline is one of the products formed from the reaction of chloramine with phenyllithium[8] or the phenyl Grignard reagent.[9] Brooks and Rudner[10] effected aminations in the heterocyclic series with chloramine. For example, pyridine and quinoline were converted to the corresponding 2-amino derivatives.

From an investigation of the trichloramine–benzene reaction, Coleman and Noyes[11] reported the formation of chlorinated anilines in low yield. The intermediate involvement of N,N-dichloroaniline was postulated.

Recent preliminary reports from this laboratory revealed that an unusual orientation arises from the amination of aromatic compounds with halamines in the presence of a Lewis acid catalyst.[12,13] In the present work we wished to investigate reaction variables and mechanistic aspects using the toluene–trichloramine–Lewis acid catalyst system.

Results and Discussion

Solutions of trichloramine in toluene were prepared from calcium hypochlorite[14] and ammonium salts by a modification of Coleman's procedure.[15] In 1929 Chapin[16] reported that the nature of the product formed was critically dependent upon pH (chloramine at pH >8.5, dichloramine at pH 4.5–5, and trichloramine at pH <4.4). In our procedure negligible amounts of positive halogen compound were present in the toluene layer at pH >8.5. Surprisingly, analytical data[17] indicated that trichloramine was the principal product extracted into the organic solvent at both pH 5 and 1.

Czech and co-workers[18] have published ultraviolet spectra of the chloramines (λ_{max} (mμ): NH_2Cl, 262; $HNCl_2$, 257, 300; NCl_3, 265, 345). When our preparations were repeated with carbon tetrachloride as solvent at pH 5 and 1, the ultraviolet spectrum of each solution indicated the presence of trichloramine, with no evidence of dichloramine. Furthermore, toluene solutions were analyzed for positive chlorine by iodometric titration in acetic acid and for nitrogen by the Kjeldahl and Dumas methods. For both solutions Cl:N atomic ratios of 2.9–3.3 were obtained. The absence of dichloramine was also demonstrated by n.m.r. investigations.

In a rationalization of the results, stability and solubility[16,18] characteristics of the halamines would be expected to play important roles. Although solutions of trichloramine generated by the two procedures behaved similarly for the most part, some slight differences were noted.

Reactions of trichloramine with toluene were generally carried out at −35° in the presence of large amounts of aluminum chloride. The toluene solution of trichloramine was added slowly to a heterogeneous

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[2] National Science Foundation Undergraduate Summer Fellow, 1963 and 1964; in part from the B.S. thesis of C. T. G., 1964.

[3] NDEA Fellow, 1964.

[4] National Science Foundation Fellow, 1963–1964; in part from the Ph.D. thesis of R. M. L., 1964.

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[12] P. Kovacic, R. M. Lange, J. L. Foote, C. T. Goralski, J. J. Hiller, Jr., and J. A. Levisky, *ibid.*, **86**, 1650 (1964).

[13] J. L. Foote, Ph.D. thesis, Case Institute of Technology, 1960.

[14] M. J. Tcherniak, *Bull. Soc. Chim.*, [2] **25**, 160 (1876).

[15] G. H. Coleman, *J. Am. Chem. Soc.*, **55**, 3001 (1933).

[16] R. M. Chapin, *ibid.*, **51**, 2112 (1929).

[17] In the preliminary stages of this work, we proceeded on the erroneous assumption that dichloramine was present in the toluene solution at pH 5 (see ref. 12).

