Lithium Metal in the α Butylation of Dimethylaniline[1a]

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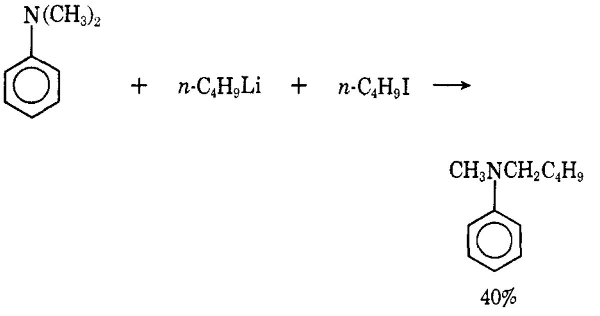
The use of lithium metal in place of *n*-butyllithium as a reagent in the direct butylation of N,N-dimethylaniline was studied. *n*-Butyl halides react with lithium in dimethylaniline to give the normally competing products in α alkylation, N-methyl-N-(1-pentyl)aniline and *n*-octane. Trace amounts of α-amine butylation were observed with 1-chlorobutane; none was reported in previous reactions with butyllithium. Bromobutane with lithium gave less alkylation and more Wurtz product than was observed with alkyllithium reagents. However, yields of N-methyl-N-(1-pentyl)aniline were 62–68% in the reactions of 1-iodobutane. An additional compound, N-methyl-N-(1-butyl)aniline, was observed in small quantities in chloro- and bromobutane reactions. The formation of *n*-butyllithium in the solvent dimethylaniline was demonstrated in the chloro and bromo reactions. Slow room temperature conversion of dimethylaniline–*n*-butyllithium mixtures into aromatic ring metalated products was evident from reaction with hexafluoroacetone.

Alkylation on carbon of a tertiary amine was recently observed in the reaction of N,N-dimethylaniline with iodobenzene and *n*-butyllithium, which produced N-methyl-N-benzylaniline and N-methyl-N-(1-pentyl)aniline.[2] Subsequent studies have demonstrated that this reaction (1) is limited to the α position of the amine,[3,4] (2) will occur with simple aliphatic amines as well as with aniline derivatives,[4] and (3) takes place when aliphatic iodides or bromides, but not chlorides, replace the original aryl halide.[5] Furthermore, investigations aimed at clarifying the reaction mechanism indicate that the reaction occurs by a direct substitution which, in most cases, does not involve α carbanion,[6] quaternary ammonium salt,[3,4] carbene, or benzyne intermediates.[7]

These alkylations (*e.g.*, eq 1) are clearly in completition with Wurtz coupling,[2-5] and the product distributions are influenced by halogen–metal interchange.[2,3,5] The diversity of the possible reactions, the question of the stability of organolithium compounds in tertiary amine solvents, and the increase in amine α alkylation with a decrease in competing or diluting solvents[3,5] led to the current investigation of organolithium generation in pure, anhydrous, tertiary amines.



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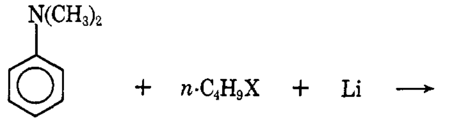


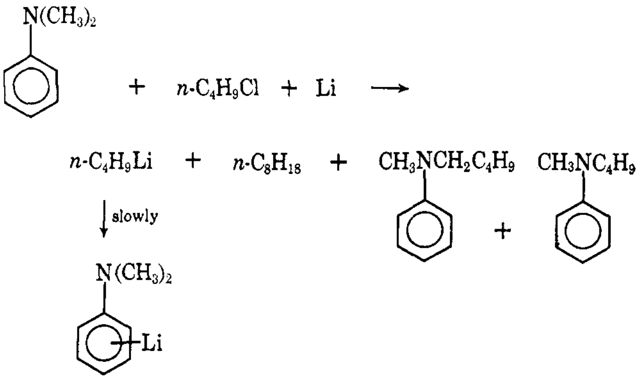
(2)

N,N-Dimethylaniline was chosen as solvent and *n*-butyl halides as the organolithium generating species (eq 2) because of the availability of pertinent data from previous related studies.[2-5]

Results and Discussion

Each of the alkyl halides, 1-chloro-, 1-bromo-, and 1-iodobutane, was allowed to react with lithium metal in N,N-dimethylaniline. Enough alkyl halide was used in each case to allow for both *n*-butyllithium generation and amine α alkylation or other carbanion consuming reactions. N,N-Dimethylaniline was used in a considerable excess to provide both reactant and supporting solvent.

