amino)biphenyl and N-methyldiphenylamine from a gc-purified sample in dimethylaniline reactions, see below.

Dimethylaniline–Fluorobenzene Preparative Reaction.—Dimethylaniline (317 ml, 2.5 moles) and 47 ml (0.5 mole) of fluorobenzene were mixed in a dry 2-l. flask, equipped with magnetic stirrer and drying tube, and cooled in an ice bath. *n*-Butyllithium, 500 ml of 1.6 *N* in hexane, was rapidly added while stirring and cooling. The solution was then allowed to come to room temperature. After 18 hr, 25 ml of methanol was carefully added with cooling. Ice, 50 g, was added and the organic phase was separated. Solvent and unreacted starting materials were distilled off. The residue which had two product gc peaks of area 10:1 and retention ratios of 0.87 and 1.03 (Table I) was extracted with concentrated hydrochloric acid. The acid layer was washed with ether and then made strongly basic by slow addition of solid sodium hydroxide while stirring and cooling. The organic products were collected by ether extraction and the ether solution was dried with anhydrous sodium sulfate, decanted, and distilled. Products, 6.7 g, were collected at 85.5–88° (3.5 mm), $n^{25}\mathrm{D}$ 1.6093. The material was purified by preparative gc for infrared, pmr, and elementary analysis. The infrared spectrum had bands at 3.30 w, 3.42 vw, 3.51 vw, 3.60 vw, 6.28 s, 6.68 s*, 6.92 vw, 7.43 m, 7.87 w, 7.98 w, 8.44 vw, 8.66 vw, 8.83 w, 9.00 vw, 9.15 vw, 9.3 vw, 9.70 vw, 10.08 vw, 10.55 vw, 11.52 w, 12.9–13.0 w, 13.3 m, and 14.4 m μ. The pmr spectrum had methyl group singlets at 2.49 and 3.25 ppm and a broad aromatic multiplet centered at 7.12 ppm with the respective area ratios of 1:3:9.7.

Anal.[23] Calcd for $C_{13}H_{13}N$: C, 85.21; H, 7.15. Found: C, 84.90; H, 6.92.

From these data, the product mixture was 86% N-methyldiphenylamine and 14% *o*-(dimethylamino)biphenyl. Both of these products were from the first peak of gc analysis. The second gc component was observed in the mixture before separation but was not recovered on distillation.

Diethylaniline–Fluorobenzene Reaction.—Dry N,N-diethylaniline (25 ml, 155 mmoles) was mixed with 5 ml (54 mmoles) of fluorobenzene and 50 ml of 1.6 *N* *n*-butyllithium in hexane was added. The reaction was stoppered and stirred for 72 hr at room temperature. After quenching with 25 ml of water, gc analysis indicated two peaks with area ratios of 1.1:1 and retention ratios of 2.80 ± 0.03 and 3.50 ± 0.04 with respect to N-(*n*-butyl)-N-methylaniline (*cf.* Table I). The solvent and starting materials were distilled off. Preparative gc on the residue gave two components for infrared, pmr, and molecular weight determinations.

The two components and samples of N-benzyl-N-ethylaniline (formula weight 211.3) and N-benzyl-N-(β-phenethyl)methylamine (formula weight 225.3) were measured to increase precision. The first gc component had a formula weight of 218 ± 3 g/mole while the second component formula weight was 224 ± 1 g/mole.

The first component had an infrared spectrum with bands at 3.30 w, 3.40 s, 3.51 m, 6.28 vw, 6.70 vw, 6.78 m, 6.8–7.0 w, 7.28 vw, 7.94 vw, 8.45 vw, 8.63 vw, 8.89 vw, 9.08 vw, 9.32 vw, 9.5 vw, 9.88 w, 10.55 vw, 10.9 vw, 12.92 w, 13.3 s, and 14.22 s* μ. The pmr spectrum of this component had complex aliphatic CH multiplets centered at 1.11 and 2.53 ppm and an aromatic multiplet centered at 7.25 ppm with the respective integrated peak area ratio of 3.5:1:4.5. Comparison of these data with other spectral data on *sec*-butyl aromatic amines lead to the assignment of N-(2-butyl)diphenylamine as the main constituent of this component. Attempts to make this compound by other reactions were unsuccessful. From the measured formula weight and spectra, the amount of N-ethyldiphenylamine in the first gc component was <25%.

The second gc component had retention ratio, formula weight, infrared, and pmr analyses identical with those of *o*-(diethylamino)biphenyl.

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[23] We are grateful to Dr. D. Chrisman of Brookhaven National Laboratory for this analysis.

α Substitution on N,N-Dialkylanilines[1a]

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Received March 10, 1966

N-(*n*-Pentyl)- and N-benzyl-N-methylaniline were formed on reaction of dimethylaniline, iodobenzene, and *n*-butyllithium. When iodobenzene was replaced with 1-iodobutane, only N-(*n*-pentyl)-N-methylaniline was observed. Either 1-iodobutane or iodobenzene reacted with phenyllithium and dimethylaniline to give N-benzylmethylaniline but no pentyl product. Reactions with *n*-butyllithium or 1-iodobutane were complete after 3 hr. Premetallation of dimethylaniline indicated that metallated species were not reaction intermediates. The action of *n*-butyllithium on N-(*n*-butyl)dimethylanilinium iodide gave dimethylaniline and N-(*n*-butyl)-methylaniline. Solvent and dilution effects on the α-substitution reaction forming N-(*n*-pentyl)methylaniline indicated the possibility of participation of an amine–organolithium complex. Restriction to the α position was shown by the formation of N-(2-hexyl)ethylaniline as the sole amine product in the reaction of diethylaniline with 1-iodobutane and *n*-butyllithium.

