responded to the intensity of this multiplet. Also the lower intensity of the methyl and methylene doublets for compound VII corresponded to the low intensity of the multiplet at $\delta = 4.98$ p.p.m. for $CH_2{=}C$.

There was also obtained 16 g. of *t*-butyl chloride, b.p. 50–54°, from experiment 9 in which 255 g. of crude, high-boiling product was obtained.

The phosphorus trichloride–vinylcyclohexene experiment was run in the batch process apparatus described above. A charge of 51.5 g. of vinylcyclohexene, freshly washed with ferrous sulfate solution and distilled over sodium and 385 g. of redistilled phosphorus trichloride, was flushed with nitrogen and then irradiated for 16 hr. at 55°. Unreacted reagents were removed by distillation at atmospheric pressure. Vacuum distillation yielded 20 g. of 1:1 product, b.p. 104–120° (4 mm.), $n^{20}D$ 1.5475. *Anal.* Calcd. for $C_8H_{12}Cl_3P$: Cl, 43.4; P, 12.6. Found: Cl, 42.5; P, 12.7. The higher boiling product left as a residue amounted to 4 g.

Phosphorus trichloride reactions with the olefins listed in Table II and with those reported above to yield little or no product were run in the batch apparatus in a manner similar to the experiments with isobutylene and vinylcyclohexene above except that product residues after removal of unreacted reagents were not distilled. An attempt to distill a portion of the phosphorus trichloride–vinyl acetate product under vacuum resulted in decomposition.

Amination of Alkylbenzenes with Trichloramine–Aluminum Chloride. Synthetic Utility and Theoretical Aspects[1,2]

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Abstract: Direct amination of monoalkylbenzenes with trichloramine in the presence of aluminum chloride provided *m*-alkylanilines as the predominant basic product. Yields varied from <5% for diphenylmethane to 53% for isopropylbenzene. *o*-Xylene gave a basic mixture consisting of 2,3-xylidine (57%) and 3,4-xylidine (43%). 3,5-Xylidine was obtained from *m*-xylene, and 2,5-xylidine from *p*-xylene. Pseudocumene provided a mixture of amines containing mainly 2,3,5-trimethylaniline. Only small amounts of mesidine were formed from mesitylene, in addition to 2,3,5-trimethylaniline. The amination reaction proves to be synthetically useful for the preparation of certain *m*-alkylanilines. Further mechanistic information, particularly in relation to steric factors, is provided for this novel reaction which is believed to proceed by σ-substitution.

The literature dealing with aromatic amination by halamines is quite sparse. Minisci and Galli[4] reported that amination of anisole with N-chloropiperidine and ferrous salt produces *p*-piperidinoanisole. Benzimidazoles are obtained from N-arylamidines by treatment with sodium hypochlorite and base.[5] The N-chloroamidine is presumed to be the intermediate involved in cyclization. Other pertinent references have been discussed previously.[6]

Recent reports from this laboratory revealed that direct amination of aromatic compounds with halamines in the presence of a Lewis acid catalyst represents a new method of aromatic substitution (σ-substitution) resulting in unusual orientation.[6,7] For example, toluene–trichloramine–aluminum chloride produced *m*-toluidine. The present study involves the alkylbenzene series with emphasis on synthetic utility and mechanistic aspects.

Results and Discussion

Reactions of trichloramine with alkylbenzenes were generally carried out in the presence of large amounts of aluminum chloride ($AlCl_3/NCl_3$ molar ratio of 2). A solution of trichloramine in *o*-dichlorobenzene was added slowly to a heterogeneous mixture of the catalyst and aromatic hydrocarbon at 10° (Table I). Benzene afforded aniline in 20% yield.

In the case of the monoalkylbenzenes, the corresponding *m*-alkylaniline constituted the principal basic product. This is in accord with the previous studies involving toluene.[6] The isolated amines are shown in the order of decreasing yield: *m*-isopropylaniline (*m*-cumidine) (53%), *m*-toluidine (36%), *m*-ethylaniline (31%), *m-sec*-butylaniline (29%), *m-n*-propylaniline (28%), *m-n*-butylaniline (18%), *m-t*-butylaniline (8%), *m*-cyclohexylaniline (<5%), 3-aminodiphenylmethane (<5%), and 3-aminobibenzyl (<5%).

