Amination of *m*-Dialkylbenzenes with Trichloramine–Aluminum Chloride[1]

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A variety of 3,5-dialkylanilines has been prepared by a convenient one-step procedure involving amination of *m*-dialkylbenzenes with trichloramine–aluminum chloride. The method proves to be satisfactory even when the *m*-dialkylbenzene is contaminated with the other isomers. Preparation of *meta*-enriched dialkylbenzene substrates is described. A σ-substitution (addition–elimination) mechanism is used to rationalize the observed orientation. Further evidence for involvement of a chlorarenonium intermediate was obtained from the *m*-xylene system. In most cases classical literature techniques for synthesis of 3,5-dialkylanilines entail two to six steps.

Prior reports from this laboratory reveal an unusual orientation resulting from amination of aromatic substrates with trichloramine in the presence of aluminum chloride catalyst. For example, the indicated transformations were observed: *m*-toluidine from toluene,[6] 3,5-xylidine from *m*-xylene,[7] *m*-chloroaniline from chlorobenzene,[8] and 3-aminobiphenyl from biphenyl.[9] Other pertinent, previous literature is treated elsewhere.[6-9]

The purpose of the present study was to investigate more fully the amination of *m*-dialkylbenzenes in this system. Our attention was focused primarily on the synthetic aspects with some consideration given to the mechanistic features. Furthermore, we were interested in carrying out the reaction with a mixture of *m*-dialkylbenzene contaminated with the other isomers.

Results and Discussion

Competitive amination of the xylenes with trichloramine–aluminum chloride revealed that *m*-xylene is six to eight times as reactive as the other isomers.[10] This observation indicated that the *meta* component could be selectively aminated in admixture with limited quantities of the isomeric hydrocarbons. In addition to the theoretical considerations, the rate difference assumes practical importance in a study of the *m*-dialkylbenzene series. We anticipated that for certain members it might prove laborious to obtain the substrate in a state of high purity. Hence, we limited ourselves to simple one- or two-step procedures for preparation of starting materials, and carried out the subsequent aminations even when as much as 20–30% of the *ortho* and *para* isomers was present.

Various procedures were used to provide the desired hydrocarbons (Table I). In the case of the xylenes, the commercially available isomeric mixture, containing 67% of the *meta* isomer, was used directly. For diethyl- and diisopropylbenzenes, fractional distillation of the purchased material (62–64% *meta*) resulted in a portion composed of 93–97% *meta*. The other starting materials were prepared by rearrangement of the *para* isomers. Isomerization of the *p*-alkyltoluenes was performed in toluene in order to minimize losses from disproportionation. Further *meta* enrichment was accomplished by subsequent rectification when necessary and feasible. Our aim was to furnish in every case a substrate containing at least 65% of the *meta* isomer. Isomeric purity fell in the range of 67–97% for the homologous series.

TABLE I

meta ENRICHMENT OF DIALKYLBENZENES[a]

C_6H_4RR'		*meta* content, %	
R	R'	Before enrichment	After enrichment
Me	Me	67	..[b]
Me	Et	0[c]	86[d]
Me	*i*-Pr	0[c]	80[d]
Me	*t*-Bu	0[c]	96[d,e]
Et	Et	64	97[f]
i-Pr	*i*-Pr	62	93[f]
t-Bu	*t*-Bu	0[c]	80[e,g]

[a] See the Experimental Section. [b] No enrichment performed. [c] *para* isomer was the starting material. [d] Isomerization effected in toluene. [e] Further *meta* enrichment accomplished by fractional distillation after isomerization. [f] Enriched by distillation. [g] Isomerization performed in *t*-butylbenzene.

Amination was effected at 0 to $-10°$ with trichloramine/aluminum chloride/dialkylbenzene in 0.1:0.2:1 molar ratio (Table II). The desired 3,5-dialkylanilines were formed in yields of 6–26%, usually in the 20–26% range. Simple work-up procedures were sufficient to attain purities of >90% in all cases. Characterization was accomplished by elemental analyses, infrared and nmr (Table III) spectra, preparation of amide (Table IV) and phenolic (Table V) derivatives, and in a few cases, comparison with authentic material.