[18] F. W. Czech, R. J. Fuchs, and H. F. Antczak, *Anal. Chem.*, **33**, 705 (1961).

mixture of the catalyst and toluene. Under these conditions *m*-toluidine of 98% isomeric purity was the major basic product, and chlorotoluene comprised the principal neutral product. *m*-Toluidine was characterized by elemental analysis and comparison with authentic material (infrared spectrum, boiling point, refractive index, and benzoyl derivative). In the various experiments *m*-toluidine made up 67–83% of the basic fraction, the remainder consisting of higher boiling material and residue. The less volatile cut contained several components including isomeric chloro-*m*-toluidines. A possible stoichiometric relationship is illustrated by the equation:

$$NCl_3 + 3C_6H_5CH_3 \xrightarrow{AlCl_3} m\text{-}H_2NC_6H_4CH_3 + 2ClC_6H_4CH_3 + HCl \qquad (1)$$

In order to gain further insight into the reaction, several variables were examined, namely, catalyst strength, temperature, $AlCl_3$:NCl_3 ratio, and diluents. From the catalyst studies the indicated order of catalyst activity was obtained, $AlCl_3 > AlBr_3 > SbCl_5 > FeCl_3,SnCl_4$ (Table I). In comparison with other systems it is important to keep in mind that the nature of the reaction plays an important part in determining the order of promoter strength.[19a] Nevertheless, in many cases the arrangement which pertains,[19a,20] $AlBr_3$, $AlCl_3 > SbCl_5,FeCl_3 > SnCl_4$, is similar to that observed in this study.

Table I. Catalyst Studies[a]

Catalyst	*m*-Toluidine, yield, %	Catalyst	*m*-Toluidine, yield, %
$AlCl_3$	42	$SnCl_4$	0
$AlBr_3$	25	$FeCl_3$	0
$SbCl_5$	3	. .	0

[a] Catalyst:NCl_3 = 2, *o*-$C_6H_4Cl_2$:catalyst = 1.5, $C_6H_5CH_3$:NCl_3 = 25, −35°. Trichloramine was prepared by method A.

The temperature effect (Table II) was investigated in the range −70 to +50°, at $AlCl_3$:NCl_3 ratios of 2 and 3 with trichloramine prepared at pH 5 (method A) and pH 1 (method B). When method A was used, the yield of *m*-toluidine attained a maximum (42%) at −35°, decreasing to low values (7–16%) at −70° and 50°. Trichloramine from method B gave very similar results except for the lower yields at −35° and at −70° ($AlCl_3$:NCl_3 = 2). The reason for this discrepancy is not known.

Table II. Temperature Effect[a]

Temp., °C.	$AlCl_3$:NCl_3, *M*	Toluidine, yield, %: NCl_3 by method A	Toluidine, yield, %: NCl_3 by method B
−70	2	7[b]	0[c]
−55	2	18[b]	18
−35	2	42[c]	30[c]
−15	2	36[b]	34[b]
10	2	30	28[d]
50	2	16	. .
−70	3	0	0
−55	3	20	20
−35	3	42[c]	31[b]
−15	3	30	32
10	3	28[c]	28[c]

[a] *o*-$C_6H_4Cl_2$:NCl_3 = 3, $C_6H_5CH_3$:NCl_3 = 25. [b] Average of 2 runs. [c] Average of 3 runs. [d] Average of 10 runs.

Studies involving variation in the $AlCl_3$:NCl_3 ratio were carried out at −35 and +10° (Table III). Also, trichloramine prepared by the two methods was used. The yield of *m*-toluidine reached a maximum at a 2:1 ratio and then remained constant or declined slightly at higher ratios. Best results (42%) were realized at −35° with trichloramine prepared at pH 5. Since basic products (aromatic amine and presumably ammonia) are formed which can coordinate with and deactivate the catalyst, the need for large amounts of aluminum chloride is understandable.

Table III. Variation in $AlCl_5$:NCl_3 Ratio[a]

$AlCl_3$:NCl_3, *M*	*m*-Toluidine, yield, %: (35°) NCl_3 by method A	*m*-Toluidine, yield, %: (35°) NCl_3 by method B	*m*-Toluidine, yield, %: (10°)[b]
1	0	15	10
2	42[c]	30[c]	28[d]
3	42[c]	31[e]	28[c]
4	35	30[c]	20[e]
5.7	39	. .	. .