With higher alkylbenzenes, the indicated results were obtained: 3,5-dimethylaniline (23%) from *m*-xylene; 2,5-dimethylaniline (22%) from *p*-xylene; 2,3-dimethylaniline (16%) and 3,4-dimethylaniline (12%) from *o*-xylene. Pseudocumene provided a mixture of bases containing mainly 2,3,5-trimethylaniline (13%). Amination of mesitylene led to formation of mesidine (2%) and 2,3,5-trimethylaniline (6%).

We have been unable to formulate a reasonable, over-all correlation between aromatic structure and yield. Various factors should be taken into account: resonance, induction, dielectric constant, solvation, polarity, etc. An important consideration may be the speed of the competing chlorination reaction which can destroy N-halamines.

$$3C_6H_5R + NCl_3 \xrightarrow{AlCl_3} 3ClC_6H_4R + 3HCl + NH_3 \quad (1)$$

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(1) Paper II, Aromatic Amination with Halamines: presented at the 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept. 1965.

(2) Taken largely from the M.S. Thesis (1965) of J. A. L.

(3) National Science Foundation Undergraduate Summer Fellow, 1964.

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

Table I. Amination of Alkylbenzenes[a]

	Principal basic product				
Aromatic reactant	Structure	Yield, %	B.p., °C. (mm.)		$n\text{D}^t$
			Found	Lit.	
Benzene	Aniline	20	54 (4)	75–77 (20)[b]	1.586^{20}[c]
Toluene	*m*-Toluidine	36	73 (5)	95–97 (16)[d]	1.568^{20}[e]
Ethylbenzene[f]	*m*-Ethylaniline	31	84 (5)	97–98 (8)[g]	1.557^{25}[h]
n-Propylbenzene	*m*-*n*-Propylaniline	28	92 (4)	107–110 (8)[g]	$1.542^{27.5}$
Isopropylbenzene	*m*-Isopropylaniline	53[i]	94–69 (6–7)	79–80 (3)[j]	$1.544^{27.5}$[k]
n-Butylbenzene	*m*-*n*-Butylaniline	18	100 (4)	124–125 (9)[g]	$1.534^{25.5}$
sec-Butylbenzene	*m*-*sec*-Butylaniline	29	97 (5)	120 (18)[l]	$1.536^{26.5}$
t-Butylbenzene	*m*-*t*-Butylaniline	8	100 (6)	83–84 (2)[j]	$1.510^{27.6}$
Diphenylmethane	3-Aminodiphenylmethane[m]	<5[n,o]	...	...	...
Cyclohexylbenzene	*m*-Cyclohexylaniline[m]	<5[n]	...	...	...
Bibenzyl	3-Aminobibenzyl[m]	<5[n]	...	...	...
o-Xylene	2,3-Dimethylaniline	16	82–86 (4)	221–222[p]	...
	3,4-Dimethylaniline	12	82–86 (4)	222–228[q]	...
m-Xylene	3,5-Dimethylaniline	23	83–85 (4)	67–70 (1.7)[r]	...
p-Xylene	2,5-Dimethylaniline	22	83 (4)	213–215[l]	...
Pseudocumene[f]	2,3,5-Trimethylaniline	13	82 (2)	...	...
Mesitylene[f]	Mesidine	2	...	230[s]	...
	2,3,5-Trimethylaniline	6	...	...	...

[a] $NCl_3/AlCl_3/o\text{-}C_6H_4Cl_2$/aromatic = 1:2:*ca.* 17.5: *ca.* 12.5, 10°, 90 min. [b] D. H. R. Barton and L. R. Morgan, *J. Chem. Soc.*, 622 (1962). [c] $n^{20}\text{D}$ 1.5863: "Tables for Identification of Organic Compounds," C. D. Hodgman, Ed., Chemical Rubber Publishing Co., Cleveland, Ohio, 1960, p. 158. [d] R. L. Russell, M. S. Thesis, Case Institute of Technology, 1964. [e] $n\text{D}^{20}$ 1.5686, see footnote *c*. [f] See the Experimental Section. [g] See ref. 16. [h] $n^{25}\text{D}$ 1.5575, authentic material. [i] Plus a small amount of a second basic component. [j] M. S. Carpenter, W. M. Easter, and T. F. Wood, *J. Org. Chem.*, **16**, 586 (1951). [k] $n^{20}\text{D}$ 1.5445, see footnote *j*. [l] R. R. Read, C. A. Hewitt, and N. R. Pike, *J. Am. Chem. Soc.*, **54**, 1194 (1932). [m] Product identification is based solely on infrared and n.m.r. analyses; 3-aminodiphenylmethane assignment is based solely on infrared analysis. [n] Based on crude product. [o] Excess *o*-dichlorobenzene was necessary to dissolve the aromatic reactant. [p] See footnote *c*, p. 159. [q] R. W. Cripps and D. H. Hey, *J. Chem. Soc.*, 14 (1943). [r] R. M. Lange, Ph.D. Thesis, Case Institute of Technology, 1964. [s] G. M. Hoop and J. M. Tedder, *J. Chem. Soc.*, 4685 (1961).