Some attention was devoted to the effect of variation in temperature (Table VI) and concentration of the *m*-dialkylbenzene (Table VII). In earlier studies with toluene,[6] it was noted that optimum yields resulted at $-35°$. Similarly in our investigations with *m*-xylene and *m*-ethyltoluene, best results were observed at $-30°$ in comparison with reactions carried out at higher temperatures. In contrast, lower temperatures in the case of diisopropyl- and di-*t*-butylbenzenes produced no enhancement in the yield of desired amine, as a result of the formation of more complex reaction products. It is interesting that the *meta* content of the isomeric substrate could be reduced to the 70–80% level without appreciably affecting the yield of 3,5-dialkylaniline.

The basic by-products which appeared from the amination reactions (Table II) originate *via* several

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

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

(8) P. Kovacic and J. F. Gormish, *ibid.*, **88**, 3819 (1966).

(9) P. Kovacic and A. K. Harrison. *J. Org. Chem.*, **32**, 207 (1967).

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

TABLE II

AMINATION OF *m*-DIALKYLBENZENES[a]

m-C_6H_4RR' R	R'	Yield, % Crude	Yield, % Purified	Bp, °C (mm)	Formula	Calcd, % C	Calcd, % H	Calcd, % N	Found, % C	Found, % H	Found, % N
Me	Me	25[b]	24.2	68 (0.5)[c]	...	...	...	...	...	...	...
Me	Et	27[d]	25.6	86 (0.9)	$C_9H_{13}N$	80.00	9.63	10.37	79.91	9.63	10.19
Me	*i*-Pr	29[e]	20	87 (1.1)	$C_{10}H_{15}N$	80.53	10.06	9.39	80.29	10.13	9.14
Me	*t*-Bu	22[f]	20	85 (1.4)[g]	$C_{11}H_{17}N$	80.98	10.43	8.59	80.73	10.55	8.67
Et	Et	27[h]	22.4	88 (0.7)	$C_{10}H_{15}N$	80.53	10.07	9.40	80.60	10.12	9.34
i-Pr	*i*-Pr	20[i]	8	90 (0.8)	$C_{12}H_{19}N$	81.35	10.73	7.90	81.45	10.81	7.81
t-Bu	*t*-Bu	8[j]	5.9[k,l]	...	...	...	...	...	...	...	...

[a] $NCl_3/AlCl_3/o$-$C_6H_4Cl_2$/total aromatic substrate = 0.1:0.2:20:10; see general procedure. [b] Contained 2,5-dimethylaniline (0.8% yield). [c] Lit. bp 67–70° (1.7 mm): R. M. Lange, Ph.D. Thesis, Case Institute of Technology, 1964. [d] Contained 2-methyl-5-ethylaniline (1.4% yield). [e] Contained *m*-toluidine (6.1% yield) and 8-amino-*p*-cymene (2.7% yield). [f] Contained 2-methyl-5-*t*-butylaniline (2% yield); see ref 10. [g] Lit. bp 133–134° (17 mm): B. M. Dubinin and N. E. Kozhevnikova, *J. Gen. Chem. USSR*, **21**, 731 (1951). [h] Contained 2,5-diethylaniline (4.6% yield). [i] Contained *m*-cumidine, bp 69° (0.6 mm) (10% yield), and 2,5-diisopropylaniline (<1% yield). [j] Contained *m*-*t*-butylaniline (2.1% yield). [k] Not highly pure. [l] Crystallized material, mp 53–53.5° [lit. mp 53–53.5°: N. L. Allinger, H. M. Blatter, L. A. Freiberg, and F. M. Karkowski, *J. Am. Chem. Soc.*, **88**, 2999 (1966)].