[a] *o*-$C_6H_4Cl_2$:NCl_3 = 3, $C_6H_5CH_3$:NCl_3 = 25. [b] Trichloramine was prepared by method B. [c] Average of 3 runs. [d] Average of 10 runs. [e] Average of 2 runs.

Various responses were observed with the diverse diluents introduced into the amination reaction mixture (Table IV). With certain additives, *o*-dichlorobenzene,[21] 1,2,4-trichlorobenzene, and water, no alteration in yield resulted. Addition of the others elicited a strong inhibitory response. Presumably the Lewis bases, nitromethane, diethyl ether, and triethylamine, render the catalyst ineffective by complex formation. A general procedure involving *o*-dichlorobenzene as diluent was adopted to permit facile extension to solid aromatic reactants.

Table IV. Effect of Diluents[a]

Diluent	*m*-Toluidine, yield, %	Diluent	*m*-Toluidine, yield, %
. . .	32[b]	CH_3NO_2	0
o-$C_6H_4Cl_2$	34[b]		
1,2,4-$C_6H_3Cl_3$	30	$(C_2H_5)_2O$	0
H_2O	30[b]	$(C_2H_5)_3N$	0
$SnCl_4$	8		

[a] $AlCl_3$:NCl_3 = 3.8, $C_6H_5CH_3$:NCl_3 = 30, diluent:$AlCl_3$ = 1.5, −35°. Trichloramine was prepared by method A. [b] Average of 3 runs.

The present investigation, as well as previous results,[22–24] demonstrated that the individual toluidine isomers are stable under simulated reaction conditions.

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(19) "Friedel-Crafts and Related Reactions," Vol. I, G. A. Olah, Ed., Interscience Publishers, Inc., New York, N. Y., 1963: (a) G. A. Olah, Chapter XI; (b) G. A. Olah and M. W. Meyer, Chapter VIII.

(20) G. A. Russell, *J. Am. Chem. Soc.*, **81**, 4834 (1959).

(21) For some unexplained reason, chloroaromatics occasionally produced a beneficial effect, as was observed in our initial studies (see ref. 12).

(22) P. Kovacic and J. L. Foote, *J. Am. Chem. Soc.*, **83**, 743 (1961).

(23) P. Kovacic, R. P. Bennett, and J. L. Foote, *ibid.*, **84**, 759 (1962).

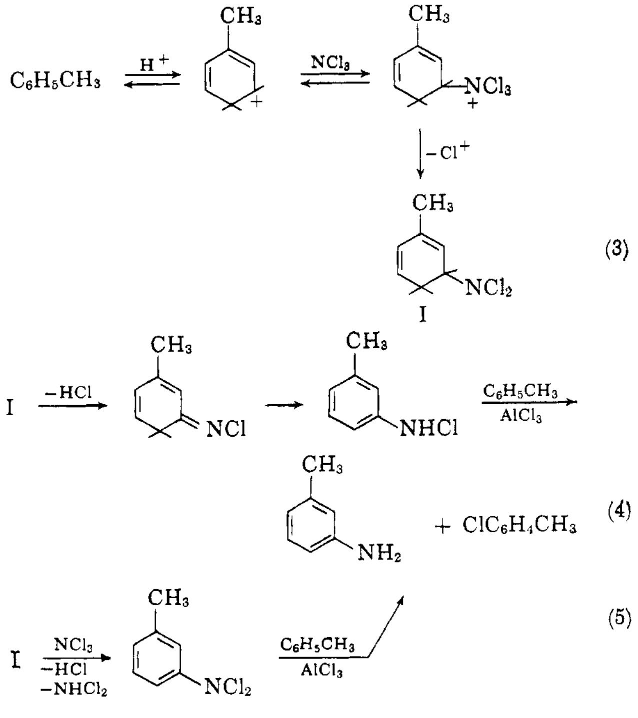
(24) P. Kovacic, R. L. Russell, and R. P. Bennett, *ibid.*, **86**, 1588 (1964).

Therefore, it appears unlikely that the observed orientation arises from rearrangement of the other isomers during reaction.