1-Chlorobutane reactions furnished the principal evidence for *n*-butyllithium formation. Initial yields of the measured reaction products were quite low despite the rapid disappearance of lithium metal.



After 24 hr, *n*-octane was the major product with 3% yield, while the α-alkylation product, N-methyl-N-(1-pentyl)aniline, was less than 1% although initially formed quite rapidly. N-Methyl-N-(1-butyl)aniline, a product not observed previously in similar reactions, was formed by the chlorobutane–lithium reaction. Initial N-(1-butyl) formation was less than N-(1-pentyl) production, but exceeded the yield of that compound after 24 hr. Thereafter, the N-(1-butyl) product continued to form slowly. These products accounted for less than 6% of the starting amounts of alkyl halide or lithium metal. The remaining material was in the form of organolithium compound.

Addition of 1-iodobutane to the 1-chlorobutane reaction mixture after 24 hr increased the formation of N-methyl-N-(1-pentyl)aniline, which varied with the tem-

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[2] A. R. Lepley and A. G. Giumanini, *Chem. Ind.* (London) 1035 (1965).

[3] A. R. Lepley and A. G. Giumanini, *J. Org. Chem.*, **31**, 2055 (1966).

[4] A. R. Lepley and W. A. Khan, *ibid.*, **31**, 2061 (1966).

[5] A. R. Lepley and W. A. Khan, *ibid.*, **31**, 2064 (1966).

[6] A. R. Lepley, W. A. Khan, A. B. Giumanini, and A. G. Giumanini, *ibid.*, **31**, 2047 (1966).

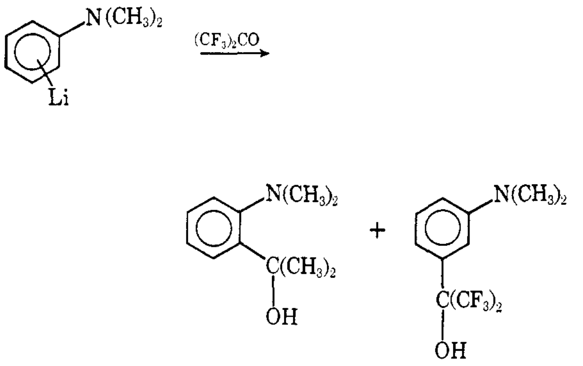
[7] A. R. Lepley, A. G. Giumanini, A. B. Giumanini, and W. A. Khan, *ibid.*, **31**, 2051 (1966).

TABLE I
N-METHYL-N-(1-PENTYL)ANILINE PRODUCTION FROM THE REACTIONS OF 1-HALOALKANES WITH LITHIUM METAL IN N,N-DIMETHYLANILINE

	Yield, %			
		n-C_4H_9I added[a]		Addition
Halide (X)	24 hr	26 hr	28 hr	temp, °C
Cl	<1	21	22	26–28
Cl	<1	30	36	0
Br	6	8	13	0
I	66	64	66	0

[a] Added immediately after removal of 24-hr sample

perature of iodide addition (Table I), to 50–90% of the amounts previously obtained[3,5] when n-butyllithium in hexane was allowed to react directly with iodobutane in dimethylaniline. Thus, the chlorobutane reaction mixture acted as if it contained a significant amount of n-butyllithium. Also, the mixture from the chlorobutane reaction, after 7 days, was treated with hexafluoroacetone and gave almost quantitative yields of o-and m-dimethylaminophenylbis(trifluoromethyl)carbinol (eq 3). Normally, metalation of N,N-dimethylaniline with n-butyllithium in hexane requires several hours of reflux.[6] The 13:1 ratio of these products, *ortho*: *meta*, was very close to the hydrogen acidities of N,N-dimethylaniline observed on potassium amide catalyzed deuterium exchanges in liquid ammonia at 25°.[8] However, these room temperature results were considerably higher than the 5:1 ratio observed after 24 hr in refluxing hexane.[6] The equilibrium established therefore is highly dependent upon temperature or solvent. Since metalated dimethylaniline was ineffectual as a base in the α-alkylation reaction,[6] the current results are an indication of excellent conversions of chlorobutane into n-butyllithium in N,N-dimethylaniline.



