α Butylation of Triethylamine[1a]

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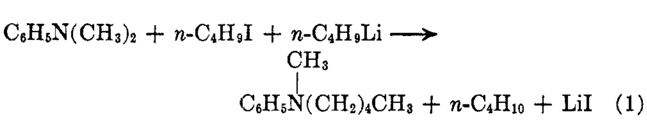
The α alkylation of triethylamine by *n*-butyllithium and 1-iodobutane gave 14 to 25% yields of N-(2-hexyl)-diethylamine. The lower the initiation temperature the more effective the α butylation was in competition with the *n*-octane forming "Wurtz" reaction. Metallation of triethylamine was carried out by prolonged reflux with *n*-butyllithium. Although products from the reactions of the metallated species were not observed, determination of the total active lithium and *n*-butyllithium showed that triethylamine metallation took place at reflux but not under conditions of α alkylation. The α alkylation also can not proceed *via* a quaternary ammonium salt intermediate.

The α alkylation reaction of tertiary amines, eq 1, has been observed with N,N-dialkylanilines.[2] Since



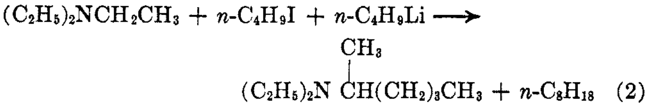
$$C_6H_5N(CH_3)_2 + n\text{-}C_4H_9I + n\text{-}C_4H_9Li \longrightarrow C_6H_5\overset{CH_3}{\overset{|}{N}}(CH_2)_4CH_3 + n\text{-}C_4H_{10} + LiI \quad (1)$$

this alkylation involves the reaction of alkyllithium and halo organic compounds with a tertiary amine, the application to a trialkylamine seemed feasible. Such reactions would be of particular interest because of recent studies on alkyllithium complexes with trialkylamines,[3-6] and suggest exploration of amine metallations under conditions of complex formation and α alkylation.

Triethylamine has been used extensively in complex studies,[4-6] and the effect of ethyllithium on the salt of triethylamine and iodobutane has been reported.[7] Therefore, we have studied the α alkylation of triethylamine.

Results and Discussions

The α alkylation of triethylamine with *n*-butyllithium and 1-iodobutane gave N-(2-hexyl)diethylamine and the "Wurtz" product *n*-octane, eq 2. Gas chromato-



$$(C_2H_5)_2NCH_2CH_3 + n\text{-}C_4H_9I + n\text{-}C_4H_9Li \longrightarrow (C_2H_5)_2N\overset{CH_3}{\overset{|}{C}}H(CH_2)_3CH_3 + n\text{-}C_8H_{18} \quad (2)$$

graphic (gc) retention ratios, Table I, were used for initial product identification and, with calibration, for quantitative analysis. Infrared comparison of the first gc component from a preparative run and commercial *n*-octane confirmed the Wurtz product structure. N-(2-Hexyl)diethylamine was prepared from 2-bromohexane and diethylamine. The infrared and proton magnetic resonance (pmr) spectra, refractive indices, and boiling point of the second gc preparative component were identical with those of the synthetic N-(2-hexyl)diethylamine.

Table I

Gas Chromatographic Retention Ratios of Compounds Related to the α Alkylation of Triethylamine

	Retention ratios[a]		
		Reaction products	
	Calibration	α alkylation[b] of $(C_2H_5)_3N$	Rearrangement[c] of $n\text{-}C_4H_9\overset{+}{N}(C_2H_5)_3I^-$
Triethylamine	0.096		0.097
n-Octane	0.195	0.191	0.193
1-Iodobutane	0.208		
N-(*n*-Butyl)diethylamine	0.270		0.268
N-(2-Hexyl)diethylamine	0.700	0.700	
N,N-Dimethylaniline	1.000[d]		

[a] 0.25 in. × 10 ft column of 20% GE-SF96 on 40–60 mesh Chromosorb W, 100°, 166 cc/min of He flow; ratios are ±0.002. [b] Reaction of triethylamine, *n*-butyllithium, and 1-iodobutane. [c] Reaction of N-(*n*-butyl)triethylammonium iodide with *n*-butyllithium. [d] Retention time for standard, 18.6 ± 0.4 min; peak width at half-height, 1.20 ± 0.03 min.