In a discussion of the theoretical aspects, the nature of N-halamines should be considered. The electronegativities of nitrogen and chlorine are reported to be equal.[25] Although the polarization has been designated[26] as $N^{\delta+}-Cl^{\delta-}$, the reactions with water[27] and ketene[28] indicate that the chlorine is positive. Our working hypothesis concerning the pathway of this unusual reaction is outlined in Scheme I. Alternatively, II may lose chlorine prior to rearrangement.

Scheme I

$$H_2O + AlCl_3 \rightleftarrows H_2O{-}AlCl_3 \rightleftarrows H^+AlCl_3(OH)^- \qquad (2)$$



In a control experiment in which aluminum chloride was omitted from the reaction mixture, no aromatic amine was formed (Table I). This result, demonstrating the vital necessity of the catalyst, strongly suggests a polar reaction mechanism. According to the proposed sequence, a Brønsted acid, such as adventitious water, functions as a co-catalyst.[29] Previous studies have shown the operation of a co-catalytic effect in the Friedel–Crafts alkylation[30] of benzene with alkyl halides or ethers, and in the polymerization of benzene.[31]

The existence of σ-complexes in mixtures of aromatics with strong Lewis acids has been well established.[19b] Nucleophilic attack of the halamine on the arenonium ion very nicely accounts for the observed orientation. A somewhat similar mechanism may be involved in the pyridine–chloramine reaction,[10] and in the oxidative cationic polymerization of benzene.[32] The over-all scheme is consistent with the observation that the reaction proceeds at very low temperatures, conditions under which σ-complexes readily form.[19b] The proposed aromatic chloramine intermediates are considered to be highly unstable,[33] and therefore would exhibit transient existence under the reaction conditions. The quite pronounced resistance of *m*-toluidine to subsequent attack is probably due to stabilization by coordination with hydrogen chloride or aluminum chloride.

If the mechanism proves to be valid, "σ-substitution" would be a convenient designation for the reaction. Failure to observe this type of transformation previously may be due to the various, strictly defined properties requisite of the reagents and catalyst.

The observed orientation cannot be satisfactorily interpreted by alternative mechanistic possibilities. Electrophilic substitution, which is characterized by *ortho–para* orientation, appears highly improbable[34] since the unusual directive influence was obtained with toluene which is categorized as an *ortho–para* director.

Operation of a free-radical mechanism during the attack step of amination can be ruled out. Radical substitution in toluene generally results in predominant *ortho–para* orientation.[35] More specifically, several amino type radicals have been investigated in their behavior toward aromatic substrates. Amino radicals, generated from hydroxylamine and titanous ions, combined with benzene or toluene to form nonconjugated products, indicating addition rather than substitution.[36] Cowley and Waters[37] obtained no evidence for aromatic substitution by dimethylamino radicals.

One should also consider the possible participation of a nitrene intermediate[38] arising from α-elimination. Recent studies of the e.p.r. spectra of nitrenes generated by thermal decomposition of azides demonstrated the radical character of these species.[39] Benzenesulfonamidation of toluene by the corresponding azide produced substitution mainly in the *ortho–para* positions.[40] Furthermore, it appears that a carbene, dichloromethylene, is involved in the Reimer–Tiemann reaction which

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(25) L. Pauling, "The Nature of the Chemical Bond," 3rd Ed., Cornell University Press, Ithaca, N. Y., 1960, p. 90.

(26) J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. VIII, Longmans, Green and Co., New York, N. Y., 1928, pp. 604, 605.

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(31) P. Kovacic and C. Wu, *J. Polymer Sci.*, **47**, 45 (1960); P. Kovacic, F. W. Koch, and C. E. Stephan, *ibid.*, **2A**, 1193 (1964).

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(33) S. Goldschmidt, *Ber.*, **46**, 2728 (1913); S. Goldschmidt and L. Strohmenger, *ibid.*, **55**, 2450 (1922).