In accompanying papers, we have studied the metallation of dimethylaniline[2] and the benzyne addition to dialkylanilines.[3] The information obtained was an adjunct to ternary reaction system studies. The ternary system included a tertiary amine, a halo-organic, and an organolithium compound. Restriction of the amine to dimethyl or diethylaniline, the halo-organic to 1-iodobutane or iodobenzene, and the organolithium species to *n*-butyllithium or phenyllithium furnished the basis for a remarkable new reaction which is the subject of this paper.

Results and Discussion

When iodobenzene was used in place of fluoro or chlorobenzene,[3] the reaction of the halobenzene with dimethylaniline and *n*-butyllithium was quite vigorous in contrast with the order of benzyne generation F > Cl > Br > I.[4] Initial cooling of the mixture to −10°, gave a smooth reaction. Two products were observed by gas chromatographic (gc) analysis of the final solution. Retention ratios were confirmation that the reaction did not proceed *via* benzyne. N-Methyldiphenylamine, *o*-(dimethylamino)biphenyl, and N-ethyldiphenylamine, the anticipated benzyne products[3] were not formed.

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[1] (a) Presented in part before the Division of Organic Chemistry, 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 1964, Abstracts, 92S; A. R. Lepley and A. G. Giumanini, *Chem. Ind.* (London), 1035 (1965); (b) to whom reprint requests should be sent: Department of Chemistry, Marshall University, Huntington, W. Va.

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

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

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

TABLE I

GAS CHROMATOGRAPHIC RETENTION RATIOS AND PROTON NUCLEAR MAGNETIC RESONANCE SPECTRA OF AROMATIC TERTIARY AMINES ASSOCIATED WITH THE α BUTYLATION OF DIALKYLANILINES

		Chemical shift[b]						
		CH_3		CH_2			CH	H
Compound	Retention ratio[a]	C	NAr	C, C	C, Ar	C, NAr	C, C, NAr	ArN
o-(n-Butyl)-N,N-dimethylaniline	0.79	1.33 m (7)	2.58 s (6)		2.75 m (2)			6.98 m (4)
N-(n-Butyl)-N-methylaniline	1.000[c]	1.05 m (7)[d]	2.75 s (3)	1.05 m (7)[d]		3.18 t (2)		6.58 m (3) 7.05 m (2)
N-(n-Butyl)-N-ethylaniline	1.265	1.07 t 1.18 m (10)[d]		1.18 m (10)[d]		3.16 t 3.25 q (4)[e]		6.53 m (3) 7.04 m (2)
N-(2-Pentyl)-N-methylaniline	1.29	1.02 d 1.07 m (10)[d]	2.57 s (3)	1.07 m (10)[d]			3.8 t (1)	6.63 m (3) 7.04 m (2)
N-(n-Pentyl)-N-methylaniline	1.64	1.30 m (9)[d]	2.82 s (3)	1.30 m (9)[d]		3.21 t (2)		6.58 m (3) 7.06 m (2)
N-(2-Hexyl)-N-ethylaniline	2.18	1.10 t 1.15 m (15)[d]		1.15 m (15)[d]		3.16 q (2)	3.7 m (1)	6.62 m (3) 7.03 m (2)

[a] 0.25 in. × 5 ft column of 20% GE-SF96 on 60–80 mesh Chromosorb W, 74 cc/min of He flow, 134°; ratios are ±0.005. [b] All peaks are relative to tetramethylsilane in parts per million; splitting: s = singlet, d = doublet, t = triplet, q = quartet, m = multplet; all J values are 7.0 ± 0.1 cps; values in parentheses are relative integrated peak ratios in compound. [c] Retention time for standard, 22 ± 2 min; peak width at half-height, 1.5 ± 0.1 min. [d] Total of all protons from CH_3 and CH_2 attached only to C in particular compound. [e] Total number of CH_2 protons from butyl and ethyl groups attached to nitrogen.

TABLE II

DIMETHYLANILINE REACTIONS WITH RI PLUS R'LI

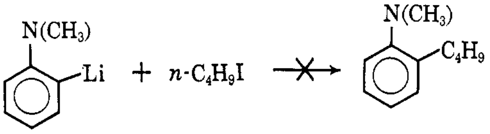
		RI		R'Li			Product yield, %	
Reaction	$C_6H_5N(CH_3)_2$, mmole	R	mmole	R'	mmole	Time, hr	$n\text{-}C_6H_{11}\overset{CH_3}{\overset{\vert}{N}}C_6H_5$	$C_6H_5CH_2\overset{CH_3}{\overset{\vert}{N}}C_6H_5$
1	100	C_6H_5	20	n-C_4H_9[a]	50	12	16.4	15
2	100		20		20	24–28	10 ± 0.5	26.5 ± 0.1
3	100		20		40	14[b]	6.5	7
4	60		40		40	7 days[c]	...	3
5	100	n-C_4H_9	20	n-C_4H_9[a]	40	2.5	33	...
6	100		40		40	2.5	27	...
7	100		20		40	2.5[d]	22	...
8	100		20		40	2.5[e]	11	...
9	100	n-C_4H_9	20	C_6H_5[f]	40	3.25	...	9
10	100	C_6H_5	20	C_6H_5[f]	40	4 days	...	1.8[g]