Initial cooling of reaction mixtures was necessary to control the reactions. Ziegler and Colonius[8] reported a vigorous reaction between *n*-butyllithium and 1-iodobutane at room temperature. In previous α butylations of dialkylanilines with *n*-butyllithium and 1-iodobutane, the reaction was calm at −10°. The reaction with triethylamine was quite vigorous at −10°, but could be controlled at lower temperatures. Although constant temperature was not maintained in these butylations, the yields of N-(2-hexyl)diethylamine decreased while *n*-octane formation increased with increasing initial reaction temperature, Table II.

Table II

Products from the Reactions of Triethylamine (100 mmoles), *n*-Butyllithium (20 mmoles), and 1-Iodobutane (20 mmoles)

Initial temp, °C	Reaction time, hr	Product yield, %	
		n-Octane	N-(2-Hexyl)diethylamine
−15	2	92 ± 8	14 ± 2
−25	2	87 ± 8	21 ± 2
−70 to −80	16	80 ± 7	25 ± 2

Since 1-iodobutane was quantitatively accounted for in the two products and since the reactions are competitive, the temperature dependence must be greater in "Wurtz" double displacement than in α alkylation.

The general nature of the α alkylation reaction is confirmed by the participation of triethylamine. The reaction with this amine also furnishes a means of over-

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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, W. Va.

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

(3) J. F. Eastham and G. W. Gibson, *J. Am. Chem. Soc.*, **85**, 2171 (1963); Z. K. Cheema, G. W. Gibson, and J. F. Eastham, *ibid.*, **85**, 3517 (1963).

(4) F. A. Settle, M. Haggerty, and J. F. Eastham, *ibid.*, **86**, 2076 (1964).

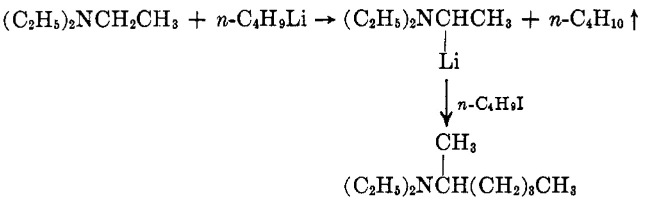
(5) T. L. Brown, R. L. Gerteis, D. A. Bafus, and J. A. Ladd, *ibid.*, **86**, 2135 (1964).

(6) C. G. Screttas and J. F. Eastham, *ibid.*, **87**, 3276 (1965).

(7) F. D. Hager and C. S. Marvel, *ibid.*, **48**, 2689 (1926).

(8) K. Ziegler and H. Colonius, *Ann.*, **479**, 135 (1940).

coming ambiguities in interpretation of metallated intermediates in the dialkylaniline α alkylations. The only identifiable products in the n-butyllithium attack on dimethylaniline were from the *ortho* and *meta* ring metallated species.[9] With triethylamine, only alkyl groups are present for metalation. Reaction should parallel the α metallation of diethyl ether with n-butyllithium.[10] The metallated species would then produce the α-alkylation product by a "Wurtz" reaction with 1-iodobutane. Support for the initial step



in this mechanism comes from the recent work of Screttas and Eastham,[6] who report that tertiary amines act as catalysts in many normally difficult metallations. In this case, the amine would act as a catalyst in its own metallation.

The metallation of triethylamine with n-butyllithium was attempted at room temperature and reflux. After prolonged reflux, the mixture took on the appearance and consistency of meringue. Although the mixture reacted rapidly with reagents previously employed,[9] we were unable to purify materials isolated from the reaction mixtures. Instead of direct product identification, indirect methods were used to determine the extent of metallation.

We determined the total amount of active lithium compounds by the double titration of Gilman and Haubein,[11] with a calibration correction for reaction of benzyl chloride and triethylamine. The amount of unreacted butyllithium was determined by conversion to 1,1-bis(trifluoromethyl)-1-pentanol with hexafluoroacetone gas and gc analysis using 1-pentanol as a standard.[9] The difference between active lithium and n-butyllithium then gave the amount of triethylamine metallation.

The active lithium and n-butyllithium results at room temperature and reflux are given in Table III. At room temperature, n-butyllithium accounted for all active lithium. Although a slight decrease in lithium compounds appears to occur after 16 hr, the value just exceeds the error of ±2 mmoles in duplicate sample preparation. At reflux, both active lithium and n-butyllithium drop off rapidly. Although a minimum of 11 ± 1 mmoles of active lithium is reached after 2 hr,[12] the amount of n-butyllithium continues to decrease until the mixture forms the meringue. An appreciable quantity of some metallated material was formed, therefore, but only under reflux. Since the α butylation required only 2 hr at temperatures not exceeding ambient after initiation at -15 or $-25°$, metallation can not participate in the α alkylation of triethylamine.