(34) Although the toluidine isomers are stable to rearrangement under simulated reaction conditions, there is the possibility that an intermediate, such as *p*-$CH_3C_6H_4NCl_2$, may be highly susceptible to isomerization. This hypothesis might be difficult to test because of the instability of N-haloaromatic amines.

(35) G. H. Williams, "Homolytic Aromatic Substitution," Pergamon Press, New York, N. Y., 1960, pp. 68, 106, and 115.

(36) E. Seaman, P. J. Taylor, and W. A. Waters, *J. Chem. Soc.*, 4690 (1954); C. J. Albisetti, D. D. Coffman, F. W. Hoover, E. L. Jenner, and W. E. Mochel, *J. Am. Chem. Soc.*, **81**, 1489 (1959); P. Davis, M. G. Evans, and W. C. E. Higginson, *J. Chem. Soc.*, 2563 (1951); Z. Yoshida, T. Matsumoto, and R. Oda, *Kogyo Kagaku Zasshi*, **65**, 46 (1962) [*Chem. Abstr.*, **57**, 16446 (1962)].

(37) B. R. Cowley and W. A. Waters, *J. Chem. Soc.*, 1228 (1961).

(38) J. Jander, *Naturwiss.*, **42**, 178 (1955); *Chem. Abstr.*, **50**, 9915, (1956); J. E. Leffler, "The Reactive Intermediates in Organic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1956, p. 47.

(39) G. Smolinsky, E. Wasserman, and W. A. Yager, *J. Am. Chem. Soc.*, **84**, 3220 (1962).

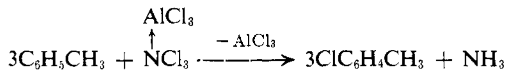
(40) J. F. Heacock and M. T. Edmison, *ibid.*, **82**, 3460 (1960).

produces the orientation expected for electrophilic attack.[41]

Direct nucleophilic substitution in the aromatic nucleus[42] is not a reasonable possibility due to the basicity of toluene and the low nucleophilicity of trichloramine.

Direct amination has also been effected under Friedel–Crafts conditions with hydroxylamine derivatives[22,23,43,44] and azides.[24,44,45] In contrast to the present method, these techniques afford orientations characteristic of electrophilic attack.

The major neutral reaction product, chlorotoluenes, possessed an isomer distribution (*ortho*:*meta*:*para* = 68:1:31) characteristic of electrophilic substitution. Since the orientation is very similar to that obtained[46] with molecular chlorine and antimony pentachloride, halogenation (aluminum chloride catalysis) might arise from chlorine generated *in situ*. Hydrogen chloride is known to produce chlorine on interaction with chloramines.[47] Alternatively, the halogenating species could conceivably be a chloramine, such as trichloramine or a reaction intermediate possessing a N–Cl bond. It is reasonable to expect Friedel–Crafts catalysis for this pathway also.



$$3C_6H_5CH_3 + \overset{\overset{AlCl_3}{\uparrow}}{NCl_3} \xrightarrow{-AlCl_3} 3ClC_6H_4CH_3 + NH_3$$

The literature contains various examples of aromatic chlorination by N-chloro compounds, including trichloramine[11] and N-chlorodiethylamine.[48] It is pertinent that the kinetics of chlorination of phenol by N-chlorodiethylamine can be interpreted in terms of interaction of phenoxide ions and diethylchlorammonium cations.[48]

Experimental[49]

Materials. Toluene (Mallinckrodt) was dried over sodium and used without further purification. *o*-Dichlorobenzene (Eastman) was distilled from calcium hydride. Granular calcium hypochlorite (Fisher, 73.5% purity) and commercial "HTH" (Monsanto Chemical Co., 70% purity) were active halogen sources. Aluminum chloride, sublimed (Matheson Coleman and Bell), was used as obtained. *o*-, *m*-, and *p*-toluidines (Eastman) were distilled for use as authentic samples.