(3)

1-Bromobutane and lithium metal gave a considerable increase in secondary reactions of the initially formed n-butyllithium. n-Octane was the principal product identified. This hydrocarbon continued to be formed smoothly after the disappearance of lithium metal from the reaction mixture. Other products showed similar behavior. The general trends were interpreted as an indication that n-butyllithium was a required reagent in the formation of all of the observed products. N-Methyl-N-(1-pentyl)aniline and N-methyl-N-(1-butyl)aniline were observed after 24 hr, in 6 and 3% yields, respectively, together with 15% n-octane.

1-Iodobutane gave the most dramatic change in this series of reactions. Only M-methyl-N-(1-pentyl)aniline was observed as an amine product; this compound was rapidly formed, reaching a maximum yield of 62–68% after 4 hr. The amount of 1-pentyl product was not enhanced on the subsequent addition of more 1-iodobutane. Since such enhancement was an indication of the formation of n-butyllithium in the reactions with 1-chlorobutane, it seems apparent that any n-butyllithium formed in the presence of 1-iodobutane rapidly underwent further reaction by either α alkylation or Wurtz coupling processes. n-Octane was observed, but was inadequately separated from the starting 1-iodobutane for quantitative gc determination; *cf.* Table II.

In the 1-bromobutane reaction, n-butyllithium was produced more rapidly than it was consumed by product forming reactions. Addition of 1-iodobutane to this reaction mixture after 24 hr gave a significant (doubling after 4 hr) enhancement of the α-alkylation product, Table I; yet the mass balance was poor. However, when 1-bromobutane was allowed to react for 2 days without 1-iodobutane addition, a 49% yield of n-octane and 4.2% yield of N-methyl-N(1-butyl)aniline were determined, which raised the mass balance to more than 60% of the starting halide. This trend toward more Wurtz reaction and less α alkylation agreed with previous studies using n-butyllithium and 1-bromobutane.[5]

Only a single new amine was observed when iodobutane was used with lithium metal. This single product accounted for more of the starting materials than all products in either the chloro or bromo reaction. Iodobutane α alkylation was more than 1.5 times that obtained with commercial n-butyllithium.[3] Concentrated n-butyllithium in hexane solutions produced up to 50% yield of α alkylation[5] but never the more than 60% currently observed with lithium metal. Three factors may contribute to this reaction control: (1) temperature, (2) low organometallic reagent concentrations, and (3) the solvent composition. The current results warrant a further study of these previously observed[5] variables.

The primary reaction process occurs on the metal surface. Generation of n-butyllithium, in hydrocarbon solvents (eq 4), is accelerated by the use of a

$$6\,n\text{-}C_4H_9X + 12Li \longrightarrow (n\text{-}C_4H_9Li)_6 + 6LiX \qquad (4)$$

metal dispersion to increase the surface for halide reaction. The surface area requirement reflects the solvation in nonpolar and nonassociative alkanes. n-Butyllithium is a hexamer[9] in hydrocarbons where the metal atoms form a cluster surrounded by the alkyl chains. However, branched chain and tertiary alkyl groups form only tetramers. The external hydrocarbon coat interacts with the similar solvent structure to solvate the organolithium clusters. The removal of the n-butyllithium from the metal surface thus depends on the formation of some minimum number of RM units capable of solvation. The greater the steric requirements to reach this number, the more dependent the reaction will be on surface conditions.

The tertiary amine significantly changes this solvation. Reactions take place readily even when the metal is not finely divided and when initially covered with a

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(8) A. I. Shatenshtein and Y. I. Ranneva, *J. Gen. Chem. USSR*, **31**, 1317 (1961).

(9) T. L. Brown, R. L. Gerteis, D. A. Bafus, and J. A. Ladd, *J. Amer. Chem. Soc.*, **86**, 2135 (1964).

