(2 ml) were withdrawn after 24, 48, and 72 hr, quenched with ice, and analyzed by gc. Three gc components had retention ratios of 0.097, 0.193, and 0.268, corresponding to triethylamine, *n*-octane, and N-(*n*-butyl)diethylamine, respectively. The structure of the major component, N-(*n*-butyl)diethylamine, was confirmed by infrared analysis on a preparative gc sample; the infrared spectrum was identical with that of the synthetic material above. Gc determination of the yields for the three components were within experimental error on duplicate samples at 48 and 73 hr. Triethylamine was formed in 13.5 ± 3%, *n*-octane 5.8 ± 0.4%, and N-(*n*-butyl)diethylamine 82 ± 2%. Traces of materials which might be N-(2-butyl)-N-(*n*-butyl)-ethylamine, N-(2-hexyl)diethylamine, and N-(3-hexyl)diethylamine were observed. The weak, broad gc peak with a maxima and a shoulder in the retention ratio region 0.66–0.72 had a calculated yield of 1.6 ± 0.5% for the isomeric Stevens rearrangement products.

General Procedure for the α Alkylation of Triethylamine.—Anhydrous triethylamine (14 ml, 0.1 mole) and 13 ml of 1.6 *N* *n*-butyllithium (20 mmoles) in hexane were mixed and cooled to the initial reaction temperature, Table II. When bath temperature was reached, 2.3 ml (20 mmoles) of 1-iodobutane was added. The stoppered stirred solution was kept in the bath which was allowed to gradually warm to ambient. After the reaction period, ice was added to quench the reaction. The organic layer was used directly for product characterization and yield measurements. The products were isolated by gc and characterized by their gc retention ratios, and infrared and pmr spectra. In all cases, comparisons were made with the properties of commercial or synthetic compounds.

Triethylamine α Alkylation at −70 to −80°.—The reagents as described above were cooled in a dewar containing a Dry Ice–acetone mixture. After addition of 1-iodobutane the reaction was allowed to warm with magnetic stirring to room temperature. The reaction was quenched with ice after 16 hr. Gc on the organic layer showed two products with retention ratios of 0.191 and 0.70 with respect to dimethylaniline.

The retention ratio and infrared spectrum of the first component were identical with those of commercial *n*-octane. The yield of *n*-octane in multiple runs was 80 ± 7%, determined by quantitative gc with calibration correction.

The second component collected from gc has a faint amine-like odor, bp 174° (Siwoloboff), and had refractive indices of $n^{20}\text{D}$ 1.4239, $n^{25}\text{D}$ 1.4213, and $n^{30}\text{D}$ 1.4192. The infrared spectrum had bands at 3.42 s*, 3.55 m, 3.60 m, 6.90 m, 7.35 m, 7.80 w, 8.40 m, 8.80 w, 9.20 w, 9.42 w, and 9.60 w μ. Pmr absorption showed two complex multiplets centered at 1.05 and 2.41 ppm, with peak area proton ratios of 18 to 5.

Anal. Calcd for $C_{10}H_{23}N$: C, 76.43; H, 14.65; N, 8.92. Found: C, 76.51; H, 14.81; and N, 9.01.

The properties of this compound are identical with those of N-(2-hexyl)-N,N-diethylamine. Gc yields were 25 ± 2%.

General Procedure for Triethylamine Metallation Studies.—A mixture of 14 ml (0.1 mole) triethylamine and 13 ml of 1.6 *N* *n*-butyllithium (20 mmoles) in hexane was stirred at ambient or reflux for a fixed time. Samples were withdrawn for active lithium determination by the double titration method.[11] The remaining solution was treated with hexafluoroacetone and the yield of butyllithium reaction product was determined by gc.

The double titration, with and without addition of benzyl chloride, was carried out on 2-ml samples of the reaction mixture. Correction for triethylamine reaction with the halide was made by using the standard double titration procedure on 2-ml samples from a mixture of 14 ml of triethylamine and 13 ml of hexane. The correction factor, which was constant within the limits of exprimental error, was subtracted from titre values in metallation reaction mixtures. Original reaction volumes were used to calculate millimoles of active lithium compounds.

The hexafluoroacetone gas was passed through the metallation mixture for about 4 hr at ambient temperature. The reaction was quenched with ice and made acidic with concentrated hydrochloric acid. Ether (10 ml) was added and the mixture was shaken well. A sample (1 ml) of the organic layer was withdrawn and added to a known weight of standard (1-pentanol); the mixture (10, 25, or 50 μl) was injected into the gc. Gc conditions and calibration factors were as previously described.[9] Yields of 1,1-bis(trifluoromethyl)-1-pentanol were used to determine millimoles of unreacted *n*-butyllithium, Table III.