TABLE III

PROTON MAGNETIC RESONANCE DATA FOR 3,5-DIALKYLANILINES

1,3,5-$H_2NC_6H_3RR'$ R	R'	Chemical shifts, δ (ppm)[a,b] ArH	ArCH	ArCHR	RCH$_3$	ArNH$_2$	Relative intensities
Me	Me	5.9–6.4	2.15 (s)	...	...	3.35 (s)	3:6:2
Me	Et[c]	5.91–6.4	2.15 (s)	2.25–2.7 (q)	0.92–1.4 (t)	3.32 (s)	2.6:5[d]:3:2
Me	*i*-Pr[c]	6.05–6.45	2.0 (s)	2.2–2.9 (h)	0.09–1.35 (d)	3.20 (s)	3:3:1.1:6:2
Me	*t*-Bu	6.2–6.6	2.22 (s)	...	1.24 (s)	3.42 (s)	3:3:9:2
Et	Et[e]	6.05–6.9	...	2.47 (q)	1.15 (t)	3.28 (s)	2.8:4:6:1.9
i-Pr	*i*-Pr[e]	6.06–6.68	...	2.3–3.0 (h)	0.9–1.37 (d)	3.29 (s)	2.7:2.4:13:2.1

[a] Tetramethylsilane was used as an external reference standard. [b] s, singlet; d, doublet; t, triplet; q, quartet; h, heptet. [c] CCl_4 solvent. [d] ArCH and ArCHR combined. [e] Tetramethylsilane solvent.

TABLE IV

3,5-DIALKYLACETANILIDES

R	R'	Mp, °C Found	Mp, °C Lit.[a]	Formula	Calcd, % C	Calcd, % H	Calcd, % N	Found, % C	Found, % H	Found, % N
Me	Me	140	140–140.5	$C_{10}H_{13}NO$	73.60	7.98	8.59	73.58	8.03	8.51
Me	Et	110	107–109	$C_{11}H_{15}NO$	74.60	8.48	7.91	74.75	8.60	7.98
Me	*i*-Pr	85.5–86	86–87	$C_{12}H_{17}NO$	75.40	8.90	7.33	75.19	8.85	7.46
Me	*t*-Bu	141.5–142	...	$C_{13}H_{19}NO$	76.10	9.27	6.83	75.97	9.33	6.90
Et	Et	115–115.5	...	$C_{12}H_{17}NO$	75.40	8.90	7.33	75.52	8.90	7.48
i-Pr	*i*-Pr	97–99	...	$C_{14}H_{21}NO$	76.71	9.59	6.40	76.61	9.45	6.42

[a] See E. C. Horning and M. G. Horning, *J. Am. Chem. Soc.*, **69**, 1907 (1947); E. C. Horning, M. O. Denekas, and R. E. Field, *J. Org. Chem.*, **9**, 547 (1944).

TABLE V

PHENOLS FROM 3,5-DIALKYLANILINES[a]

1,3,5-$H_2NC_6H_3RR'$ R	R'	3,5-Dialkylphenol mp, °C Found	3,5-Dialkylphenol mp, °C Lit.
Me	Et	50[b]	51–52[c]
Me	*i*-Pr	46–49[d,e]	50–50.5[f]
Me	*t*-Bu	...[d,g]	...
Et	Et	74–75	76–77[h]
i-Pr	*i*-Pr	...[d]	...

[a] See the Experimental Section. [b] Identified by comparison of the infrared spectrum with that published: R. A. Friedel, *J. Am. Chem. Soc.*, **73**, 2881 (1951). [c] E. C. Horning, *ibid.*, **67**, 1421 (1945). [d] Identified by comparison with authentic material. [e] R. J. Hopper, Ph.D. Thesis, Case Institute of Technology, 1966. [f] M. S. Carpenter and W. M. Easter, *J. Org. Chem.*, **20**, 401 (1955). [g] Bp 245° (740 mm) [lit. bp 127° (11 mm)]: footnote *g*, Table II. [h] Z. P. Aleksandrova, *J. Gen. Chem., USSR*, **12**, 522 (1942); *Chem. Abstr.*, **37**, 2723 (1943).