[a] 15% solution in n-hexane (1.6 N n-C_4H_9Li). [b] n-C_4H_9Li plus $C_6H_5N(CH_3)_2$ refluxed for 4 hr before cooling and addition of C_6H_5I; time given is reaction time after final addition. [c] As in b but 24 hr of reflux before reaction; measurements also made after 1 and 3 days. [d] Diluted with 15 ml of n-pentane. [e] Diluted with 15 ml of anhydrous ether. [f] 20% solution in 3:1 (v/v) benzene–ether (2.16 N C_6H_5Li). [g] Other products include 5% o-terphenyl and 1.7% of another product which may be o-dimethylaminobiphenyl or N-methyldiphenylamine per gc retention ratio.

The two products were characterized by their retention ratios and infrared and proton magnetic resonance (pmr) spectra. One of these products, the second gc component, was fortuitously identified as N-benzyl methylaniline by comparison with our tables of tertiary amine pmr spectra.[5]

Elementary analysis of the first gc component was in agreement with $C_{12}H_{19}N$. The substitution of a butyl group, C_4H_9, for a hydrogen in dimethylaniline would give this empirical formula. Therefore, rational means for such a substitution were considered.

The reaction of the principal metallated species, o-(dimethylamino)phenyllithium,[2] with 1-iodobutane or of the halogen–metal exchange product of this metallated species, o-iodo-N,N-dimethylaniline, with butyllithium might give o-butyl-N,N-dimethylaniline. Although such a product does not agree with the absence of n-butylbenzene in reactions of iodobenzene and n-butyllithium or phenyllithium and 1-iodobutane,[6] o-butyl-N,N-dimethylaniline was prepared. n-Butylbenzene was treated with nitric and sulfuric acids.[8] The o-nitrobutylbenzene obtained was reduced catalytically[9] using hydrazine hydrate and the products were methylated with trimethyl phosphate. The physical properties of o-(n-butyl)-N,N-dimethylaniline (Table I) did not correspond to those of the $C_{12}H_{19}N$ compound.



Since 1-iodobutane is formed from the halogen–metal interchange between iodobenzene and n-butyllithium,[6] products from the rearrangement of the quaternary salt formed by dimethylaniline and 1-iodobutane were considered. The extraction of a proton from the carbon attached to nitrogen in N-(n-butyl)dimethylanilinium iodide would produce the butyl or methyl ylide (Scheme I). Methyl migration in the methyl ylide would give

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(5) see Appendix A of A. R. Lepley and R. H. Becker, *Tetrahedron*, **21**, 2365 (1965).

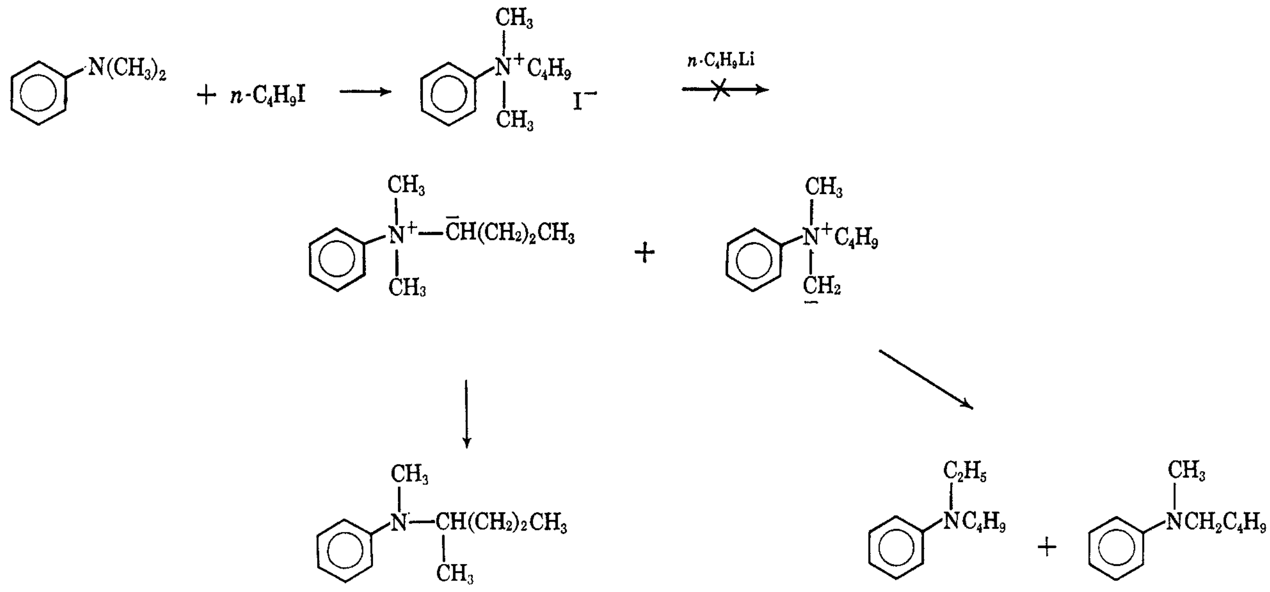
(6) A. R. Lepley and A. G. Giumanini, *Chim. Ind.* (Milan), 408 (1965).[7]

(7) No o-butyl-N,N-dimethylaniline was observed in attempts to treat 1-iodobutane with metallated[2] dimethylaniline.