Studies on the α Alkylation of Dimethylaniline[1a]

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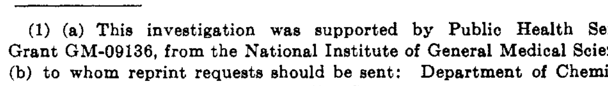
The effect of the haloalkane on the α alkylation of N,N-dimethylaniline has been investigated. The yield of alkylated products and reaction rates were found to decrease with increasing electronegativity of the halogen atom. Distributions of alkylated products and hydrocarbons from "Wurtz" coupling result from a prereaction halogen–metal interchange of the organolithium compound with the 1-iodoalkane. A discontinuity in the product dependence on dimethylaniline concentrations evinces the participation of a 1:1 *n*-butylithium–amine complex in the alkylation. When 1-bromopentane reacted with dimethylaniline and *n*-butyllithium, only limited halogen–metal exchange was evident. A 1.1:1 ratio of N-(*n*-pentyl)- to N-(*n*-hexyl)-N-methylaniline was formed despite the limited exchange. The ratio of yields for these products was comparable with that of the hydrocarbons *n*-octane to *n*-decane. However, the actual yields of the alkylation products were 3.5 times greater than those of the exchanged "Wurtz" products. These results were interpreted as reflecting a transition state in which the *n*-butyllithium–dimethylaniline complex participates in halogen–metal interchange and in which the amine and hydrocarbon distributions are dependent on the amount of exchanged halides escaping from the complex before alkylation occurs. Since exchange most probably precedes alkylation, it is not possible to determine whether the lithium or bromo compound furnishes the alkylating group.

Recently[2] the formation of N-(*n*-pentyl)-N-methylaniline has been reported by the action of *n*-butyllithium and 1-iodobutane on N,N-dimethylaniline.



$$C_6H_5N(CH_3)_2 + n\text{-}C_4H_9Li + n\text{-}C_4H_9I \longrightarrow C_6H_5\underset{\displaystyle CH_3}{\underset{|}{N}}(CH_2)_4CH_3 + n\text{-}C_4H_{10} + LiI \quad (1)$$

The reaction was shown to be limited to attack at the alkyl carbon atom adjacent to nitrogen for N,N-diethylaniline. A Stevens rearrangement mechanism was excluded (1) by the reaction of N,N-dimethyl-N-(*n*-butyl)anilinium iodide with *n*-butyllithium giving only N,N-dimethylaniline, and (2) the use of iodobenzene in place of 1-iodobutane, eq 1, with the formation of N-benzyl-N-methylaniline

Several reactions are known between pairs of reagents present in eq 1. Dimethylaniline reacts with 1-iodobutane[2,3] forming the quaternary salt, N,N-

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[1] (a) This investigation was supported by Public Health Service Grant GM-09136, from the National Institute of General Medical Sciences; (b) to whom reprint requests should be sent: Department of Chemistry, Marshall University, Huntington, West Va.

[2] (a) A. R. Lepley and A. G. Giumanini, *Chem. Ind.* (London), 1035 (1965); (b) *J. Org. Chem.*, **31**, 2055 (1966).

[3] L. Y. Chow and R. M. Fuoss, *J. Am. Chem. Soc.*, **80**, 1095 (1958).

dimethyl-N-(*n*-butyl)anilinium iodide. At reflux, *o*-dimethylaminophenyllithium is slowly formed from dimethylaniline and butyllithium[2,4] by a direct metallation reaction.[5] The combination of 1-iodobutane and *n*-butyllithium undergoes two double displacement reactions, halogen-metal interchange,[6,7] and "Wurtz" coupling.[8]

These reactions may occur simultaneously with the new α-alkylation reaction and may play an important part in the alkylation reaction mechanism. Alternatively, a reaction which does not participate in the mechanism may complicate the detection of that mechanism. Therefore, we have undertaken a series of studies aimed at the detection of competitive reactions and the elucidation of the reaction mechanism. In the current study, the influence of haloalkane and reagent concentration were determined for eq 1.

Results and Discussion

1-Halobutanes in combination with N,N-dimethylaniline and *n*-butyllithiun give a new amine, eq 1. In this new amine, one of the methyl protons has been replaced by a butyl group, *i.e.*, N-(*n*-pentyl)-N-methylaniline. The order of halogen reactivity, I > Br ≫ Cl (Table I), corresponds to either halogen displacement or proton extraction[9] on the alkyl halide. Thus, carbenes could participate in the formation of the amine.

TABLE I

N-(*n*-PENTYL)-N-METHYLANILINE FROM THE 1-HALOBUTANE (40 MMOLES) REACTIONS OF DIMETHYLANILINE (200 MMOLES) AND *n*-BUTYLLITHIUM (40 MMOLES)[a]

Halide	I	Br	Cl
% yield[b]	42	16	0

[a] This reactivity directly parallels the reaction order found in the "Wurtz" reaction,[8] eq 2. [b] All values after 4 hr.

$$n\text{-}C_4H_9Li + n\text{-}C_4H_9X \longrightarrow n\text{-}C_8H_{18} + LiX \qquad (2)$$

The 1-iodobutane reaction, eq 1, was complete in 2.5 hr (Figure 1), when initiated at −10°; while at room temperature, the exothermic reaction could not be controlled. 1-Bromobutane was slower to react. After 4 hr, the amine formation was complete for − 10° initiation (Figure 1) and room temperature (Figure 2) reaction. The reaction temperature profile for −10° initiation showed a temperature increase of approximately 0.4°/min and was within 3° of the final temperature, 32 ± 1°, after 90 min.

Although the final amine yields from the bromobutane reaction are not significantly different under the two conditions, 16 (−10°) and 14% (32°), the 42% yield from 1-iodobutane indicates an appreciable decrease in the effectiveness of reactions competing with the carbon alkylation, eq 1. If the "Wurtz" reaction, eq 2, were the only competing reaction, the relative rates for eq 1/eq 2 must be greater for alkyl iodides than for bromides. Other competitive reactions may be significant in the bromobutane case.