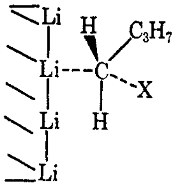
TABLE II

GAS CHROMATOGRAPHIC RETENTION RATIOS FOR PRODUCTS AND OTHER COMPOUNDS RELATED TO THE REACTIONS OF 1-HALOBUTANES WITH LITHIUM METAL IN N,N-DIMETHYLANILINE

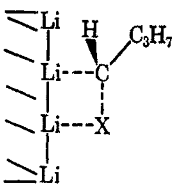
	Retention ratios			
	Silicon rubber[a]		GE-SF96[b]	
Compd	Calibration	Reaction products	Calibration	Reaction products
1-Chlorobutane	0.117			
1-Bromobutane	0.168			
n-Octane	0.199	0.197–0.200 (Cl, Br)		
1-Iodobutane	0.210			
1-Bromopentane	0.276			
n-Nonane	0.323		0.378	
n-Decane	0.570		0.524	
n-Undecane	0.705			
N,N-Dimethylaniline	0.711		0.704	
n-Dodecane	1.000[c]		1.000[d]	
m-Dimethylaminophenylbis(trifluoromethyl)carbinol	1.14		1.15	
o-Dimethylaminophenylbis(trifluoromethyl)carbinol	1.38		1.58	
N-Methyl-N-(1-butyl)aniline		1.43–1.48 (Cl, Br)	1.66	1.68 (Cl)
N-Methyl-N-(1-pentyl)aniline	1.71	1.69–1.79 (Cl, Br, I)	2.41 ± 0.03	2.37 (Cl) 2.35 (I)
N,N,N′,N′-Tetramethylbenzidine		1.77 (I)		3.07 (I)
N-Methyl-N-(1-hexyl)aniline	2.08		3.27	
Benzhydryldimethylamine			4.52	4.32 (added to I)

[a] Commercial column supplied by F & M, 0.25 in. × 4 ft, programmed from 80 to 180° at 5°/min, 50 cc/min He flow (80°). [b] A 0.25 in. × 10 ft column of 20% GE-SF96 on 40–60 mesh Chromosorb W; at 185°, 100 cc/min He flow. [c] Standard for qualitative and quantitative analysis, retention time 10.6 ± 0.5 min, peak width at half-height 0.43 ± 0.04 min. [d] Standard for qualitative and quantitative analysis, retention time 3.5 ± 0.3 min, peak width at half-height 0.20 ± 0.05 min.

thin oxide and nitride coat. Thus freshly cut metal, after exposure to the laboratory atmosphere for 5 to 10 min, can be used with the halide in dimethylaniline. This solvent does not appreciably solvate halide ions; *cf.* the insolubility of trialkylanilinium halides. Thus, *n*-butyllithium formation requires a four-center mechanism where both halide and alkyl groups associate with the metal surface as in B rather than the displacement



A



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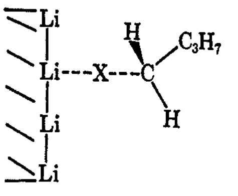

C

type intermediate A. However, *n*-butyl group displacement in C favors the free-radical formation observed[10,11] with iodo and to a lesser extent with bromo compounds.

The enhanced solubility of *n*-butyllithium is then accounted for by an alternative solvation process. The nonbonding, lone pair electrons of the solvent forms an outersphere complex[9,12] with the metal of the alkyllithium. This complex (*e.g.*, the trimer in eq 5) con-

$$2\ n\text{-}C_4H_9X + 4Li + R_3N{:} \longrightarrow (n\text{-}C_4H_9Li)_2{:}NR_3 + 2LiX \quad (5)$$

tains a solvent molecule which aids solvation. Limited precipitation, apparent during the initial reaction period except when the iodide was used, is consistent with complex formation since halides form weak complexes with organolithium compounds.[13] Organolithium–amine complexes were only studied with trialkylamines;[9,12] thus, the extent of dialkylaniline participation is not yet known.