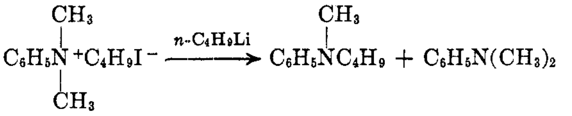
(8) R. R. Read and D. B. Mullin, *J. Am. Chem. Soc.*, **50**, 1763 (1928).

(9) M. J. S. Dewar and T. Mole, *J. Chem. Soc.*, 2556 (1956).

SCHEME I



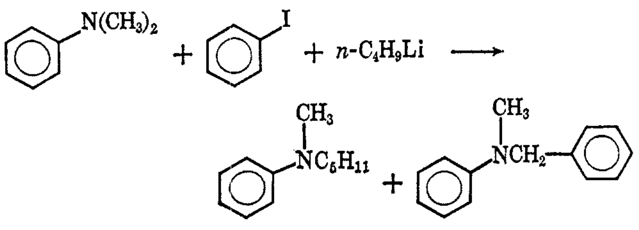
N-(n-butyl)ethylaniline, and butyl migration would give N-(n-pentyl)methylaniline. Methyl migration on the butyl ylide would lead to N-(2-pentyl)methylaniline. Although selective formation of a particular product in the Stevens rearrangement is not unheard of,[10] Hofmann elimination[11,12] or nucleophilic substitution[12] should compete to form N-(n-butyl)methylaniline and reform some dimethylaniline. The tertiary amines from these several reaction routes were prepared by the reaction of N-methylaniline and the appropriate bromoalkanes. Characterization of these compounds, Table I, allowed identification of the first gc component in the original reaction as N-(n-pentyl)methylaniline.



$$C_6H_5\overset{CH_3}{\underset{CH_3}{N}}{}^+C_4H_9I^- \xrightarrow{n\text{-}C_4H_9Li} C_6H_5\overset{CH_3}{N}C_4H_9 + C_6H_5N(CH_3)_2$$

The quaternary salt route to this particular product was checked by preparation of N-(n-butyl)trimethylanilinium iodide from dimethylaniline and 1-iodobutane. As was the case under Hofmann conditions,[12] only dimethylaniline, 20%, and N-(n-butyl)methylaniline, 7%, were formed on treatment of the liquid salt with n-butyllithium.

The reaction of dimethylaniline with iodobenzene and n-butyllithium (1 and 2 of Table II) produced N-(n-pentyl)methylaniline and N-benzylmethylaniline. The relative amounts of n-pentyl- and benzylmethylaniline were dependent on the initial concentrations of reactants. However, the ratio was much smaller (1:1 to 1:3) than one might have anticipated from the equilibrium constant,[13] $K = 7.6 \times 10^3$, for the halogen–metal interchange of iodobenzene with n-butyllithium.



When dimethylaniline and n-butyllithium were refluxed for 4 or 24 hr before addition of iodobenzene (reactions 3 and 4, Table II), the yields of α-substitution products decreased significantly. In the latter case, metallated dimethylaniline[2] must be the lithium compound participating in the reaction since no butyl substitution occurred. After only 4 hr of reflux, n-butyllithium did not completely react in the metallation process as demonstrated by the formation of 5.5% n-pentyl compound. With o-(dimethylamino)phenyl- (reaction 4) or phenyllithium (10) as the base, reaction was exceedingly slow and accompanied by the formation of other compounds observed in benzyne reactions.[3] Although 9% N-benzylmethylaniline was observed in the reaction (9) of dimethylaniline, 1-iodobutane, and phenyllithium, no n-pentyl product was present after 3.25 hr. The continued slow increase in the benzyl species after cessation of N-(n-pentyl)-methylaniline formation, Figure 1, may thus depend on a number of combinations of organometallic and iodo compounds. Strikingly, the absence of n-pentyl product in reaction 9 corresponded to very low n-butyllithium concentrations; the concentration of n-butyllithium was not appreciable since the halogen–metal interchange equilibrium[6,13] is unfavorable. These observations seemed to suggest that the organometallic species is the alkylating agent. However, a strong dependence on the halo compound was evident; *cf.* reactions 9 and 10. The rate of benzyl product formation was much faster when 1-iodobutane was used with phenyllithium as opposed to iodobenzene. These results suggest an α-position metallation followed by a

$$C_6H_5I + n\text{-}C_4H_9Li \rightleftharpoons C_6H_5Li + n\text{-}C_4H_9I$$

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[10] H. E. Zimmerman "Molecular Rearrangements," part I, P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, pp 378–382; A. R. Lepley and R. H. Becker, *Tetrahedron*, **21**, 2365 (1965).

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

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

[13] Calculated from the results of D. E. Applequist and D. F. O'Brien, *J. Am. Chem. Soc.*, **85**, 743 (1963).