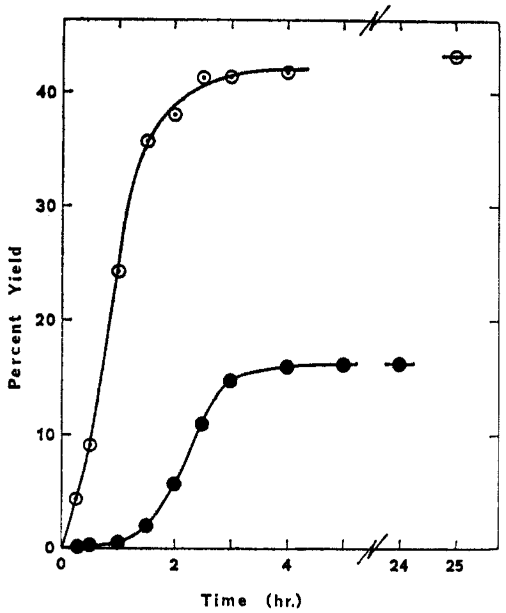

Figure 1.—The rate of formation of N-(*n*-pentyl)-N-methylaniline from 1-iodobutane (⊙) or 1-bromobutane (●) when reaction was initiated at −10°. Initial concentrations were 3.77 *M* dimethylaniline, 0.75 *M* *n*-butyllithium, and 0.75 *M* 1-halobutane.

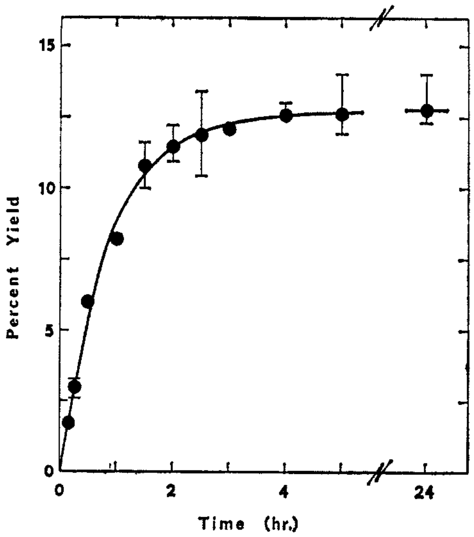

Figure 2.—The rate of formation of N-(*n*-pentyl)-N-methylaniline from 1-bromobutane at 32 ± 1°. Initial concentrations are the same as in Figure 1.

The formation of N,N-dimethyl-N-(*n*-butyl)anilinium iodide was not a rapid reaction, but the attack of base on the quaternary salt regenerates dimethylaniline[2] *via* a Hoffmann elimination,[10] Scheme I.

SCHEME I

$$\begin{array}{c} C_6H_5N(CH_3)_2 + n\text{-}C_4H_9I \longrightarrow C_6H_5\overset{+}{N}(CH_3)_2C_4H_9\,I^- \\ \Big\downarrow n\text{-}C_4H_9Li \\ CH_2{=}CHCH_2CH_3 + n\text{-}C_4H_{10} + C_6H_5N(CH_3)_2 + LiI \end{array}$$

This particular route need not be the exclusive means of 1-butene formation. β-proton abstraction on the 1-halobutane or reduction of the halocarbon with butyllithium can also give the alkene.[11] The alkene

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[4] *Cf.* G. Wittig and H. Merkle, *Chem. Ber.*, **75**, 1491 (1942).

[5] H. Gilman and J. W. Morton, *Org. Reactions*, **8**, 258 (1954).

[6] R. G. Jones and H. Gilman, *ibid.*, **6**, 339 (1951).

[7] D. E. Applequist and D. F. O'Brien, *J. Am. Chem. Soc.*, **85**, 743 (1963).

[8] K. Ziegler and H. Colonius, *Ann.*, **479**, 135 (1930).

[9] J. Hine "Divalent Carbon," Ronald Press Co., New York, N. Y., 1964, p 40.

[10] A. C. Cope and E. R. Trumbull, *Org. Reactions*, **11**, 317 (1960).

[11] See ref 9, p 102–104.

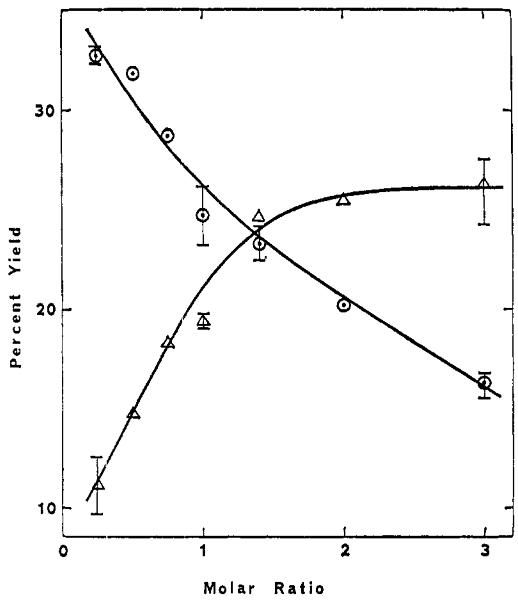


Figure 3.—Variation in the yields of N-(*n*-pentyl)-N-methylaniline (⊙) and N-(*n*-hexyl)-N-methylaniline (△) with increasing 1-iodopentane–*n*-butyllithium molar ratio. An initial 5:1 molar ratio of dimethylaniline–*n*-butyllithium (10 mmoles) was used in all reactions.

yields are not readily determined in the presence of a carbanionic polymerization catalyst such as *n*-butyllithium. However, defects in a more complete mass balance may give some information on competition of the various alkene formation paths with eq 1 and 2.