The secondary reaction processes lead to amine and hydrocarbon products. The yields of N-methyl-N-(1-pentyl)aniline are significantly higher in the 1-iodobutane–lithium reaction than those obtained from *n*-butyllithium in hexane indicating product may occur at the metal surface. However, yields do increase with amine concentration,[5] and the optimum yields now obtained do not exceed those anticipated for this concentration. Thus, there is no evidence supporting direct participation of the metal in this most important, secondary reaction.

The 1-pentyl product was much less important in the chloro- and bromobutane reactions. *n*-Octane from Wurtz coupling (eq 6) accounted for 15% of the bromo compound after 14 hr of reaction and 49% after 48 hr of reaction. The octane formation after lithium

$$2\ n\text{-}C_4H_9X + 2Li \longrightarrow n\text{-}C_8H_{18} + 2LiX \quad (6)$$

metal disappearance (second day) was evidence for the initial formation of *n*-butyllithium and its subsequent reaction with a second mole of the halide (eq 7). However, octane formation reached 3.6% in 24 hr and increased to 4.3% at 48 hr, when chlorobutane was allowed to react with metallic lithium. Since disappearance of the metal was slower and *n*-butyllithium concentrations after 1 day were higher than with bromobutane, the predominant formation of *n*-octane from chlorobutane evidently occurs in the presence of the metal. An alternative to free-radical *n*-octane formation which occurs with bromobutane[11] is thus bimo-

$$\begin{aligned} n\text{-}C_4H_9X + 2Li &\longrightarrow n\text{-}C_4H_9Li + LiX \\ n\text{-}C_4H_9X + n\text{-}C_4H_9Li &\longrightarrow n\text{-}C_8H_{18} + LiX \end{aligned} \quad (7)$$

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(10) A. R. Lepley, *Chem. Commun.*, 64 (1969); A. R. Lepley and R. Landau, *J. Amer. Chem. Soc.*, **91**, 748 (1969); A. R. Lepley, *ibid.*, **90**, 2710 (1968).

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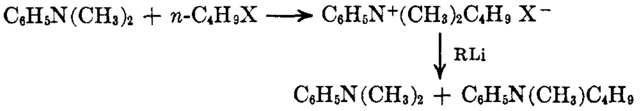
(12) J. F. Eastham and G. W. Gibson, *J. Amer. Chem. Soc.*, **85**, 2171 (1963); Z. K. Cheema, G. W. Gibson, and J. F. Eastham, *ibid.*, **85**, 3517 (1963); F. A. Settle, M. Haggerty, and J. F. Eastham, *ibid.*, **86**, 2076 (1964); C. G. Screttas and J. F. Eastham, *ibid.*, **87**, 3276 (1965).

(13) W. Glaze and R. West, *ibid.*, **82**, 4437 (1960).

lecular reaction of the halide absorbed on the metal surface or reaction with a surface layer of previously formed alkyllithium.

The final product, N-methyl-N-(1-butyl)aniline, was formed in small amounts and was evident only in the chloro- and bromobutane reactions. The highest yields of this product occurred in bromobutane reactions, where the yield after 24 hr slowly increased to 4% at 48 hr. In the chlorobutane reaction, the N-butyl compound was observed at less than 2% after 1 day and increased to only 2.5% with an additional day of reaction. Three possible mechanisms might be anticipated: (1) quaternary salt formation followed by elimination; (2) dealkylation followed by addition to the secondary amine formed; or (3) some type of double displacement or direct alkyl group exchange. Although the occurrence of amine dealkylation has been suggested to result from treatment of some tertiary amines with alkyllithium reagents, only alkyl groups with protons β to the amino nitrogen atom participate,[14] thus excluding the current reactant dimethylaniline. The major formation of N-pentyl product occurs where N-butyl compound is absent and is only comparable to the latter in the chlorobutane reactions. Thus initial formation of the pentyl compound followed by dealkylation and addition steps is improbable. Since a double displacement is uncommon in tertiary amines, including the anilines, a quaternary anilinium salt intermediate seems most plausible. The N,N-dimethyl-N-butyl salt does not form readily,[3] but such salts can undergo displacement reactions as well as Hofmann elimination.[15] The participation of *n*-butyllithium in such displacement reactions has been considered elsewhere.[16] This salt can revert to dimethylaniline by either butene elimination or by displacement, giving *n*-octane. These paths may thus account for part of the hydrocarbon observed. The N-butyl product under consideration is the result of methyl, rather than butyl, group displacement. However, if a significant amount of quaternary salt occurred, other products such as N-methyl-N-(*sec*-pentyl)aniline might be expected from a Stevens rearrangement. Thus limited salt formation is indicated by both the absence of other products and low yield of N-butyl product.