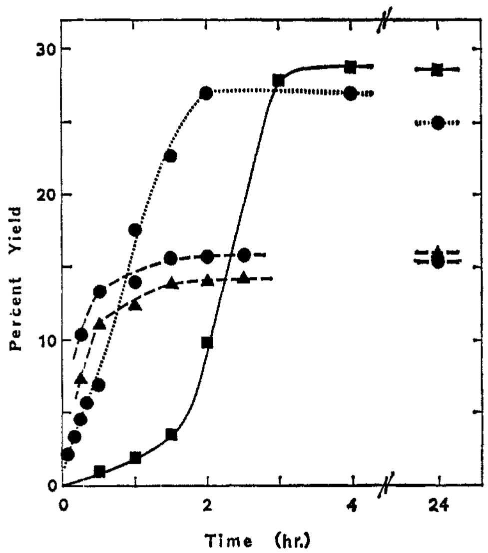
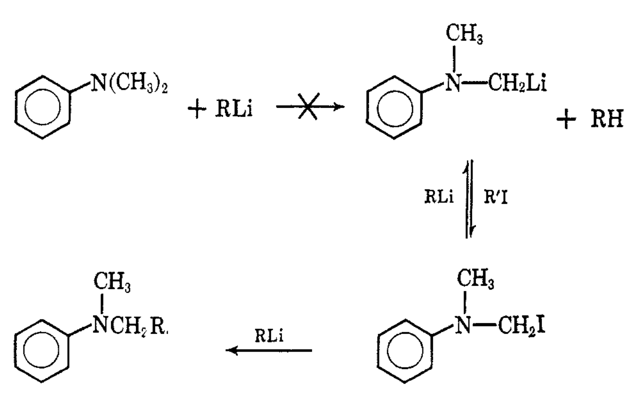
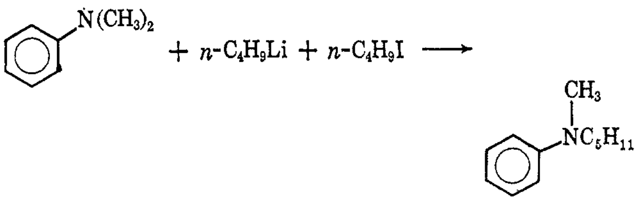


Figure 1.—Yields of α-substitution products with time for parallel reactions of 100 mmoles of tertiary amine, 20 mmoles of iodo compound, and 40 mmoles of *n*-butyllithium: N-(*n*-pentyl)-methylaniline (●) and N-benzylmethylaniline (▲) from the reaction (– – – –) of dimethylaniline and iodobenzene; N-(*n*-pentyl)methylaniline (●) from the reaction of dimethylaniline and 1-iodobutane (··········); N-(2-hexyl)ethylaniline (■) from the reaction of diethylaniline and 1-iodobutane (————).

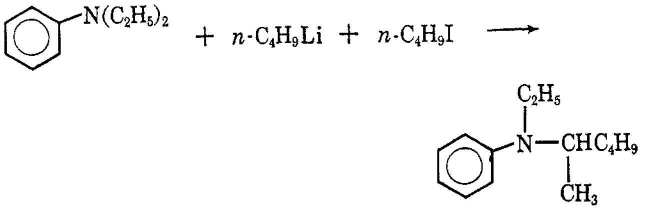
halogen–metal interchange and final double displacement reaction on the α-halo species; the reaction would depend on the rates in both forward and reverse reactions. Unfortunately the mechanism is untenable because the first step, as shown by reactions 3 and 4 and supported by other metallation[2] and deuterium exchange studies,[14] does not occur readily. This fact becomes more obvious when one compares the time for α substitution, Figure 1, with the metallation reaction. Metallation is an irreversible process and was incomplete when the strong base, *n*-butyllithium, was used after 4 hr at reflux (reaction 3). On the other hand, when *n*-butyllithium was used, α substitution was complete after 3 hr even in the slowest case, Figure 1.



Further information was obtained by considering the simpler reaction (5–8) of dimethylaniline with *n*-butyllithium and 1-iodobutane. Only N-(*n*-pentyl)-methylaniline was observed as an aniline product in this reaction. The yield decreases on doubling the 1-iodobutane concentration, which suggests a stronger competition from the normal Wurtz coupling to form *n*-octane.[6] When a fixed reaction period greater than that required for reaction completion, Figure 1, was taken for the reaction, dilution with *n*-pentane decreased the N-(*n*-pentyl)methylaniline yields. If the species participating in the reaction are the same in all cases and the principal competing reaction is octane formation, then the α substitution may be of higher order. When an equivalent dilution with ether was used, the yield decreased to 11%, half that observed with *n*-pentane dilution. Recent studies have shown the formation of complexes between *n*-butyllithium and tertiary amines.[15,16] If a complex between dimethylaniline and *n*-butyllithium were required for the α-substitution process, the reaction concentration dependence should be larger than usual and the presence of competing complexing agents would have an extreme effect. The decreased yields on addition of *n*-pentane (reaction 7) and diethyl ether (8) would be compatible with an intermediate complex. The mixed solvent, benzene–ether, may have a similar effect on the reactions (9 and 10) when phenyllithium is used.



The above reactions were restricted to substitution at the α-alkyl carbon atom on dimethylaniline. The reaction of *n*-butyllithium and 1-iodobutane with diethylaniline demonstrated that this restriction was inherent in the substitution, not in the reagents. N-(2-hexyl)ethylaniline was the only product observed from this reaction as identified from the physical properties of the synthetic material, Table I. As with the other reactions, Figure 1, this reaction was complete after 3 hr. The yield, 29%, was comparible with those of the better dimethylaniline reactions (2, 3, and 5). The slow initiation of this reaction, Figure 1, was probably an artifact of temperature rise rates which varied somewhat from reaction to reaction.