A further reaction which does not destroy reagents but complicates the mechanism studies is the halogen–metal interchange reaction.[6] In the α-amine alkylation, the alkyl group added to the reacting amine might be presumed to come from either the organolithium or the halocarbon but not both. Since the alkyl groups are the same their source cannot be determined in the reactions with *n*-butyllithium and 1-halobutanes. However, the use of another 1-iodoalkane and *n*-butyllithium would allow (1) the determination of the alkylating group and/or (2) the extent of halogen–metal interchange occurring before alkylation.

1-Iodopropane and 1-iodopentane were, therefore, used in the reaction. The reactions were carried out for 2 hr with a molar ratio of 5:2:1 for dimethylaniline, *n*-butyllithium, and 1-iodoalkane (Table II). Gas chromatography of the known predicted products indicated (Table III) the feasibility of qualitative and quantitative determination by these techniques. The reaction of each iodide (Scheme II) gave two products which were identified as the predicted products by retention ratios, and infrared and proton magnetic resonance spectra. The ratio of product from 1-iodopropane ($C_5H_{11}:C_4H_9$), 2.2:1, and 1-iodopentane ($C_5H_{11}:C_6H_{13}$), 1.7:1, can be interpreted as evidence for halogen–metal interchange since these ratios are within reproducibility errors for the reagent ratio (2:1). Additional support for the exchange comes from a series of experiments with 1-iodopentane.

SCHEME II

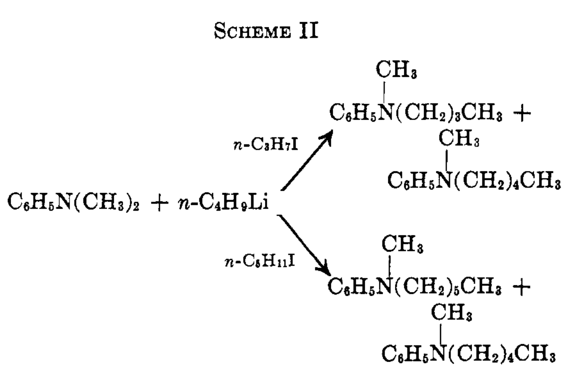


TABLE II

AMINE PRODUCTS FROM THE 1-IODOALKANE (20 MMOLES) REACTIONS OF DIMETHYLANILINE (100 MMOLES) AND *n*-BUTYLLITHIUM (40 MMOLES)

Product $C_6H_5NCH_3R$	% yield[a] from 1-iodoalkane		
	n-C_3H_7	*n*-C_4H_9	*n*-C_5H_{11}
R = *n*-C_4H_9	7.6		
R = *n*-C_5H_{11}	16.5	23.5	14.3
R = *n*-C_6H_{13}			8.2

[a] All values after 2 hr.

TABLE III

GAS CHROMATOGRAPHIC RETENTION RATIOS[a] OF REACTANTS, PRODUCTS, AND STANDARDS IN THE α ALKYLATION OF DIMETHYLANILINE

Compound	Retention ratios		
		Reaction products[b] from	
	Calibration	*n*-C_5H_{11}Br	*n*-C_5H_{11}I
At 100°[c]			
1-Bromobutane	0.136		
n-Octane	0.218	0.221 (I)	0.217 (I)
1-Iodobutane	0.233		
1-Bromopentane	0.248		
n-Nonane	0.400	0.402 (II)	0.400 (II)
1-Iodopentane	0.432		
n-Decane	0.750	0.755 (III)	0.740 (III)
n-Butylbenzene	1.000[d]		
At 185°[e]		*n*-C_3H_7I	*n*-C_5H_{11}I
N-(*n*-Butyl)-N-methylaniline	0.360	0.375 (A)	
N-(*n*-Pentyl)-N-methylaniline	0.518	0.518 (B)	0.518 (C)
N-(*n*-Hexyl)-N-methylaniline	0.770		0.764 (D)
N-Benzhydryldimethylamine	1.000[f]		

[a] 0.25 in. × 10 ft column of 20% GE-SF96 on 40–60 mesh Chromosorb W, 170 cc/min of He flow. [b] Product designation in parentheses. [c] Ratios at this temperature are ±0.005. [d] Retention time for standard, 16.1 ± 0.4 min; peak width at half-height, 1.04 ± 0.04 min. [e] Ratios at this temperature are ±0.007. [f] Retention time for standard, 14.6 ± 0.7 min; peak width at half-height, 1.07 ± 0.05 min.