TABLE III

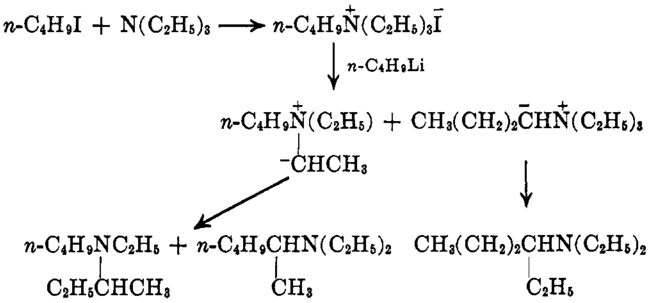
METALLATION OF TRIETHYLAMINE

	Metallated species, mmole			
	Room temp, °C		Reflux	
Time, hr	Total[a] active Li	n-C$_4$H$_9$Li[b]	Total[a] active Li	n-C$_4$H$_9$Li[b]
0	22	22 (43)[c]	..	...
0.25	20	20 (38)	20	15 (30)
2	22	23 (44)	11	6 (12)
4	24	24 (46)	12	<2 (<4)
16	17	17 (34)	10	0 (<0.5)

[a] Active lithium, from C–Li compounds, was determined by the double titration method,[11] with a correction for amine. [b] Reaction with hexafluoroacetone; yields of 1,1-bis(trifluoromethyl)-1-pentanol, given in parentheses, were determined by quantitative gc with calibration corrections.[9] [c] Blank for calculation of yield-mmole correlation.

An alternative to metallation in a stepwise reaction process is the formation of a quaternary salt which rearranges under basic conditions (Scheme I). Under

SCHEME I



the conditions of the Stevens rearrangement an α proton could be extracted from either an ethyl or butyl group in the salt formed by triethylamine and 1-iodobutane. Three products would be possible if no changes occur in the alkyl groups migrating to form the final tertiary amine. The observed α-butylation product of triethylamine, N-(2-hexyl)diethylamine, is among the products. However, there is no obvious reason why N-(2-butyl)-N-(n-butyl)ethylamine and N-(3-hexyl)diethylamine would not be formed simultaneously. If this is the reaction route, perhaps our initial identification of the amine product was not adequate, and perhaps earlier workers[7] on the alkyllithium attack on N-(n-butyl)-triethylammonium iodide failed to find these products.

We, therefore, prepared the quaternary salt by reaction of triethylamine with 1-iodobutane.[13] The properties of the salt agreed with the literature[7,13] and the pmr spectrum confirmed functional groups including the anticipated nitrogen splitting of CH$_3$ on the ethyl groups. Treatment of the salt with n-butyllithium in ether[14] gave triethylamine, n-octane, and N-(n-butyl)diethylamine, Table I, in 13 ± 3, 5.8 ± 0.4, and 82 ± 2% yields, respectively. N-(n-Butyl)diethylamine was confirmed by comparison with the amine prepared from 1-bromobutane and diethylamine. Both amines had been suggested by Hager and Marvel[7] in studies of the salt reaction with ethyllithium. However, they were unable to observe hydrocarbon products because of the solvent, petroleum ether.

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[9] A. R. Lepley, W. A. Khan, A. B. Giumanini, and A. G. Giumanini, *J. Org. Chem.*, **31**, 2047 (1966).

[10] K. Ziegler and H.-G. Gellert, *Ann.*, **567**, 185 (1950).

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

[12] Reaction with nitrogen in the closed reaction system may account for the initial loss of active lithium.

[13] W. G. Young, I. D. Webb, and H. L. Goering, *J. Am. Chem. Soc.*, **73**, 1076 (1951).

[14] *Cf.* A. R. Lepley and R. H. Becker, *Tetrahedron*, **21**, 2365 (1965); *J. Org. Chem.*, **30**, 3888 (1965).

$$n\text{-}C_4H_9\overset{+}{N}(C_2H_5)_3\overset{-}{I} + n\text{-}C_4H_9Li \xrightarrow{-C_4H_{10}} \begin{cases} n\text{-}C_4H_9N(C_2H_5)_2 + CH_2{=}CH_2\uparrow \\ N(C_2H_5)_3 + CH_2{=}CHCH_2CH_3\uparrow \end{cases} \tag{3}$$

$$n\text{-}C_4H_9\overset{+}{N}(C_2H_5)_3\overset{-}{I} + n\text{-}C_4H_9Li \longrightarrow \begin{cases} n\text{-}C_4H_9N(C_2H_5)_2 + n\text{-}C_6H_{14} \\ N(C_2H_5)_3 + n\text{-}C_8H_{18} \end{cases} \tag{4}$$

All products[15] are the result of Hofmann elimination,[16,17] eq 3, or nucleophilic substitution,[17] eq 4. *n*-Hexane was the solvent for *n*-butyllithium preventing the observation of eq 4 as a route to N-(*n*-butyl)diethylamine formation. The octane yield indicates that about half the triethylamine was formed by nucleophilic attack by the base.