Although we have not unraveled the mechanism, a new substitution reaction on the α position of dialkylanilines has been observed. Alkyl or aryl iodides were used with alkyl or aryllithium compounds. Benzyne intermediates were not essential in the reaction. Neither α-metallated species nor quaternary salts participated in the process. However, a complex between dialkylaniline and organolithium may play some role in the substitution.

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

[15] T. L. Brown, R. L. Gerteis, D. A. Bafus, and J. A. Ladd, *J. Am. Chem. Soc.*, **86**, 2135 (1964); J. F. Eastham and G. W. Gibson, *ibid.*, **85**, 2171 (1963); C. G. Screttas and J. F. Eastham, *ibid.*, **87**, 3276 (1965).

[16] 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).

Experimental Section[17]

Gas Chromatography.—The retention ratios and product yields were determined using an internal standard method.[19] An Aerograph A-90P was used with a 0.25 in. × 5 ft column of 20% GE-SF96 on 60–80 mesh Chromosorb W. The flow rate was maintained at approximately 74 cc/min of helium for analyses at 134°. Retention ratio reproducibility was ±0.005. Retention time of N-(*n*-butyl)methylaniline was 22 ± 2 min; the standard peak had a width of 1.5 ± 0.1 min at half-height. Retention ratios for the dialkylanilines are given in Table I. A F & M Model 500 with a 0.25 in. by 10 ft column packed with 20% GE-SF96 on 40–60 mesh Chromosorb W was used for analyses at 185°. Retention ratios and characteristics are reported elsewhere.[3,18]

Chemicals.—Methyl and dimethylaniline, N-methyldiphenylamine, N-benzylmethylaniline, iodobenzene, 1-iodobutane, 1-bromobutane, and 1-bromopentane were obtained from Eastman. Ethyl- and diethylaniline, *n*-butylbenzene, 2-bromopentane, and 2-bromohexane came from Matheson Coleman and Bell. Monofree dimethyl and diethylaniline were dried over sodium before use. Foote Mineral 15% *n*-butyllithium in hexane and 20% phenyllithium in 3:1 (v/v) benzene–ether were titrated[20] to determine active lithium concentrations.

***o*-(*n*-Butyl)-N,N-dimethylaniline.**—*o*-Nitrobutylbenzene was prepared by the nitration of butylbenzene in sulfuric acid as previously described.[8] The doubly distilled *o*-nitro compound (3.8 g, 19 mmoles) was dissolved in 40 ml of absolute ethanol and 50 mg of 10% palladium on charcoal was added. Hydrazine hydrate (15 ml) was slowly added to the stirred refluxing solution and reflux was continued for an additional 2 hr. After cooling, the solution was filtered and solvent was distilled off. The crude product, having only one gc peak, was dissolved in ether and dried over anhydrous sodium sulfate. The ether was evaporated, 5 ml of trimethyl phosphate was added, and the solution was refluxed for 2 hr. Aqueous sodium hydroxide was added and the mixture was refluxed for 15 min. The oil obtained was distilled giving 1.5 g (41%) of a pure (gc) (*n*-butyl)-N,N-dimethylaniline: bp 100°(6 mm) [lit.[21] 108–118° (8 mm)]; n^{20}_{D} 1.5071, n^{25}_{D} 1.5052, n^{30}_{D} 1.5028.

Anal. Calcd for $C_{12}H_{10}N$: C, 81.29; H, 10.81; N, 7.90. Found: C, 81.54; H, 10.77; N, 7.68.

The infrared spectrum had bands at 3.4 w, 3.51 s*, 3.60 m, 3.71 m, 6.32 w, 6.76 s, 6.96 s, 7.74 w, 8.45 w, 8.70 w, 9.02 w, 9.60 w, 10.55 s, 13.04 m, 13.40 m, and 14.0 w μ.

N-(2-Hexyl)-N-ethylaniline.—N-Ethylaniline, 24 g, and 2-bromohexane, 20 g, were mixed in a stoppered flask and heated on a steam bath for 36 hr. The cooled solution was poured into 50 ml of water and solid sodium hydride, 25 g, was slowly added while stirring and cooling. The oil that separated and an ether extract were combined and dried over anhydrous sodium sulfate. Distillation gave 11.5 g (38% yield) of a chromatographically pure product: bp 118–119° (3.5 mm); n^{20}_{D} 1.5201, n^{25}_{D} 1.5180, n^{30}_{D} 1.5159, d^{20}_{4} 0.941.

Anal. Calcd for $C_{14}H_{23}N$: C, 81.88; H, 11.24; N, 6.82. Found: C, 81.80; H, 11.59; N, 6.61.

Infrared analysis showed bands at 3.25 vw, 3.38 s, 3.49 m, 6.26 s, 6.67 s*, 6.88 w, 7.20 m, 7.29 m, 7.43 m, 7.56 w, 7.71 w, 7.88 m, 8.02 w, 8.24 w, 8.40 m, 8.65 vw, 8.87 w, 9.24 w, 9.62 w, 10.10 w, 11.60 vw, 12.70 vw, 13.38 s, and 14.47 m μ.