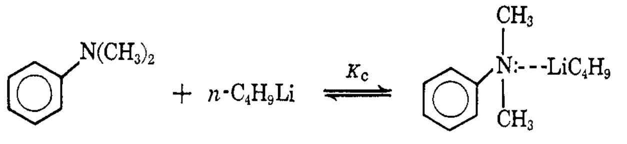
When the concentration of a single variable (either *n*-butyllithium or 1-iodopentane) was changed in reactions in which a 5:1 ratio was maintained for dimethylaniline to the other reagent (1-iodopentane or *n*-butyllithium, respectively), the relative amounts of *n*-hexyl and *n*-pentyl products shift over a wide range. With 1-iodopentane as the variable, a decrease in *n*-pentyl product and an increase in the *n*-hexyl product occurs with an increase in the molar ratio of I/Li, Figure 3. The ratio of *n*-pentyl–*n*-hexyl products was plotted for the *n*-butyllithium variation Li/I, Figure 4. The linearity of this function is interpreted as arising from a prereaction equilibrium condition with an equilibrium constant equivalent to the slope, approximately 1. This agrees with the direct measurement of related equilibrium constants by Applequist and O'Brien[7] and requires that the rate of halogen–metal

$$n\text{-}C_5H_{11}I + n\text{-}C_4H_9Li \overset{k_1}{\rightleftharpoons} n\text{-}C_5H_{11}Li + n\text{-}C_4H_9I$$

interchange be much greater than the rate of amine alkylation.

Although it was not possible to distinguish the role of iodo and lithium compounds in the alkylation, some information on the mechanism was obtained by varying amine concentrations. All the experiments discussed thus far were carried on in the presence of a large excess of dimethylaniline. When the ratio of n-butyllithium and 1-iodopentane was 1:1 and their initial concentrations were constant, the amount of dimethylaniline present was varied, Figure 5. At large molar ratios (>6) of dimethylaniline to n-butyllithium, the product ratios did not increase so rapidly as in the range 1–6. The trend however was positive over the entire range 1–8. If the species reacting is the same under all conditions, simple mass action considerations apply and the yield of amine products should be directly proportional to the concentration (or some power of the concentration) in all ranges of the amine ratio. However the yield of amine, based on the reaction limiting reagent, increases at ratios of <1. Such a discontinuity is reasonable where a species required for the reaction is principally formed at ratios 1, where the formation of this species is essentially complete at 1:1 molar ratio, and where normal kinetic concentration dependence is observed at higher ratios. The formation of a 1:1 complex between amines and n-butyllithium has been studied recently.[12] The complex, Scheme III, would be preferentially formed at low dimethylaniline concentrations if K_c was large. Above the point at which the amine or the lithium compound is completely complexed, the mass action principle should apply. This will only show up in reaction product yields if the complex participates in the reaction. When a strong complex which does not participate in the reaction is formed initially, yields of product will be a minimum and remain constant or increase very slowly with concentration. They will not begin to follow normal concentration dependencies until the complex formation is complete.

SCHEME III



The participation of a complex in the reaction is also reasonable on a kinetic basis. If the reaction is a third-order process in eq 1, the reaction rate must be fantastically high to account for the appreciable amounts of α alkylation. Second-order processes such as the Wurtz reaction may be very vigorous at room temperature.[8,13] Since third-order processes are not common[14] and halide attack on/by the complex is possible, this second-order process is more probable.

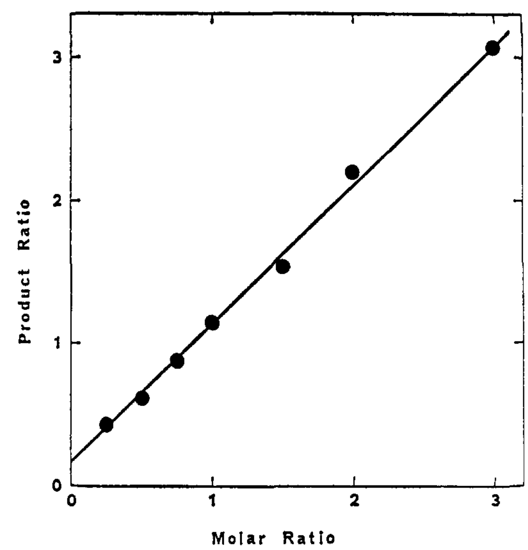


Figure 4.—Shifts in the ratio of N-(n-pentyl)- to N-(n-hexyl)-N-methylaniline with n-butyllithium to 1-iodopentane molar ratio. Controlled dilutions with n-hexane gave 0.37 M initial iodo compound concentration. The molar ratio of dimethylaniline–1-iodopentane was 5:1.

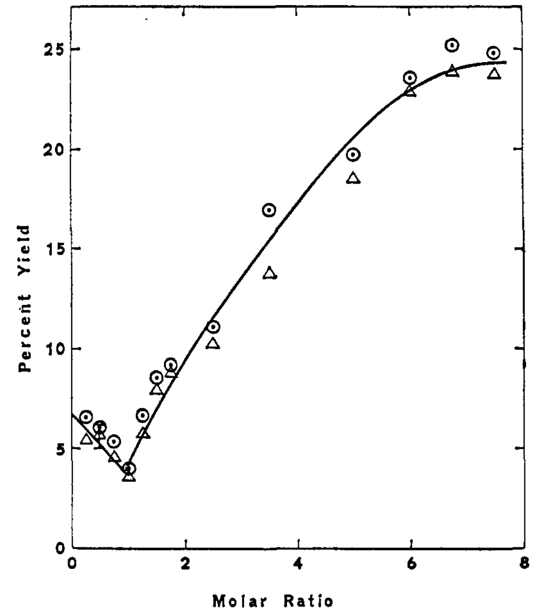


Figure 5.—Increase in yields of N-(n-pentyl)-N-methylaniline (⊙) and N-(n-hexyl)-N-methylaniline (△) with an increase in the initial molar ratio of dimethylaniline to n-butyllithium on 1-iodopentane. Controlled dilutions with the solvent, n-hexane, were used to establish initial 0.72 M iodo and lithium compound concentrations in all reactions.