$$\begin{tikzcd}
C_6H_5N(CH_3)_2 + n\text{-}C_4H_9X \arrow[r] & C_6H_5N^+(CH_3)_2C_4H_9\ X^- \arrow[d, "RLi"] \\
 & C_6H_5N(CH_3)_2 + C_6H_5N(CH_3)C_4H_9
\end{tikzcd}$$

Experimental Section

Physical Properties.—Proton magnetic resonance (pmr) spectra of synthetic material were measured on a Varian A-60A spectrometer using 0.5-ml samples of 20% v/v solutions in carbon tetrachloride with approximately 1% tetramethylsilane (TMS) as an internal standard. Reaction products were collected from gc as 5–10-mg samples, diluted to 35 μl with 1% TMS in carbon tetrachloride, and measured in a 30-μl spherical cavity tube.

Infrared (ir) measurements were made on the pure liquids or on potassium bromide disks for solids using a Perkin-Elmer Model 137 spectrophotometer. Wavelengths and intensities are given as previously described.[17]

Gas Chromatography.—Columns and conditions used on an F & M Model 700 chromatograph are given in Table II. Retention ratios, peak resolution, and product yields (see tables) were determined using an internal standard method.[5,17] Qualitative and quantitative analyses were made on 0.4 and 1.0 μl of samples from the reaction mixtures. The weighed dodecane, introduced initially in preparing reaction mixtures, was used as the standard for quantitative analysis. Calibration factors for weight ratios of particular classes of compounds were alkanes 1.00, N,N-dialkylanilines and 1-haloalkanes 0.68, and *o*- or *m*-(dimethylamino)phenylbistrifluoromethylcarbinols 0.46. Measured variation in calibration factors was ±0.04. Calculated yields are ±3% of the value given (*e.g.*, 20.0 ± 0.6).

Preparative gc samples were obtained from an F & M Model 500 using a 0.25 in. × 10 ft GF-SF96 column with operating conditions as in Table II. Samples of 50–200 μl were injected and the individual products collected, as each emerged, in cooled 1.5–2.0 × 100 mm open-ended capillary tubes. Normally, several samples were run to collect the 10–15 mg of a product required for ir and pmr spectra and, where appropriate, melting points.

Chemicals.—*n*-Nonane, *n*-decane, *n*-undecane, *n*-dodecane (olefin free, 99%+), and 1-iodobutane were obtained from Matheson Coleman and Bell. *n*-Octane, 1-bromobutane, and 1-bromopentane came from Eastman. 1-Chlorobutane and reagent grade N,N-dimethylaniline were from Fisher Scientific. The latter was dried over sodium wire before use. N-Methyl-N-(1-butyl)aniline, N-methyl-N-(1-pentyl)aniline, N-methyl-N-(1-hexyl)aniline, benzhydryldimethylamine, and *o*- and *m*-dimethylaminophenylbis(trifluoromethyl)carbinol were available from previous studies.[6] Hexafluoroacetone was obtained from Columbia Organic Chemicals and Foote Mineral 0.5 in. × 1 ft lithium metal rod was used. N,N,N′,N′-Tetramethylbenzidine was obtained from Aldrich.

General Procedure for α Alkylation of N,N-Dimethylaniline Using Lithium Metal.—An alkyl halide (0.1 mol) was added to a freshly prepared magnetically stirred mixture of freshly cut lithium metal (0.7 g, 0.1 g-atom), dry N,N-dimethylaniline (38 ml, 0.3 mol), and an accurately weighed amount of *n*-dodecane (*ca.* 3 g) in a 100-ml round-bottomed flask fitted with a drying tube. Samples (1 ml) were removed at various intervals and quenched immediately with distilled water (3 ml). The organic phase was decanted and used for gc analysis. The gc retention ratios of the products were compared with those of synthetic materials. Identification was made through pmr and ir spectra of the products isolated by preparative gc.