N-(*n*-Butyl)-N-methylaniline.[22,23]—N-Methylaniline, 20 g, and 1-bromobutane, 20.5 g, were treated as in the preparation of N-(2-hexyl)-N-ethylaniline. The light yellow product, 13.3 g, 55% yield, boiled at 95–96 (3.1 mm) [lit. 114–116 (12 mm),[24] 144–147 (30 mm)[25]] and had refractive indices of n^{20}_{D} 1.5327 (lit.[25] n^{20}_{D} 1.5300), n^{25}_{D} 1.5302, n^{30}_{D} 1.5285. The material gave only a single gas chromatographic peak. The infrared spectrum had bands at 3.31 w, 3.40 m, 3.49 m, 6.23 s, 6.63 s*, 6.88 w, 7.4 m, 7.79 w, 8.12 w, 8.29 w, 8.7 w, 9.0 vw, 9.2 w, 9.67 w, 10.08 w, 10.42 vw, 10.74 w, 11.6 vw, 13.35 s, and 14.47 m μ.

N-(*n*-Pentyl)-N-methylaniline.[26]—N-Methylaniline, 20 g, and 1-bromopentane, 22.5 g, were treated as in the preparation of N-(2-hexyl)-N-ethylaniline. The light yellow product, 17.2 g, 67% yield, boiled at 111–114° (3.6 mm) [lit.[26] 129–131° (15 mm)], and had refractive indices of n^{20}_{D} 1.5266, n^{25}_{D} 1.5247, n^{30}_{D} 1.5226, d^{20}_{4} 0.918. The material gave only a single gas chromatography peak. Infrared analysis showed bands at 3.32 w, 3.42 s, 3.50 m, 6.24 s, 6.64 s*, 6.83 w, 7.32 m, 7.68 vw, 7.88 w, 8.18 w, 8.38 w, 8.64 w, 8.97 vw, 9.18 w, 9.64 w, 10.07 w, 10.51 w, 11.6 vw, 13.35 s, and 14.47 m μ.

N-(*n*-Butyl)-N-ethylaniline.[27]—N-Ethylaniline, 23 g, and 1-bromobutane, 20 g, were treated as in the preparation of N-(2-hexyl)-N-ethylaniline. The colorless oil product, 13.6 g, 51% yield, boiled at 107° (4.4 mm), and had refractive indices of n^{20}_{D} 1.5281, n^{25}_{D} 1.5259, n^{30}_{D} 1.5232, d^{20}_{4} 0.908. Gas chromatography indicated <1% impurity. Infrared analysis showed bands at 3.32 w, 3.40 s, 3.51 m, 6.28 s, 6.39 w, 6.67 s*, 6.87 w, 7.20 w, 7.32 m, 7.42 m, 7.78 m, 8.18 w, 8.40 m, 8.68 w, 9.11 w, 9.33 vw, 9.64 w, 9.94 vw, 10.10 w, 10.5 vw, 11.18 vw, 11.62 vw, 12.6 vw, 13.39 s, and 14.45 m μ.

N-(2-Pentyl)-N-methylaniline.—N-Methylaniline, 20 g, and 2-bromopentane, 22.5 g, were treated as in the preparation of N-(2-hexyl)-N-ethylaniline. The pale yellow product, 11.5 g, 44% yield, boiled at 110–111.5° (5.5 mm), and had refractive indicies of n^{20}_{D} 1.5278, n^{25}_{D} 1.5258, n^{30}_{D} 1.5237, d^{20}_{4} 0.918. The material gave only a single gas chromatographic peak. The infrared spectrum had bands at 3.3 w, 3.38 s, 3.47 m, 3.56 w, 6.23 s, 6.64 s*, 6.90 w, 7.21 m, 7.42 w, 7.6 m, 7.9 vw, 8.09 w, 8.28 w, 8.64 vw, 8.82 m, 9.39 vw, 9.65 w, 10.08 w, 10.6 vw, 11.15 vw, 11.6 vw, 13.32 s, 14.46 m μ.

Anal. Calcd for $C_{12}H_{19}N$: C, 81.29; H, 10.81; N, 7.90. Found: C, 81.20; H, 10.84; N, 8.17.

Preparation and *n*-Butyllithium Reaction of N-(*n*-Butyl)-dimethylanilinium Iodide.—Dimethylaniline (12.5 ml, 0.1 mole) and 11.5 ml (0.1 mole) of 1-iodobutane were mixed and kept at room temperature for 4 days in a stoppered flask. A tacky syrup separated which was triturated with anhydrous ether and dry hexane. Attempts to crystallize the salt from methanol, ethanol, and ethanol–ether mixture[28] were unsuccessful; only the original syrup being successfully obtained. The syrup was insoluble in ether and hexane, slightly soluble in water, and readily soluble in methanol and ethanol. The pmr spectrum of this material in D_2O had a broad CH_3 and CH_2 of butyl multiplet at 1.06 ppm, a methyl on nitrogen singlet centered on a broad CH_2 on nitrogen of butyl at 3.90 ppm, and a complex aromatic multiplet centered at 7.80 ppm. The integrated peak areas agreed with the respective proton ratio of 7:8:5.

Attempts to prepare a solid product by heating the same mixture for 16 hr with 20 ml of anhydrous ether gave the syrup. Gc on the liquid layer of this mixture showed the formation of a trace of N-(*n*-butyl)methylaniline (1/200th of the concentration of unreacted dimethylaniline). When the original mixture of 1-iodobutane and dimethylaniline was heated for 16 hr on a steam bath a crystalline material precipitated, 6.2 g. This salt could be recrystallized from methanol or ethanol. It decomposed on heating to 228–230° and gave no depression of melting point when mixed with trimethylanilinium iodide prepared from methyl iodide and dimethylaniline. The pmr spectrum in D_2O had a methyl on nitrogen singlet at 3.85 ppm and a broad aromatic multiplet centered at 7.93 ppm; peak integral proton equivalence was 9:5, respectively.