Analytical Procedures. Qualitative and quantitative analyses were made with Beckman IR-5A, IR-7, and IR-8 infrared spectrophotometers. Qualitative spectra were obtained neat or with potassium bromide pellets, whereas all quantitative determinations were made in cyclohexane solution. Gas chromatographic work was carried out with the Aerograph Model A-90-P. Dr. G. Weiler and Dr. F. B. Strauss, Oxford, England, performed the elemental analyses.

Iodometric determinations of active halogen were made as follows: 1.0 ml. of trichloramine solution was pipetted into a solution of 2.0 g. of potassium iodide or sodium iodide in 50 ml. of 80% acetic acid. When a stronger acid was used, the trichloramine solution (1.0 ml.) was added to 3 ml. of 0.1 *N* hydrochloric acid and 10 ml. of water. The liberated iodine in each case was then titrated with 0.100 *N* sodium thiosulfate. The Volhard method was applied after reduction with sodium bisulfite.

Kjeldahl analysis for nitrogen was accomplished by refluxing 15.0 ml. of trichloramine solution with 100 ml. of concentrated hydrochloric acid for 6 hr. After careful neutralization with 50% caustic, the evolved ammonia was distilled into 250.0 ml. of 0.100 *N* hydrochloric acid. The excess acid was then back-titrated with 0.100 *N* caustic. Dumas nitrogen analyses were performed with a Coleman Model 29 nitrogen analyzer.[50]

Results from the analyses are summarized in Table V. The various determinations were carried out with a single solution prepared at the indicated pH.

Table V. Analysis[a] of Trichloramine in Toluene

Method	Prepared at pH 5		Prepared at pH 1	
	Cl	N	Cl	N
Iodometric (HCl)	2.26[b]		2.18[b]	
Iodometric (HOAc)	3.44[b]		3.56[b]	
Volhard	4.92[c]		4.28[c]	
Kjeldahl		1.14		1.18
Dumas		1.17		1.13

[a] Results in mmoles/ml. [b] Positive chlorine. [c] Total chlorine.

The Varian A-60 instrument was used for the n.m.r. analyses (Table VI). The trichloramine solutions showed no proton resonance peaks (other than those of the aromatic solvent) in the region 10 to $-22\ \tau$.

Table VI. Proton Resonance Spectra

Compound[a]	NH proton, τ
Ammonia[b]	9.48
m-Toluidine	7.1
t-Butylamine[c]	8.84
N-Chloro-*t*-butylamine[d]	5.38
Trichloramine[e,f]	. . .

[a] In *o*-dichlorobenzene; tetramethylsilane as reference. [b] Liquid (neat). [c] CH protons:NH protons = 4.5:1. [d] CH protons:NH proton = 9:1. [e] Also in carbon tetrachloride. [f] Prepared at both pH 1 and 5.

Preparation of Trichloramine Solutions. Method A. Commercial "HTH" (70% purity, 90 g., 0.4 mole) was suspended in 250 ml. of water in a three-neck flask equipped with a stirrer, water condenser, thermometer, and addition funnel. After addition of the toluene (300 ml.), a solution consisting of 27.2 g. (0.2 mole) of sodium acetate, 27 ml. (0.4 mole) of glacial acetic acid, and 30.8 g. (0.4 mole) of ammonium acetate in

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(42) J. F. Bunnett and R. E. Zahler, *Chem. Rev.*, **49**, 273 (1951).

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(48) L. O. Brown and F. G. Soper, *ibid.*, 3576 (1953).

(49) Melting points and boiling points are uncorrected.

(50) We are indebted to Dr. John Crano of Pittsburgh Plate Glass Co. for these analyses.

150 ml. of water was introduced slowly below 10° with vigorous stirring during 30 min. The mixture was stirred for an additional 15 min., the layers were separated, and the bright yellow organic phase was dried over anhydrous sodium sulfate after a water wash. The concentration of trichloramine was then determined. Preparations in carbon tetrachloride were carried out similarly. The solutions of trichloramine exhibited satisfactory stability for at least several hours at ice-bath temperatures.