Table II. Proton Magnetic Resonance Data on Amine Products

	Chemical shifts, p.p.m.[a,b]					
Amine	Ar*H*	ArC*H*	RC*H*₂R	RC*H*₃	ArN*H*₂	Relative intensities
Aniline	6.1–7.25	...	...	...	3.25	5:2
m-Toluidine	5.8–6.8	2.1(s)	...	...	3.2 (s)	4:3:2
m-Ethylaniline	5.9–6.9	2.2 (q)	...	0.9 (t)	3.2 (s)	4:2:3:2
m-*n*-Propylaniline	5.9–6.9	2.2 (t)	1.3 (se)	0.6 (t)	3.15 (s)	4:2:2:3:2
m-Isopropylaniline	5.9–6.9	2.6(h)	...	1.1 (d)	3.2 (s)	4:0.9:6.1:2
m-*n*-Butylaniline	5.9–6.9	(Complicated spin–spin coupling)			3.2 (s)	4:2
m-*sec*-Butylaniline	5.9–6.9	2.3 (se)	1.5 (qi)	0.75 (t)/ 1.2 (d)	3.25 (s)	4:1:2:3/3:2
m-*t*-Butylaniline	5.9–6.9	...	...	1.1 (s)	3.2 (s)	4:9:2
m-Cyclohexylaniline[c]	6.1–7.1	(Complicated spin–spin coupling at 1.1–2.5)			4.4 (s)	
3-Aminobibenzyl[c]	6.2–7.3	2.85 (s)	...	...	3.55 (s)	8.6:4.2:2
2,3- and 3,4-Dimethylaniline	5.9–6.9	2.15 (s); 1.85 (s)	...	...	3.35 (s)	3:6:2
3,5-Dimethylaniline	5.9–6.4	2.15 (s)	...	...	3.35 (s)	3:6:2
2,5-Dimethylaniline	6.25–7.15	2.15 (s); 1.85 (s)	...	...	3.35 (s)	3:6:2
Mesidine[c]	6.5	1.9 (s); 2.2 (s)	...	...	3.2 (s)	2:3:6:2
2,3,5-Trimethylaniline[c]	6.1 (s); 6.2 (s)	1.9 (s); 2.2 (s)	...	...	3.2 (s)	2:3:6:2
3,5-Diethylaniline[c]	6.05–6.9	2.47 (q)	...	1.15 (t)	3.28 (s)	2.8:4:6:1.9

[a] Tetramethylsilane was used as external reference standard. [b] s, singlet; d, doublet; t, triplet; q, quartet; qi, quintet; se, sextet; h, heptet. [c] CCl_4 was used as solvent.

Various means were employed in characterizing the amine products, including elemental analysis, infrared and n.m.r. spectra, comparison with authentic material, boiling point, and derivatives. All of the anilines derived from monoalkylbenzenes exhibited infrared spectra characteristic of *meta* substitution.[8] Comparison with authentic material was made with aniline, *m*-toluidine, *m*-ethylaniline, the xylene products, and mesidine. An isomeric purity of >95% was generally indicated for the distilled aromatic amines.

For n.m.r. analyses of the *m*-alkylanilines, *m*-toluidine was used as a model. The observed spin–spin coupling pattern in the aromatic region was the same for all of the monoalkylanilines. Comparison of the coupling data for the alkyl side chains in the parent aromatic hydrocarbons with that for the amine products indicated the absence of skeletal rearrangement. The results are summarized in Table II.

In addition to the principal basic material, the amine fraction usually contained <10% of a higher boiling cut and <8% of distillation residue. The ethylbenzene reaction yielded a by-product which is believed to be 3,5-diethylaniline. Although the higher boiling substances were not generally studied, previous investigations of this fraction in the toluene reaction revealed the presence of isomeric chlorotoluidines.[6]

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(8) See ref. 2 for the detailed data.