The alkylation reactions effectiveness in competition with "Wurtz" coupling was determined by determining hydrocarbon and amine product yields. These products were all analyzed by gas chromatography, Table III. Possible interference with halide peaks was avoided by using 5:1.5:1 molar ratios of dimethylaniline, n-butyllithium, and 1-halopentane. The product distribution differences for iodo and bromopentane reactions are given in Table IV. The total amine yields, 13% from Br and 40% from I, were comparable with those from the 1-halobutane reactions, Table I.

The ratio of amine products for 1-iodopentane, 1.5:1 (n-C$_5$:n-C$_6$), was in agreement with the prehalogen metal equilibrium and with a pseudo-first-order (in

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(12) T. L. Brown, R. L. Gerteis, D. A. Bafus, and J. A. Ladd, *J. Am. Chem. Soc.*, **86**, 2135 (1964); F. A. Settle, M. Haggerty, and J. F. Eastham, *ibid.*, **86**, 2076 (1964).

(13) J. Hine, "Physical Organic Chemistry," McGraw Hill Book Co., Inc., New York, N. Y., 1956, p 235.

(14) J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1963, Chapter 4.

TABLE IV

PRODUCTS FROM THE 1-HALOPENTANE (20 MMOLES) REACTIONS OF DIMETHYLANILINE (100 MMOLES) AND *n*-BUTYLLITHIUM (30 MMOLES)

Product	% yield[a] from 1-Halopentane	
	Br	I
Hydrocarbons		
n-Octane	1.86	16.6
n-Nonane	32.6	27.0
n-Decane	1.74	10.7
Amines: $C_6H_5NCH_3R$		
$R = n\text{-}C_5H_{11}$	7.0	23.9
$R = n\text{-}C_6H_{13}$	6.1	15.8

[a] All values after 18 hr.

halide or lithium) reaction. The total hydrocarbon yield in the same reation was 54% and the ratio of *n*-octane–*n*-nonane–*n*-decane was 1.5:2.5:1. The following four reactions give the observed products.

$$n\text{-}C_4H_9X + n\text{-}C_4H_9Li \longrightarrow n\text{-}C_8H_{18} + LiX$$

$$n\text{-}C_4H_9X + n\text{-}C_5H_{11}Li \longrightarrow n\text{-}C_9H_{20} + LiX$$

$$n\text{-}C_5H_{11}X + n\text{-}C_4H_9Li \longrightarrow n\text{-}C_9H_{20} + LiX$$

$$n\text{-}C_5H_{11}X + n\text{-}C_5H_{11}Li \longrightarrow n\text{-}C_{10}H_{22} + LiX$$

The product ratio corresponds to the initial reactant ratio from the first and fourth equations and the sum of this ratio from the second and third.

The 1-bromopentane reaction lacks the distribution characteristic of halogen–metal preequilibration. Although the yield ratio of all hydrocarbon to all amine products is twice that for 1-iodobutane, the ratio of C_8:C_9:C_{10} hydrocarbons was 1.1:18.7:1. Hence, the third Wurtz reaction must be much faster than halogen–metal interchange even though the over-all reaction rate is slower (*cf.* Figure 1). If the relative contribution from exchange to the formation of *n*-nonane was the same as with iodopentane, 3.1–4.3% or $\sim\frac{1}{10}$th of the *n*-nonane came from exchange. The ratio 1.1:1 in *n*-octane–*n*-decane and in C_5:C_6 amine products reflects the restriction in approach to/or a change in the equilibrium ratio. Since the equilibration is a 1:1 exchange process, a 1:1 ratio rather than an equilibrium value will be observed when the interchange is restricted. The total hydrocarbon ratio for I:Br was 1.5:1, while the total amine ratio was 3.1:1. This distribution for amines, however, retains the exchange ratio. Thus, though the exchange ratio in the hydrocarbons decreased by a factor of about 7.5, the exchange ratio as seen in the amines decreased by only a factor of 3. If free exchange occurred, the hydrocarbon and amine formation reactions should decrease by comparable amounts. If the bromopentane or *n*-butyllithium was the specific reagent giving the alkyl group to the amine product, the amine product ratio should not be dependent on the halogen–metal exchange ratio. In the alkylation reaction, therefore, the reactive *n*-butyllithium–dimethylaniline complex must not be able to distinguish between the alkyl group on the *n*-butyllithium and 1-iodopentane. Indeed the complex probably acts as a catalyst for the halogen–metal interchange. The hydrocarbon distribution would then be dependent on the amount of exchanged bromoalkane which escapes from the complex before alkylation of the amine can occur.

Experimental Section[15]