TABLE VI

EFFECT OF TEMPERATURE ON YIELD OF 3,5-DIALKYLANILINE[a]

C_6H_4RR' R	R'	% *meta*	Temp, °C	3,5-Dialkylaniline yield, % Crude	3,5-Dialkylaniline yield, % Pure
Me	Me	67	−30	30.4	29.8
Me	Me	67	0	25	24.2
Me	Et	100	−30	27	24.8
Me	Et	100	25	17.7	16.6
i-Pr	*i*-Pr	62	−30	28[b]	3.7
i-Pr	*i*-Pr	62	0	22[b]	7.7
t-Bu	*t*-Bu	80	−30	13.3[b]	5
t-Bu	*t*-Bu	80	0	8[b]	5.9

[a] $NCl_3/AlCl_3/o$-$C_6H_4Cl_2$/total aromatic substrate = 0.1:0.2:20:10. [b] Product not distilled.

routes. 2,5-Dialkylanilines, generated in <2% yield, were derived from *p*-dialkylbenzenes originally present or arising from isomerization. In one of our earlier investigations *p*-xylene was converted to 2,5-xylidine.[7] Disproportionation proved to be an important factor with certain of the hydrocarbons which bear an isopropyl or *t*-butyl group. For instance, cymene yielded *m*-toluidine (6%), diisopropylbenzene furnished *m*-cumidine (10%) as the predominant amine product, and di-*t*-butylbenzene gave *m*-*t*-butylaniline. Disproportionation products have also been observed in related studies.[7,10] Amination of cymene and diisopropylbenzene afforded minor amounts of side-chain amine. This intriguing amination of an alkane structure is described elsewhere in detail for *p*-cymene.[11]

(11) See Table VII, footnote *c*.

TABLE VII

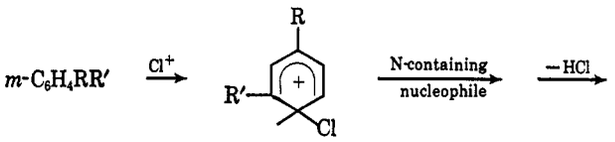
EFFECT OF *m*-DIALKYLBENZENE CONTENT ON THE YIELD OF 3,5-DIALKYLANILINE[a]

C_6H_4RR'		%	3,5-Dialkylaniline yield, %	
R	R'	*meta*	Crude	Pure
Me	Me[b]	100	23	22.3
Me	Me	67	25	24.2
Me	*i*-Pr[c]	100	26	18.7
Me	*i*-Pr	80	26	21
Me	*i*-Pr	71	29	20
Et	Et	97	27	22.4
Et	Et	81	25	21.5
Et	Et	72	23	19.3
Et	Et	65	20	15.8
i-Pr	*i*-Pr	92	22[d]	7.7
i-Pr	*i*-Pr	62	21[d]	6.7

[a] $NCl_3/AlCl_3/o\text{-}C_6H_4Cl_2$/total aromatic substrate = 0.1:0.2:20:10, 0°. [b] See ref 7. [c] See P. Kovacic and R. J. Hopper, *Tetrahedron*, in press. [d] Product not distilled.

Distillation residue made up less than 10% of the basic material in every case.

A σ-substitution (addition–elimination) mechanism[10] has been advanced for the amination reaction 1 (illustrated with *m*-dialkylbenzene). Although the nature



3,5-dialkylaniline (1)

of the nucleophile is not known with certainty, we currently prefer NCl_2^- as a working hypothesis.[12]

Relative rate studies provide good evidence for intermediacy of a σ complex as part of the rate-determining step.[10] Two species have been considered for the electrophilic attack, the proton[6] and chloronium ion.[7,10] Mounting evidence lends credence to the latter postulate.[8,10] The unlikelihood that protonation plays a vital role is corroborated by experiments with the xylenes.

A mixture of xylene (*ortho/meta/para* = 19:67:14) with aluminum chloride was exposed to excess hydrogen chloride so as to favor formation of the protoarenonium ion. Subsequent to amination with trichloramine, analysis of the ensuant xylidines revealed 76% of the 3,5 isomer in marked contrast to the value of 97% obtained from the general procedure. One is led to the conclusion that protonation converts the aromatic substrate to an inactive form. It is well established that of the three isomers the *meta* undergoes this transformation with greatest facility.[13] Thus, the net effect is an increase in the ratio of (*o*- + *p*-)/*m*-xylene in the system. Apparently the free hydrocarbon suffers initial attack by chloronium ion in the amination sequence. The decreased yield of crude amine in the presence of hydrogen chloride can be rationalized by the known decomposing action of acid upon trichloramine.[14]