Since no N-(*n*-butyl)diethylamine was observed in the α butylation of triethylamine and since no N-(2-hexyl)diethylamine was observed in the reaction of N-(*n*-butyl)triethylammonium iodide with *n*-butyllithium, the formation of a quaternary salt can not be a step in the α alkylation of triethylamine.

Although the quaternary salt and metallation intermediate do not participate, the α alkylation of triethylamine effectively competes with the "Wurtz" reaction between 1-iodobutane and *n*-butyllithium. α alkylation, therefore, would appear to be a general reaction of tertiary amines with a mechanism as yet undetermined.

Experimental Section

Physical Constants.—Unless otherwise specified, proton magnetic resonance (pmr) spectra were measured on 20% by volume solution in carbon tetrachloride with approximately 1% tetramethylsilane as an internal standard. A Varian A-60 instrument was used for all measurements. Splittings (J_H) were 7.0 ± 0.1 cps. Infrared measurements were made on the pure liquids or on potassium bromide disks of the solids using a Perkin-Elmer Model 137 spectrophotometer. Wavelengths are given in microns; intensities indicated relative to the most intense peak (*) as equivalent to 100% are s = strong 76–100%, m = medium 51–75%, w = weak 26–50%, and vw = very weak 10–25% (very weak bands are given only when quite sharp and characteristic).

Gas Chromatography.—This was carried out at 75 and 100° on an F & M Model 500 using a 10 ft × 0.25 in. column packed with 20% GE-SF96 on 40–60 mesh Chromosorb W. The flow rate was maintained between 160 and 170 cc/min. of helium. Retention ratios and product yields were determined with an internal standard method.[19] Retention ratio reproducibility was ±0.002 at 100°, Table I. Quantitative analyses were made using peak heights and peak widths at half-height. With dimethylaniline as a standard at 100°, calibration factors were 0.97 for N-(*n*-butyl)diethylamine and 0.684 for *n*-octane. Amounts of triethylamine in the quaternary salt rearrangement were determined at 75° by a secondary standard method using the value of N-(*n*-butyl)diethylamine found at 100°. 1-Pentanol was used at 75° as the standard for quantitative determination of 1,1-bis(trifluoromethyl)-1-pentanol, 1.69 calibration factor.[9] Minimum resolution for gc analysis was calculated as previously described.[20] The retention time for dimethylaniline was 18.6 ± 0.4 min; the width at half-height for this standard was 1.20 ± 0.03 min.

Chemicals.—Diethylamine, dimethylaniline, *n*-octane, 1-iodobutane, 1-bromobutane, and benzyl chloride were obtained from Eastman. Triethylamine, 2-bromohexane, and 1-pentanol came from Matheson Coleman and Bell; the triethylamine was dried over sodium before use. Hexafluoroacetone was from Columbia Organic Chemicals. Foote Mineral 15% *n*-butyllithium in hexane was titrated[11] for active lithium concentration before use.

N-(2-Hexyl)-N,N-diethylamine.—Diethylamine (21 ml, 0.2 mole) was dissolved in 28 ml of 95% ethanol and 14 ml (0.1 mole) of 2-bromohexane was added. After the flask was tightly stoppered and heated on a steam bath for 4 days, a crystalline solid separated. The reaction mixture was cooled well and made strongly basic with concentrated aqueous sodium hydroxide. The organic layer was separated and the aqueous layer was extracted with ether. The combined organic phases were washed several times with water, dried over anhydrous sodium sulfate, decanted, and distilled. N-(2-Hexyl)-N,N-diethylamine (80%, gc) was obtained as a colorless oil, bp 40° (55 mm). The infrared spectrum of this compound was identical with that of the second gc product peak in the α substitution on triethylamine. The pmr spectrum had broad multiplets centered at 1.05 and 2.41 ppm. Distinct features in this spectrum were CH_3 on CH doublet at 0.85 ppm, CH_3 of ethyl triplet at 0.97 ppm, and asymmetrically split CH_2 on N of ethyl quartets at 2.38 and 2.45 ppm. The integral of the multiplets gave the respective proton ratios of 18:5.