Gas Chromatography.—Retention ratios and product yields were determined using an internal standard method.[16] An F & M Model 500, gas chromatograph was used with 0.25 in. × 10 ft column of 20% GE-SF96 on 40–60 mesh Chromosorb W. The flow rate was maintained between 160 and 170 cc/min of helium for analyses at either 100° or 185°. Retention ratio (rr) reproducibility was ±0.005 at 100° and ±0.007 at 185°. Minimum resolution (mr) for qualitative and quantitative analyses was calculated using the factors (*qf*) of 1.25 and 1.5, respectively. The standard's retention time (*t*) and peak width at half-height (*w*) were used to calculate the separation that was required for mr of two peaks of the same height, eq 3 following. If rr

$$\text{mr} = qf(1 - (t - w)/t)rr \tag{3}$$

is the value for any peak of analytical interest, mr is the minimum separation from any other value rr for analyses. At 100° the values for the standard, *n*-butylbenzene, were $t = 16.1 \pm 0.4$ min and $w = 1.04 \pm 0.04$ min. N-Benzhydryldimethylamine at 185° had values of $t = 14.6 \pm 0.7$ min and $w = 1.07 \pm 0.05$ min. Quantitative analyses were accomplished by adding 1.00 ml of the organic layer from a reaction mixture to an accurately weighed amount of the appropriate standard. The mixture was shaken well and a specific volume (normally 10–50 μl.) was injected into the gas chromatograph. Areas of peaks, calculated from peak heights and peak widths at half-height, were used to determine the milligrams of product formed, *n*. The per cent of theory was then calculated using eq 4 following

$$\%\ \text{yield} = \frac{nV100}{fwm} \tag{4}$$

where *V* was the total volume of the organic phase in ml, *fw* was the formula weight of product, and *m* was the number of millimoles of the reaction limiting reagent. This technique generally gave values reproducible to within ±3% of the per cent yield measured (*i.e.*, 10.0 ± 0.3%).

The yields of hydrocarbon products were determined by the same method using *n*-butylbenzene at 100°.

Chemicals.—N-Methylaniline, all alkyl halides, and hydrocarbons were commercially available. N-(*n*-butyl)-N-methylaniline, and N-(n-pentyl)-N-methylaniline were available from previous studies.[2b] Commercial monofree N,N-dimethylaniline and *n*-hexane were dried over sodium before use. *n*-Butyllithium (Foote Mineral, 20% in hexane) was titrated by the double titration method for active lithium content[17] before use.

N-(*n*-Hexyl)-N-methylaniline.—N-Methylaniline (19.3 g, 0.18 mole) and 1-bromohexane (24.7 g, 0.15 mole) were mixed in a 125-ml erlenmeyer flask, stoppered well, and heated on steam bath at 98° for 48 hr. The reaction mixture was cooled and treated with a concentrated solution of sodium hydroxide until a distinct oily layer separated. The oily layer was collected separately and the aqueous solution was extracted with ether. The oil and ether solution were mixed, washed well with water, dried over anhydrous sodium sulfate, and distilled. Pure N-methyl-N-(*n*-hexyl)aniline distilled at 154–156° (40 mm), yield 19.0 g (67%); refractive indices were $n^{20}\text{D}$ 1.5221 (lit.[18] 1.5229), $n^{25}\text{D}$ 1.5203, and $n^{30}\text{D}$ 1.5181.

The retention ratio against benzhydryldimethylamine standard was found to be 0.770.

The infrared spectrum had the following absorption bands: 3.28 w, 3.38 s, 3.45 s, 6.22 s, 6.62 s*, 6.81 m, 7.30 m, 7.65 w, 7.75 w, 7.96 w, 8.20 m, 8.40 m, 8.66 w, 8.96 w, 9.19 w, 9.69 w, 10.10 m, 10.55 w, 11.65 w, 13.38 s, 14.49 s μ.

In the nmr spectrum the alkyl-chain protons showed a multiplet centered at 1.05 ppm and protons of methyl group attached to N gave a singlet at 2.72 ppm. A multiplet centered at 3.15 ppm was due to methylene protons adjacent to nitrogen. The intensity ratio was 11:3:2, respectively. The aromatic protons split into two multiplets centered at 6.56 and 7.08 ppm with the integral ratio of 3:2.

General Procedure for the α Alkylation of N,N-Dimethylaniline.—A measured volume of anhydrous mono-free N,N-

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[15] Physical properties, infrared and pmr spectra, and refractive indices were measured in the standardized manner previously described: A. R. Lepley and R. H. Becker, *Tetrahedron*, **21**, 2365 (1965).

[16] A. R. Lepley, *Anal. Chem.*, **34**, 322 (1962).

[17] H. Gilman and A. Haubein, *J. Am. Chem. Soc.*, **66**, 1515 (1944).

[18] J. Willenz, *J. Chem. Soc.*, 1677 (1955).

dimethylaniline in a 100-ml stoppered flask was cooled to −10° using an ice–salt bath. *n*-Butyllithium was then added and the homogeneous solution was stirred with cooling for 1 min. The alkyl halide was added all at once. The stoppered stirred solution was kept in the bath and the temperature of the bath was allowed to increase gradually for 1 hr. The bath was removed and the reaction mixture was stirred at 32 ± 2° for another hour. After the second hour, the flask was cooled in an ice–water bath. Ice was added, with stirring, until the precipitate formed during the reaction dissolved. The clear organic and aqueous layers were separated. The organic layer was used directly for product characterization and yield measurements. The products were isolated by gc and characterized by their gc retention ratios and infrared and pmr spectra. In all cases, comparisons were made with the properties of commercial or synthetic compounds.

Amines from the 1-Halobutane Reactions.—N,N-Dimethylaniline (24.4 ml, 0.20 mole) was treated with *n*-butyllithium (26 ml of 1.6 *N*, 0.040 mole) and 0.040 mole of a 1-halobutane. Samples (2 ml) were withdrawn at intervals and quenched with ice. The yield of the product, N-(*n*-pentyl)-N-methylaniline, was measured in each sample by quantitative gc using N-benzhydryldimethylamine as an internal standard, Figures 1 and 2.