Method B. Commercial "HTH" (70% purity, 90 g., 0.4 mole) was suspended in 200 ml. of water as described in method A, and 300 ml. of toluene was added. A solution of 22 g. (0.4 mole) of ammonium chloride, 50 ml. of concentrated hydrochloric acid, and 150 ml. of water was added slowly below 10°. The work-up was similar to that used in method A.

Preparation of N-Chloro-t-butylamine Solution. Method A was followed. Sodium hypochlorite (1 mole) was added during 30 min. to *t*-butylamine (1 mole) in *o*-dichlorobenzene (150 ml.) at 0–5°.

Amination of Toluene with Trichloramine. General Procedure. A cold toluene solution (200 ml.) of trichloramine (0.088 mole) prepared by method A was added with stirring during 30 min. to a mixture of toluene (233 ml.), *o*-dichlorobenzene (0.264 mole), and aluminum chloride (0.176 mole) at $-35°$. After an additional hour at $-35°$, the reaction mixture was added to cold dilute hydrochloric acid, the layers were separated, and the organic phase was washed with dilute hydrochloric acid. Following ether extraction of the combined acid solutions, the aqueous portion was made strongly basic in the cold with caustic. Ether extraction, removal of the solvent, and then distillation provided 3.83 g. of *m*-toluidine (41% yield),[51] b.p. 69–73° (5 mm.), lit.[52] b.p. 95–97° (16 mm.). The infrared spectrum was identical with that of the authentic substance. Additional characterization (n^{20}D 1.5679, lit.[53] n^{20}D 1.5686) was carried out with corresponding material obtained from another experiment. *Anal.* Calcd. for C_7H_9N: C, 78.50; H, 8.41; N, 13.08. Found: C, 78.49; H, 8.48; N, 13.17. The benzoyl derivative melted at 123–124°, lit.[54] m.p. 125°.

The distillation also produced 0.5 g. of higher boiling, basic product, b.p. 130–140° (5 mm.), and 0.49 g. of distillation residue.

The higher boiling material was subjected to gas chromatography [6-ft. Ucon polar (2.5%, 5% sodium hydroxide) column, 135°, 40 ml. of helium/min.; 1-ft. Apiezon L (14%; 5% sodium hydroxide) column, 150°, 30 ml. of helium/min.)]. Amination at $-35°$ gave four peaks of which the first two, comprising about 40% of the total area, were ascribed to 2-chloro-5-methylaniline and 3-methyl-4-chloroaniline by comparison (retention times and infrared spectra) with the authentic materials. From the 10° reaction the chlorotoluidines and the third component were present, but the last peak was absent.

After the neutral layer was dried and freed of excess toluene, fractional distillation provided chlorotoluenes, 14.8 g. (67% yield),[51] n^{25}D 1.5219, b.p. 153–163°, lit.[55] boiling points for the authentic isomers fall in the range 159–162°. A sample from another experiment was analyzed.

Anal. Calcd. for C_7H_7Cl: Cl, 28.0. Found: Cl, 27.7.

A higher boiling fraction, 2.1 g., b.p. 112–136° (5 mm.), and residual material, 2.4 g., were also obtained.

Isomerization Studies. A cold solution of *o*-toluidine (6 g., 0.56 mole) and toluene (150 ml.) was added with stirring during 30 min. to a mixture of toluene (98 ml.), *o*-dichlorobenzene (24.7 g., 0.168 mole), aluminum chloride (22.4 g., 0.168 mole), and water (2 drops) at 10–12°. Ten minutes after the addition was started hydrogen chloride was slowly introduced into the reaction mixture. After an additional hour at 10–12° the reaction mixture was added to dilute hydrochloric acid, and then worked up according to the general procedure. Distillation gave *o*-toluidine, 5.84 g. (97.5% recovery), with no evidence (infrared spectroscopy) for the presence of the other isomers. The residue weighed 0.06 g.

By the same procedure, *p*-toluidine was obtained unchanged (96% recovery).

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[51] Based on trichloramine according to eq. 1.

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