This method for the direct amination of alkylbenzenes constitutes a preferred, one-step procedure for synthesis of the corresponding *m*-alkylanilines in certain cases. The best examples comprise *m*-isopropylaniline, *m-sec*-butylaniline, *m-n*-propylaniline, and *m-n*-butylaniline in which modest to fair yields (20–55%) resulted. *m-t*-Butylaniline presents a less favorable situation (8% yield). Of course, a number of the products are commercially available: aniline, *m*-toluidine, *m*-ethylaniline, the xylidines, and mesidine.

Presence of the aromatic amine functionality provides an opportunity for synthesis of various derivatives by replacement, *via* the diazo intermediate, with other atoms or groups, *e.g.*, hydroxyl, halogen, and cyano. This then represents a two-step pathway based on the aromatic hydrocarbon starting material. The *m*-alkylcarboxylic acids would then arise by a three-step sequence by way of the nitrile precursor. In many cases, classical literature procedures for the preparation of these amines and the corresponding replacement products require six to nine steps.[8] Clearly, σ-amination makes available a simple, improved route leading to a variety of *meta*-substituted aromatics.

Let us now turn our attention to the theoretical aspects. Valuable information relative to steric factors is provided by the isomer distribution from the *o*-xylene reaction. Of the basic product, about 57% was 2,3-dimethylaniline and about 43% comprised 3,4-dimethylaniline. Quantitative figures are available for a number of electrophilic substitutions in *o*-xylene. *t*-Butylation afforded 100% 1,2,4-substitution in the systems *t*-butyl bromide–stannic chloride–nitromethane and isobutylene–aluminum chloride–nitromethane.[9] In Friedel–Crafts isopropylation, isopropyl bromide–aluminum chloride–nitromethane yielded 54% of the 1,2,4-isomer and 46% of the 1,2,3-isomer, and propylene–aluminum chloride–nitromethane gave 60% of 1,2,4 and 40% of 1,2,3.[10]

If trichloramine were the aminating species in our studies, one would expect a steric factor slightly smaller than that of the *t*-butyl cation, *i.e.*, various studies indicate a somewhat greater bulk for methyl *vs.* chloro.[11] Predominant formation of the most hindered isomer from *o*-xylene amination suggests that steric factors are not high. Therefore, some other nitrogen-containing species in the reaction mixture is most likely the actual attacking entity. Possibilities that come to mind are dichloramine, chloramine, ammonia, and the corresponding amide anions, Cl_2N^-, $ClNH^-$, and NH_2^-. The nucleophiles might be formed as portrayed by the indicated examples

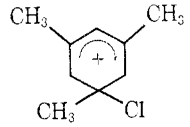
$$C_6H_5R + NCl_3 \xrightarrow{AlCl_3} ClC_6H_4R + HNCl_2 \qquad (2)$$

$$C_6H_5R + ClNH_2\cdots AlCl_3 \longrightarrow [ClC_6H_5R]^+ + [H_2NAlCl_3]^- \longrightarrow ClC_6H_4R + H_2NAlCl_2 + HCl \qquad (3)$$

All of these entities would be stronger nucleophiles than trichloramine.

For this novel reaction, a σ-substitution mechanism (addition–elimination)[12] has been advanced[6] entailing σ-complex formation, nucleophilic attack involving a nitrogen-containing entity, and then rearomatization *via* elimination.[13] Currently, we favor participation of chlorarenonium ion in this sequence.[13] Although several Lewis acids, including aluminum chloride, hydrogen chloride, and σ-complex, would be in competition for the nucleophile, apparently combination with the carbonium ion is energetically favored. The nature of certain of the amination reactions provides evidence for the presence of arenonium ions in these systems: 3,5-diethylaniline from ethylbenzene, and 2,3,5-trimethylaniline from mesitylene. Furthermore, the neutral fraction from mesitylene amination consisted of a complex mixture (g.l.p.c. analysis) indicating the occurrence of gross rearrangement and disproportionation.

Arguments against alternative mechanistic possibilities have been presented previously.[6] The nature of the mesitylene reaction provides additional evidence against direct electrophilic amination. Only 2% of mesidine was formed. It is clear that for a highly bulky attacking entity, *e.g.*, that in *t*-butylation, mesitylene, as well as *p*-xylene, is resistant to attack. However, such an adverse steric situation does not pertain to amination as illustrated by the *o*- and *p*-xylene data. On the assumption that a hydrogen *ortho* or *para* to the position of electrophilic attack is a requisite for σ-substitution, the poor result in mesitylene amination appears rational. The minor extent of reaction leading to mesidine may arise from the presence of a small amount of the energetically unfavorable form of the σ-complex I.



I (Cl^+ = electrophile)

On the other hand, perhaps direct electrophilic substitution is occurring to a slight degree.