Reaction of 1-Iodobutane, N,N-Dimethylaniline, and Lithium.—1-Iodobutane (11.4 ml, 0.10 mol) was allowed to react with lithium (0.79 g, 0.12 g-atom) and N,N-dimethylaniline (38 ml, 0.3 mol) as described in the general procedure. The mixture became warm initially and was allowed to react at room temperature. Samples for analysis were removed after 0.5, 2, and 4 hr, and 1, 2, and 9 days. One gc peak with retention ratio 1.70, (silicon rubber) or 2.35 (GE-SF96) was rapidly formed. After 4 hr the peak was almost as large as that observed after 1 day. By 9 days the peak had slowly decreased in intensity to about two-thirds of its maximum. The ir and pmr spectra of a preparative gc sample of this peak were identical with the spectra[3] of N-methyl-N-(1 pentyl)aniline. Based on this assignment, maximum yield varied from 62 to 68%. Since the starting material, 1 iodobutane, was inadequately separated from a second peak which preceded it, direct qualitative or quantitative identification was not made. However, based on previous experiments using *n*-butyllithium, this peak was assumed to be that of *n*-octane. After 9 days the reaction mixture turned deep blue and an additional peak appeared at a gc retention ratio of 1.77 (silicon rubber) or 3.07 (GE SF96). A preparative gc sample of this material had a melting point of 72°, and pmr bands were at δ 2.82 (CH$_3$ on aryl nitrogen) and a symmetric pair of aromatic multiplets were centered at 6.27 and 7.24 ppm, with relative intensity ratios of 3:1:1, respectively. The ir spectrum in KBr had bands at 2910 w, 2830 w, 1600 m, 1500 m, 1450 w, 1360 m, 1230 w, 1200 w, 1135 w, 1170 w, 952 vw, 810 s*, and 750 cm^{-1} w. Both the pmr spectrum and ir bands, except that at 750 cm^{-1}, were comparable with data measured for a commercial sample of N,N,N′,N′-tetramethylbenzidine. This product and the blue color of the reaction mixture indicate that air oxidation takes place under the conditions of these studies only long after completion of the organometallic and amine reactions.

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Reaction of 1-Bromobutane, N,N Dimethylaniline, and Lithium.—1-Bromobutane (13.7 ml, 0.13 mol) was allowed to react with lithium (0.85 g, 0.12 g-atom) and N,N-dimethylaniline (38 ml, 0.3 mol) as described in the general prodedure. No heat evolution was observed. Samples were taken and analyzed after 0.5, 4, and 18 hr, and 1, 2, 7, and 22 days. The halide with retention ratio 0.164 (silicon rubber) decreased to less than one-third its original concentration during the first day. Thereafter, its disappearance was very gradual, reaching one-sixth the initial amount after 3 weeks. *n*-Octane was adequately separated (retention ratio 0.23, silicon rubber) from the halide for quantitative analysis. This hydrocarbon formation lagged behind the halide loss rate, accounting for only 15.4% after 24 hr and 49% after 2 days. During the subsequent reaction period the increase in octane was no more than 10% that of the first 48 hr. A compound which was not apparent in the iodobutane reaction appeared during the first day and then slowly increased for the first week. Its retention ratios were 1.38 (silicon rubber) and 1.68 (GE-SF96) and the ir spectrum of a gc separated sample was identical with that of N-methyl-N-(1-pentyl)aniline except for the lack of a band at 950 w and the presence of a band at 930 cm^{-1} w. The pmr spectrum had a multiplet of two major parts centered at δ 1.08 ppm (aliphatic CH_3 + CH_2's), a singlet at 2.74 (CH_3 on aryl N), a triplet at 3.18 (CH_2 on aryl N), and parts of the aromatic multiplet centered at 6.49 and 6.97 ppm. The relative integrated intensity ratio for these peaks was 7:3:2:3:2, respectively. Both spectra and retention ratios are comparable with the data for N-methyl-N-(1-butyl)aniline.[3] On the basis of this assignment, yield were 3.0, 4.2, and 5.1% at 1, 2, and 7 days, respectively. A slightly greater amount of a second amine, N-methyl-N-(1-pentyl)aniline, was formed more gradually. This product with a retention ratio of 1.64 (silicon rubber) at 4 hr, 1, 2, and 7 days was produced in 3.6, 6.4, 9.2, and 10.6% yields, respectively. If higher molecular weight compounds were present, they were below the level of gc detection under the conditions employed.