This novel method possesses marked synthetic utility for most of the 3,5-dialkylanilines in this series. Although the yields are generally modest (20–30%), the procedure consists of a simple, one-step amination employing readily available starting materials. The advantage is further enphasized by comparison with literature preparations entailing classical techniques. Horning and co-workers made a number of 3-methyl-5-alkylanilines, *e.g.*, methyl, ethyl, and isopropyl, in the form of the acetanilide derivatives.[15] The six-step pathway resulted in yields of about 5%. 3-*t*-Butyl-5-methylaniline has been prepared in less than 10% yield by a six-step method.[16] Recently Allinger and co-workers described the conversion of 3,5-di-*t*-butyltoluene into 3,5-di-*t*-butylaniline (52% yield) in two steps,[17] which appears to be the method of choice for relatively large quantities.

(12) P. Kovacic and M. K. Lowery, *Chem. Commun.*, 651 (1966).
(13) D. A. McCaulay, B. H. Shoemaker, and A. P. Lien, *Ind. Eng. Chem.*, **42**, 2103 (1950).
(14) W. A. Noyes, *J. Am. Chem. Soc.*, **42**, 2173 (1920).

Experimental Section

Materials.—Technical *o*-dichlorobenzene was fractionally distilled from calcium hydride. The reagents were high-purity commercial materials which were used as obtained, unless otherwise specified. Sources for the various authentic materials are indicated: 3-*t*-butyl-5-methylphenol, K & K Laboratories; *p*-diethylbenzene, Aldrich Chemical Co.; *p*-ethyltoluene, Chemical Procurement Laboratories; 2,5- and 3,5-xylidines, Eastman Organic Chemicals. *m*-Diethylbenzene (Aldrich Chemical Co.) and *m*-ethyltoluene (Chemical Procurement Laboratories) were used for determination of isomer distributions. We are grateful to Hooker Chemical Co. for 3,5-diisopropylphenol, to Dr. Roger Hopper for 8-amino-*p*-cymene and 7-amino-*p*-diisopropylbenzene, and to Mr. Joseph Levisky for *m*-cumidine. *p*-Di-*t*-butylbenzene was obtained in 61% yield by the method of Fieser,[18] mp 74° (lit. mp 75°,[19] 77–79°[18]).

Analytical Procedures.—Infrared spectra were obtained with Beckman IR-5A or IR-8 spectrophotometers or a Perkin-Elmer Model 337 Infracord on neat samples unless otherwise indicated. Spectra of the reaction products and authentic materials were taken after purification by glpc. Gas chromatographic work was carried out on an Aerograph A-90-P or Perkin-Elmer Model 800 with the indicated columns: (A) 6 ft × 0.25 in., Apiezon L (14%) on Chromosorb P (30–60 mesh; 5% NaOH); (B) 20 ft × 0.25 in., Bentone-34 (9.5%) and Dow Corning silicone oil 550 (4.5%) on Chromosorb P (60–80 mesh), (C) 6 ft × 0.25 in., Carbowax 6000 (20%) on Chromosorb W (35–60 mesh) (5% NaOH); (D) 5 ft × 0.25 in., Carbowax 20M (15%) on Chromosorb W (35–60 mesh, 5% NaOH); (E) 11 ft × 0.25 in., Bentone-34 (5%) and dioctyl phathalate (5%) on firebrick (60–80 mesh); (F) 10 ft × 0.25 in., Apiezon L (15%) on Chromosorb P (60–80 mesh); (G) 5 ft × 0.25 in., Apiezon N (10%) on Chromosorb G (60–80 mesh). The basic products were separated and collected by means of the indicated columns: column A, xylidines, 3-methyl-5-ethylaniline, and 3-methyl-5-isopropylaniline; column C, 3,5-diethylaniline; column D, diisopropylanilines, 3-methyl-5-*t*-butylaniline, and 3,5-di-*t*-butylaniline. Analysis of the xylene substrate was effected with column E, *t*-butyltoluenes with column G, and cymenes and diethylbenzenes with column B. Nmr spectra were obtained with a Varian A-60 or A-60A instrument. Galbraith Laboratories, Knoxville, Tenn., performed the elemental analyses. Melting points and boiling points are uncorrected.