N-(*n*-Butyl)-N,N-diethylamine.[7]—Diethylamine (21 ml, 0.2 mole) was mixed with 32 ml (0.3 mole) of 1-bromobutane and the mixture was heated on a steam bath in a sealed tube for 2 days. The mixture was worked up as described for N-(2-hexyl)-N,N-diethylamine (82%, gc) distilled at 137° (lit.[7] 136–137°), had a retention ratio against dimethylaniline of 0.270 at 100°, and had refractive indices of n^{20}_{D} 1.4134, n^{25}_{D} 1.4115, and n^{30}_{D} 1.4091. The product gave infrared absorption bands at 3.36 s*, 3.48 m, 3.58 s, 6.85 m, 6.95 w, 7.29 m, 7.78 w, 8.34 m, 8.81 w, and 9.2–9.38 m μ. Pmr peaks were CH_3 of ethyl triplet at 0.98 ppm, superimposed on a broad CH_3 and CH_2 of butyl multiplet with the integral for all centered at 1.17 ppm; the butyl CH_2 and ethyl CH_2 on nitrogen gave a multiplet centered at 2.45 ppm with the quartet of the latter at 2.48 ppm. The integrated areas of the multiplets corresponded to 13 and 6 protons, respectively.

N-(*n*-Butyl)triethylammonium Iodide.—A mixture of 14 ml (0.1 mole) triethylamine and 11 ml (0.1 mole) of 1-iodobutane was refluxed for 1 hr and allowed to stand overnight. After filtration, the crude salt was purified by dissolution in methanol and then reprecipitated by adding ether. N-(*n*-Butyl)triethylammonium iodide (15 g, 40% yield) was washed well with ether and dried *in vacuo:* mp 204–205° (lit.[7,13] 205°). The infrared spectrum of the salt had peaks at 3.39 s, 3.48 m, 6.84 s*, 6.93 s, 7.17 s, 7.3 w, 7.64 w, 8.51 s, 9.22 w, 9.7 w, 12.3 w, and 12.54 m μ. The pmr was measured in deuterium oxide with H_2O as a standard at 4.78 ppm with respect to TMS. Salt pmr values with respect to TMS are a CH_3 of ethyl triplet split into three equal parts by nitrogen at 1.36 ppm (J_N = 2.0 ± 0.1 cps) and superimposed on a broad CH_3 and CH_2 of butyl multiplet with the integral for all centered at 1.39 ppm, and an overlapping triplet, 3.30 ppm, and quartet, 3.39 ppm, from butyl and ethyl CH_2 on nitrogen, respectively. The relative integrated areas of the two sets of overlapping bands were 2:1 corresponding to 16 and 8 protons, respectively.

Reaction of N-(*n*-Butyl)triethylammonium Iodide with *n*-Butyllithium.—The dry, finely powdered quaternary salt (5.7 g, 20 mmoles), 74 ml of anhydrous ether, and 26 ml of 1.6 *N* *n*-butyllithium (40 mmoles) were mixed with stirring at 32°. Samples

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(15) A trace amount of 1.6 ± 0.5% (by gc) of material which might be Stevens rearrangement products was observed with retention ratios 0.66–0.72; *cf.* Table I.

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

(17) D. A. Archer and H. Booth, *J. Chem. Soc.*, 322 (1963).

(18) Analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. Melting and boiling points are uncorrected.

(19) A. R. Lepley, *Anal. Chem.*, **34**, 322 (1962).

(20) A. R. Lepley and W. A. Khan, *J. Org. Chem.*, **31**, 2064 (1966).

(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 $n^{20}\mathrm{D}$ 1.4239, $n^{25}\mathrm{D}$ 1.4213, and $n^{30}\mathrm{D}$ 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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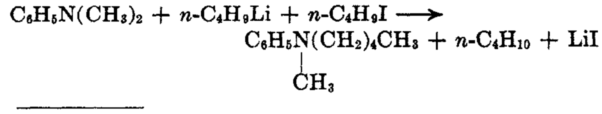
The effect of the haloalkane on the α alkylation of N,N-dimethylaniline has been investigated. The yield of alkylated products and reaction rates were found to decrease with increasing electronegativity of the halogen atom. Distributions of alkylated products and hydrocarbons from "Wurtz" coupling result 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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