There is good reason for believing that an N-chloroaromatic amine is not formed as an intermediate. If such a species were present, one would expect substantial nuclear chlorination through intramolecular rearrangement.[14] However, in all cases no more than minor amounts of chlorinated anilines were evident. 2-Chloro-5-methylaniline and 3-methyl-4-chloroaniline have been observed as by-products in toluene amination.[6] Nuclear halogen might be introduced in a side reaction by chlorination of the aromatic amine or *via* formation of small amounts of ArNHCl. Alternatively, chlorotoluenes, the major neutral product, may well undergo amination to a slight extent.

Experimental Section[15]

Warning: exercise the necessary precautions in working with halamines.

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(11) H. C. Yuan and R. Adams, *ibid.*, **54**, 4434 (1932); R. Adams and J. B. Hale, *ibid.*, **61**, 2825 (1939); R. W. Stoughton and R. Adams, *ibid.*, **54**, 4426 (1932).

(12) For other examples which apparently fit in this category, see P. B. D. de la Mare and R. Koenigsberger, *J. Chem. Soc.*, 5327 (1964); P. C. Myhre and G. S. Owen, Abstracts of Papers, 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept. 1965.

(13) The mechanistic aspects are treated more fully in a subsequent paper: P. Kovacic and J. A. Levisky, *J. Am. Chem. Soc.*, in press.

(14) R. S. Neale, R. G. Schepers, and M. R. Walsh, *J. Org. Chem.*, **29**, 3390 (1964).

(15) Melting points and boiling points are uncorrected. Elemental analyses were performed by Dr. Weiler and Dr. Strauss, Oxford, England, and Galbraith Laboratories, Knoxville, Tenn.

Table III. Elemental Analysis of *m*-Alkylanilines

R in *m*-$RC_6H_4NH_2$	Formula	Anal., % Calcd. C	H	N	Found C	H	N
n-Propyl	$C_9H_{13}N$	80.00	9.63	10.37	80.09	9.56	10.51
Isopropyl	$C_9H_{13}N$	80.00	9.63	10.37	80.12	9.51	10.44
n-Butyl	$C_{10}H_{15}N$	80.54	10.06	9.40	80.83	9.99	9.37
sec-Butyl	$C_{10}H_{15}N$	80.54	10.06	9.40	80.26	9.80	9.56
t-Butyl	$C_{10}H_{15}N$	80.54	10.06	9.40	80.59	10.18	9.59

Materials. Cumene, *t*-butylbenzene, and *o*-dichlorobenzene (containing 10% of the *para* isomer) were fractionally distilled from calcium hydride. The other reagents were high-purity commercial materials which were used as obtained. Gas chromatographic examination indicated that purity of the aromatic reagents was generally >99%. By this method mesitylene was shown to contain trace amounts of pseudocumene.

Analytical Procedure. Infrared analyses were made with Beckman IR-5A and IR-8 spectrophotometers on neat samples unless otherwise indicated. Gas chromatographic work was carried out on a homemade unit. The indicated columns (40–60 mesh) were used for analysis of the products from the monoalkylbenzenes, and *o*-, *m*-, and *p*-xylene: (1) 12 ft. × 0.25 in., Apiezon L (14%) on Chromosorb P (5% NaOH); (2) 6 ft. × 0.25 in., Ucon Polar 50 HB2000 (5%) on Chromosorb W (5% NaOH); (3) 12 ft. × 0.25 in., sodium dodecylbenzene sulfonate (20%) on Chromosorb W (5% NaOH). Separation of the *o*-xylidine isomers was effected with column 3.

Preparation of Trichloramine Solutions. A published procedure[6] (method B) was used with *o*-dichlorobenzene as solvent.

Amination of Alkylbenzenes with Trichloramine. The apparatus consisted of a 1-l., three-neck flask equipped with stirrer, condenser, thermometer, and dropping funnel. A cold solution of trichloramine (0.1 mole) in *o*-dichlorobenzene (200 ml.) was added with vigorous stirring during 30 min. to a heterogeneous mixture of alkylbenzene (1.25 moles) and aluminum chloride (0.2 mole) at 10°. After 1 additional hr. at 10°, the dark reaction mixture was stirred with a mixture of ice and dilute hydrochloric acid. After standing (usually overnight), the neutral organic phase was separated from the acidic, aqueous layer. Washing of the neutral layer with dilute hydrochloric acid, followed by ether extraction of the combined aqueous fractions, resulted in separation of the amine salt and any water-soluble material from the reaction mixture. On addition of 50% caustic to the aqueous fraction, a dark oil came to the surface. Just enough caustic was added to effect complete solution of the aluminum-containing precipitate. Ether extraction of the chilled mixture, followed by solvent removal, provided the crude amine product. Distillation was carried out through a Bantam Ware "Minilab" distillation apparatus at reduced pressure. The higher-boiling fraction comprised about 10% of the total basic product. In general distillation residue made up <8% of the basic material, except in the *t*-butylbenzene (14%) and mesitylene (12%) reactions. Yields are based on trichloramine. A minimum of two runs was made in each case; there was generally good agreement in the results.