Reaction of 1-Chlorobutane, N,N-Dimethylaniline, and Lithium.—A reaction was run using 10.3 ml (0.10 mol) of 1-chlorobutane and 0.91 g (0.13 g-atom) of lithium as described in the general procedure. Samples were taken and analyzed after 1.5, 5, and 18 hr, and 1, 2, 3, and 5 days. The chlorobutane present, retention ratio 0.115 (silicon rubber), decreased to one-quarter its initial amount during the first day and thereafter remained essentially constant. All of the products observed in the 1-bromobutane reaction were present in this reaction, but the yields were significantly lower. All reached maximum amounts after 2 days. *n*-Octane was present in 2.2% at 5 hr and in 3.6% after 1 day, and increased to 4.3% after 2 days. N-Methyl-N-(1-butyl)aniline was less than 2% at 24 hr and 2.5% at 2 days, while N-methyl-N-(1-pentyl)aniline was less than 1% and increased to 1.2% at these same two times. After 7 days, hexafluoroacetone was bubbled through the reaction for 6.5 hr. When this mixture was quenched with water and analyzed with gc, two major product peaks were observed. The first of these, retention ratios 1.14 (silicon rubber) and 1.15 (GE-SF96), was present in 6.4% yield, while the second, retention ratios 1.38 (silicon rubber) and 1.58 (GE-SF96), was formed in 82% yield. These peaks and melting points of collected products were identical with those of *m*- and *o*-(dimethylamino)phenylbistrifluoromethylcarbinol,[6] respectively.

General Procedure for α Alkylation of N,N-Dimethylaniline with Addition of 1-Iodobutane at 24 Hr.—These reactions used the amounts and general procedure described above. All reactions were carried out at 20 ± 2° by running tap water through a copper coil in an insulated water bath. Heating from the magnetic stirrer, surroundings, and exothermic reaction was thus limited. After 24 hr a sample was removed and the mixture was cooled in an ice bath for 15 min before adding 11.4 ml (0.10 mol) of 1-iodobutane. Reaction was allowed to continue for 2 hr (total time 26 hr) in the ice bath. A sample was then taken and the ice bath was replaced with the original water bath. A final sample was taken after 2 hr (total time 28 hr) in the water bath. Gc analysis was used for both qualitative and quantitative determination of N-methyl-N-(1-pentyl)aniline, which was the only product monitored in this series of reactions. Identification was based on comparisons with results from previous experiments. The ice cooling procedure, applied to reactions of the chloro-, bromo-, and iodobutane, was based on the observations in the following example experiments. The results of this series of reactions are summarized in Table I.

Reaction of 1-Chlorobutane, N,N-Dimethylaniline, and Lithium with Addition of 1-Iodobutane.—1-Chlorobutane (10.3 ml, 0.10 mol) was allowed to react with lithium (0.74 g, 0.11 g-atom) and N,N-dimethylaniline (38.1 ml, 0.30 mol) as described in the general procedure with addition of 1-iodobutane (11.4 ml, 0.10 mol) to the cooled mixture at 24 hr.

The reaction was smooth and controllable, giving the yields of N-methyl-N-(1-pentyl)aniline listed in Table I. When the reaction was run without ice cooling prior to iodobutane addition [*i.e.*, run in water bath (20°) for all stages of reaction], 1 min after iodobutane addition the reaction became quite vigorous and exothermic. The color of this reaction rapidly changed from the usual dark brown to a bright coral and an unidentified coral solid separated on prolonged standing (1 day). Yields of N-methyl-N-(1-pentyl)aniline were approximately two-thirds those obtained when cooling was applied prior to iodobutane addition (see Table I). Therefore, the precooling procedure was used in reactions with 1-bromo- and 1-iodobutane.

Registry No.—N,N-Dimethylaniline, 121-69-7; N-methyl-N-(1-pentyl)aniline, 3299-39-6.