Meta Enrichment of Dialkylbenzenes. A. Isomerization.—Anhydrous aluminum chloride (0.15 mole) and toluene (1 mole) were stirred for 2 hr at 25° while a stream of hydrogen chloride was passed through the mixture. After rapid addition of the *p*-dialkylbenzene (0.35 mole), stirring was continued for an additional 10 min. The dark reaction mixture was poured into ice and dilute hydrochloric acid, and the *meta*-enriched hydrocarbon was separated by fractional distillation. *t*-Butylbenzene was substituted for toluene in the rearrangement of *p*-di-*t*-butylbenzene. In some cases (Table I) further *meta* enrichment

(15) See Table IV, footnote *a*.
(16) Footnote *g*, Table II.
(17) Footnote *l*, Table II.
(18) L. F. Fieser, "Organic Experiments," D. C. Heath and Co., Boston, Mass., 1965, p 184.
(19) Handbook of Chemistry and Physics, C. D. Hodgman, Ed., 39th ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1957–1958, p 776.

was realized by subsequent fractionation of the dialkylbenzene product.

In the cymene case an 85% recovery was realized of material possessing a *meta/para* ratio of 4:1. From *p*-di-*t*-butylbenzene, the composition was 52% *meta* and 48% *para*, with a 10% loss to disproportionation. In a literature report[20] involving different conditions the same isomer distribution was found, but the loss was 50%.

B. Distillation.—*meta* enrichment of the dialkylbenzene fractions was accomplished with a 36 × 0.75 in. column packed with glass helices and equipped with a variable take-off head.

Preparation of Trichlormine Solution.—A published procedure (method B) was used with *o*-dichlorobenzene as solvent.[6] Positive halogen analysis was carried out as previously described.[6] *Caution, use the necessary precautions when working with N-halamines.*

Amination of Dialkylbenzenes. General Procedure.—The apparatus consisted of a 1-l., three-necked flask equipped with a mechanical stirrer, thermometer, condenser, dropping funnel, and drying tube. The *meta*-enriched dialkylbenzene (1 mole) was cooled to 0° which was the temperature maintained throughout the reaction. Aluminum chloride (0.2 mole) was added in one portion producing an orange-brown, heterogeneous mixture and a slight temperature rise. A cold solution of trichloramine (0.1 mole) in *o*-dichlorobenzene was added dropwise into this mixture with stirring. After addition of the trichloramine (approximately 30 min) and subsequent mixing (30 min), the contents were stirred into a mixture of ice and dilute hydrochloric acid. After standing the organic layer was separated from the aqueous phase and treated twice with 100-ml portions of dilute hydrochloric acid. Following ether extraction of the combined aqueous fractions, treatment of the acid solution with cold, 50% sodium hydroxide liberated the free amine. Just enough base was added to cause dissolution of the amphoteric, aluminum-containing precipitate. The amine was extracted with ether and dried over anhydrous sodium sulfate. Evaporation of the solvent on the steam cone yielded the crude basic product. Distillation was carried out through a Bantam Ware "Minilab" distillation apparatus under nitrogen at reduced pressure. Duplicate runs in all cases gave good agreement in results. The yields are based on an equimolar relationship between the distilled product and trichloramine.

The distilled amine mixtures were further purified by fractionation under reduced pressure through a 25-plate spinning-band column. In all cases the 3,5-dialkylanilines were obtained in >90% purity. The infrared spectra exhibited absorption maxima near 697 and 828 cm^{-1} characteristic of 1,3,5-substitution.[21]

Amine Derivatives. A. Acetanilides.—The acetanilide was prepared by dissolving 0.5 g of the freshly distilled amine in 25 ml of 5% hydrochloric acid. Portions of 5% sodium hydroxide were added until the solution became turbid. The turbitidy was removed by a small amount of 5% hydrochloric acid followed by addition of 5 ml of acetic anhydride with swirling. After a solution of 5 g of sodium acetate trihydrate in 5 ml of water was introduced in one portion, the resulting white crystals were isolated and recrystallized from 95% ethanol.