Yield data and physical constants are shown in Table I. Elemental analyses for *m*-alkylanilines are presented in Table III.

Aromatic Amine Derivatives. A. Picrate. The picrates were prepared in ethanol and recrystallized from benzene: from *m*-*n*-propylaniline, m.p. 154–155° (lit.[16] m.p. 155°); from *m*-*n*-butylaniline, m.p. 143.5° (lit.[17] m.p. 144–145°).

B. Acetyl Derivative. This derivative of *m*-*n*-propylaniline, prepared with acetyl chloride, gave a melting point of 53° (lit.[18] m.p. 52–53°).

C. Conversion to Phenols. A solution of sodium nitrite (2.2 g.) in 10 ml. of water was added with stirring below 5° to a solution of the aromatic amine (0.03 mole) in 20 ml. of water and 3 ml. of concentrated sulfuric acid. The mixture was then brought slowly to 50° and maintained at that temperature until nitrogen evolution ceased. The reaction mixture, which contained a black oil, was poured slowly into a 20% sodium hydroxide solution. Ether extraction, followed by acidification of the basic fraction, afforded the phenol. After extraction with ether and removal of solvent, the crude product was subjected to gas chromatographic analysis (10 ft. × 0.25 in. column, Apiezon L (15%) on acid-washed Chromosorb P). The major component was collected and identified by comparison of the infrared spectrum to that of the authentic material (K & K Laboratories). The indicated derivatives were prepared: (a) *m*-isopropylphenol from *m*-isopropylaniline and (b) *m*-*t*-butylphenol from *m*-*t*-butylaniline.

3,5-Diethylaniline. Ethylbenzene was aminated in accordance with the general procedure. The undistilled, basic product consisted of ethylaniline (60%) (91% *meta* and 9% *ortho*) and diethylanilines (40%). The major component (74%) of the diethylaniline fraction is believed to possess the 1,3,5-structure on the basis of (1) infrared analysis, characteristic band at 850 cm.$^{-1}$; (2) n.m.r. spectrum (Table II); and (3) elemental analysis. *Anal.* Calcd. for $C_{10}H_{15}N$: C, 80.53; H, 10.07; N, 9.40. Found: C, 80.58; H, 10.23; N, 9.45.

2,3,5-Trimethylaniline. A. From Amination of Mesitylene. Amination of mesitylene according to the general procedure gave a mixture, b.p. 98–104° (10 mm.), consisting of mesidine and 2,3,5-trimethylaniline. The 2,3,5-trimethylaniline was separated by gas chromatography or crystallization at Dry Ice temperatures. After purification by recrystallization from petroleum ether, the solid melted at 38.5–39.5° (lit.[19] m.p. 38–39°). *Anal.* Calcd. for $C_9H_{13}N$: C, 80.00; H, 9.63; N, 10.37. Found: C, 79.88; H, 9.70; N, 10.47.

The n.m.r. spectral data are presented in Table II. The infrared spectrum exhibited an absorption maximum at 285 cm.$^{-1}$ characteristic of an isolated nuclear hydrogen.

The distilled mixture of amines was converted to the phenolic derivatives as described in a preceding section. The principal component, separated by g.l.p.c., possessed an infrared spectrum identical with that of authentic 2,3,5-trimethylphenol (K & K Laboratories).

B. From Amination of Pseudocumene. The standard procedure was followed yielding crude amines in 18% yield, b.p. 83° (2 mm.). Gas chromatography (8 ft. × 0.25 in. column, Carbowax 6000 on base-coated (5%) Chromosorb W, 60–80 mesh) provided the indicated components: (1) 2,3,5-trimethylaniline (75%), with infrared spectrum identical with that of the major product from mesitylene amination; (2) 2,4,5-trimethylaniline (16%), identified by comparison (infrared spectrum) with the authentic substance; (3) unidentified material (9%).

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