The 1-iodobutane reaction was carried out using the general procedure and gave a maximum yield of product after 2.5 hr 1-Bromobutane reactions were followed under the general conditions and at room temperature because of the mildness of the reaction. In both cases with the bromide, reaction was complete after 4 hr. 1-Chlorobutane failed to give any N-(*n*-pentyl)-N-methylaniline after several days at room temperature.

Amines from the 1-Iodoalkane Reactions.—N,N-Dimethylaniline (12.2 ml, 0.10 mole) was treated with 26 ml (0.040 mole) of *n*-butyllithium and 0.020 mole of 1-iodoalkane for 2 hr as described in the general procedure.

When 1-iodopropane was used, the organic layer showed two product peaks by gc. The retention ratios of the products A and B were 0.375 and 0.518, respectively, *vs.* the benzyhydryldimethylamine standard. The product A had infrared and pmr spectra identical with those of N-(*n*-butyl)-N-methylaniline, while the product B corresponded in all properties to N-(*n*-pentyl)-N-methylaniline. Quantitative gc gave 7.6 and 16.5% as the respective yields of A and B.

Two product gc peaks were also observed when 1-iodopentane was used. These two peaks C and D had retention ratios of 0.518 and 0.760, respectively. The product C was identical with the product B from the 1-iodopropane reactions (*i.e.*, N-(*n*-pentyl)-N-methylaniline), while the product D corresponded in all properties to N-(*n*-hexyl)-N-methylaniline as prepared above. Yields of C and D were 14.3 and 8.2%, respectively.

Hydrocarbons and Amines from the 1-Halopentane Reactions.—N,N-Dimethylaniline (12.2 ml, 0.10 mole) was treated with 19 ml (0.030 mole) of *n*-butyllithium and 0.020 mole of a 1-halopentane at −10°. Instead of stopping the reaction after 2 hr as in the general procedure, the reaction was continued at 32° for 18 hr. After quenching, the organic layer was analyzed for hydrocarbon products by gc at 100° using *n*-butylbenzene as a standard. Amine yields were determined as in the preceeding experiments.

1-Iodopentane gave three gc product peaks at 100° with retention ratios of 0.217, 0.400, and 0.740. These compounds I, II, and III were identical with *n*-octane, *n*-nonane, and *n*-decane, respectively. The hydrocarbon products I, II, and III had respective yields of 16.6, 27.0, and 10.7%. Amine products as determined at 185° were C, 23.9%, and D, 15.8%.

1-Bromopentane gave the same products with yields for I, II, III, C, and D of 1.86, 32.6, 1.74, 7.0, and 6.1%, respectively.

Influence of Reactant Concentration on Amine Yields.—The reaction system, N,N-dimethylaniline, *n*-butyllithium, and 1-iodopentane, was studied by changing a single concentration variable.

A. **Dependence on N,N-Dimethylaniline.**—*n*-Butyllithium and 1-iodopentane were used in 1:1 molar proportions; 20 mmoles of each were used in all experiments. The total solution volume was kept at 27.7 ml by changing the relative proportions of dimethylaniline and *n*-hexane. The 1.6 *N* *n*-butyllithium in hexane solution was concentrated under vacuum to allow measurements at the higher dimethylaniline concentrations. In the concentrated solutions active lithium concentrations were determined by double titration.[18] Reactions were carried out following the general procedure and amine product yields (Figure 5) were measured by the usual gc technique.

B. **Dependence on 1-Iodopentane.**—N,N-Dimethylaniline (0.10 mole) and 20 mmoles of *n*-butyllithium were used in all experiments. The total solution volume of the reaction mixture was kept at 33.1 ml by varying the relative proportions of 1-iodopentane and *n*-hexane. The standard reaction and analysis procedures were used. The results are given in Figure 3.

C. **Dependence on *n*-Butyllithium.**—N,N-Dimethylaniline and 1-iodopentane were used in 5:1 ratio, 0.10 and 0.020 mole, respectively. The reaction mixture total volume was maintained at 53.8 ml by adding varying amounts of *n*-hexane and 1.6 *N* *n*-butyllithium in *n*-hexane. Procedures were as described in A and B. The amine product distributions are given in Figure 4.

The Sodium Amide Catalyzed Rearrangement of Some Acetylenes in Ethylenediamine[1a]

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Any of the isomeric normal C_6 acetylenes and allenes yield the same "equilibrium" mixture when treated with sodium amide in ethylene diamine at room temperature. The required equilibration time depends on the starting substrate and amounts of sodium amide. Different quantities of sodium amide produce an "equilibrium" mixture of different composition. The novel branched dialkyl acetylenes I and II were prepared and rearranged. There was no evidence that rearrangement proceeded past the branching.

The base-catalyzed rearrangement of acetylenes is well known. In the past it was frequently accomplished in the presence of alcoholic potassium hydroxide at elevated temperatures. Thus, Jacobs[2] equilibrized the isomeric pentynes at 175° and the reaction mixture consisted of 1.3% 1-pentyne, 3.5% 1,2-pentadiene, and 95.2% 2-pentyne. Such rearrangements were frequently accompanied by side reactions such as polymerization and/or addition of solvent to the unsaturated bonds, as evidenced by the fact that not more than 70% of the hydrocarbons was recovered.[2] The rearrangement of octynes and octadienes with sodium amide in hot benzene to 2-octyne was also described.[3] Sodium and potassium *t*-butoxide in *t*-butyl alcohol near 200° were used for the rear-

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