B. Phenolic Derivative.—The diazonium acid sulfate was formed by addition of a solution of sodium nitrite (1.4 g) in 7 ml of water to the aromatic amine (0.015 mole) in 2 ml of concentrated sulfuric acid and 14 ml of water. The addition was carried out at 3° and discontinued when a positive test for nitrous acid by starch–potassium iodide paper persisted. The resulting dark red diazonium mixture was warmed to 25° and 2 g of urea was added to destroy the excess nitrous acid. After the evolution of nitrogen ceased, the mixture was warmed to 55°, whereupon an oil separated. The system was made basic with 20% caustic, ether was added, and the layers were separated, The basic fraction was acidified with dilute hydrochloric acid. After extraction of the crude phenol with ether and subsequent removal of solvent, the product was subjected to glpc analysis (column F). The major component was collected and identified (Table IV).

2,5-Dialkylanilines.—To a solution of the *p*-dialkylbenzene (0.13 mole) in 20 ml of acetic anhydride and 26 ml of glacial acetic acid, 12 g of 90% nitric acid was added dropwise while the temperature was maintained below 50° by cooling. After 24 hr of stirring the product was poured into water and the yellow, organic portion was separated from the aqueous layer. The crude nitro compound was dissolved in 200 ml of 95% ethanol and reduced with hydrogen at 3 atm with 0.15 g of palladium-on-charcoal catalyst. After hydrogenation the solution was filtered and freed of ethanol by evaporation. The major component of the residual amine was collected by glpc (column A) and compared with the corresponding 2,5-dialkylaniline obtained from amination: 2,5-diethylaniline from diethylbenzene, and 2,5-diisopropylaniline from diisopropylbenzene.

Effect of Hydrogen Chloride on Xylene Amination.—The apparatus consisted of a 1-l., three-neck flask equipped with stirrer, thermometer, condenser, drying tube, and gas inlet. Hydrogen chloride was passed through a mixture of xylene (*ortho/para* = 20:80) (1 mole) and aluminum chloride (0.25 mole) for 11 hr at 50°. An aliquot[22] on treatment with water and subsequent infrared analysis revealed the composition, *ortho/meta/para* = 19:67:14.

Trichloramine (0.08 mole) in *o*-dichlorobenzene was added to the reaction mixture at 0–5° during 30 min. After an additional 30 min, work-up provided crude xylidines (13.4%):3,5-xylidine (76%), 2,5-xylidine (22%), and *m*-toluidine (2%).

In a control experiment, amination of xylene possessing the isomeric make-up, *ortho/meta/para* = 19:67:14, under standard conditions, in the absence of added hydrogen chloride, gave crude xylidines (23%). The base consisted of 3,5-xylidine to the extent of 97%.

Registry No.—*m*-C_6H_4RR' (R = Me, R′ = Me), 108-38-3; (R = Me, R′ = Et), 620-14-4; (R = Me, R′ = *i*-Pr), 535-77-3; (R = Me, R′ = *t*-Bu), 1075-38-3; (R = Et, R′ = Et), 141-93-5; (R = *i*-Pr, R′ = *i*-Pr), 99-62-7; (R = *t*-Bu, R′ = *t*-Bu), 1014-60-4; 1,3,5-$H_2NC_6H_3RR'$ (R = Me, R′ = Me), 108-69-0; (R = Me, R′ = Et), 7544-53-8; (R = Me, R′ = *i*-Pr), 7544-54-9; (R = Me, R′ = *t*-Bu), 6399-08-2; (R = Et, R′ = Et), 1701-68-4; (R = *i*-Pr, R′ = *i*-Pr), 7544-57-2; *m*-$C_6H_3RR'NHCOCH_3$ (R = Me, R′ = Me), 2050-45-5; (R = Me, R′ = Et), 7544-58-3; (R = Me, R′ = *i*-Pr), 7544-59-4; (R = Me, R′ = *t*-Bu), 7544-60-7; (R = Et, R′ = Et), 1701-67-3; (R = *i*-Pr, R′ = *i*-Pr), 7544-61-8; C_6H_4RR' (R = *t*-Bu, R′ = *t*-Bu), 2380-36-1.

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(22) Analysis of the entire reaction mixture in another experiment gave the same result as for the aliquot.