The purified syrup (5.3 g, 17 mmoles) was placed in a flask with 20 ml of dry hexane and 21 ml of 1.6 *N* (34 mmoles) *n*-butyllithium in hexane. The mixture was agitated frequently during 16 hr at ambient. Exposure of the syrup surface to the attacking base was poor. Samples (1 ml) were taken from the

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[17] Physical properties (infrared and pmr spectra and refractive indices) were measured in the standardized manner described in the accompanying papers.[3,18] Specific gravities were measured with a Fisher–Davidson Gravitometer using ethylbenzene as a standard. Analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. Melting and boiling points are uncorrected.

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[28] Reference 12 reports use of this mixture for crystallization of the salt formed from N-(*n*-butyl)-N-methylaniline and methyl iodide, mp 97°.

hexane layer before and after decomposition of *n*-butyllithium and concurrent dissolution of the salt with ice–water. The prequench sample was treated with ice before analysis. Gc showed two product peaks at 0.394 and 0.775 with respect to N-(2-pentyl)methylaniline. The retention ratios and infrared were identical with dimethylaniline and N-(*n*-butyl)methylaniline. The total peak areas after final dissolution indicate reaction of 27% of the starting syrup. The molar ratio of dimethylaniline to N(*n*-butyl)methylaniline was 3.2:1 in the prequench sample and 3.0:1 in the final mixture. The total amount of tertiary amines in the prequench mixture was one-fourth that after dissolution of the salt

General Procedure for α-Substitution Reactions.—A measured volume of sodium dried, mono-free N,N-dialkylaniline in a 100-ml round bottom flask containing a Teflon-covered magnetic stirring bar was cooled to −10° in a salt–ice bath. *n*-Butyllithium, 1.6 *N* in hexane, was then added rapidly with cooling to the stirred amine. After 5 min, the iodo compound was rapidly added. The stirred reaction was allowed to warm gradually and after 1 hr the melted cooling mixture was removed. After 1.5 hr the temperature of the mixture reached 32°. This temperature ±2° was maintained during the remainder of the reaction. The reaction was terminated by the addition of crushed ice with rapid stirring. The mixture was allowed to stand without stirring for 2 hr before withdrawing samples, 1 ml each, for qualitative and quantitative gc. The products were isolated by preparative gc and characterized by their gc retention ratios and infrared and pmr spectra. In all cases, comparisons were made with properties of commercial or synthetic compounds.

Reactions of Dimethylaniline, Iodobenzene, and *n*-Butyllithium.—N,N-Dimethylaniline (12.2 ml, 0.1 mole), 2.2 ml (20 mmole) of iodobenzene and 32.5 ml of 1.6 *N* (50 mmoles) *n*-butyllithium in *n*-hexane were treated as described in the general procedure. After 12 hr, the reaction was quenched and analyzed by gc at 134 and 185°. The lower temperature gc indicated the presence of one product with a retention ratio of 1.64 relative to N-(*n*-butyl)methylaniline. The infrared and pmr spectra of a preparative gc sample of this product are identical with the spectra of N-(*n*-pentyl)methylaniline. Product yield was 16.4%.

Anal. Calcd for $C_{12}H_{19}N$: C, 81.30; H, 10.80; and N, 7.90. Found: C, 81.33; H, 11.05; and N, 7.70.

At 185°, gc analysis indicates two product peaks with retention ratios of 0.605 and 1.67 relative to N-methyldiphenylamine. The first gc component was the previously identified N-(*n*-pentyl)methylaniline. The infrared spectrum of the second component had peaks at 3.33 w, 3.51 w, 3.62 w, 6.30 s, 6.69 s*, 6.96 m, 7.35 m, 7.45 m, 8.04 w, 8.31 w, 8.45 w, 8.70 vw, 9.02 w, 9.34 vw, 9.73 w, 10.61 w, 11.62 vw, 13.34 s, 13.63 m, and 14.48 s μ. The pmr spectrum had a methyl on nitrogen of aniline singlet at 2.64 ppm, a benzyl methylene attached to nitrogen at 4.16 ppm, and a broad aromatic multiplet of two parts centered at 6.59 and 7.01 ppm. The proton equivalence of the integrated peaks was 3:2:3:7, respectively. These physical constants were identical with those of commercial N-benzylmethylaniline. The yield of the second component was 15%.

The reaction, using 25 ml of 1.6 *N* (40 mmoles) *n*-butyllithium, was sampled at frequent intervals, Figure 1. Multiple reactions with only 12.5 ml of 1.6 *N* (20 mmoles) *n*-butyllithium were run for 24–28 hr. The reproducibility of yields was 10 ± 0.5 for N-(*n*-pentyl)methylaniline and 26.5 ± 0.1 for N-benzylmethylaniline.

Premetallation.—Dimethylaniline (12.2 ml, 0.1 mole) and 25 ml of 1.6 *N* (40 mmoles) *n*-butyllithium in hexane were mixed at room temperature and heated to reflux for 4 hr. The solution was then cooled to −10° and 2.2 ml (20 mmoles) of iodobenzene was added. The reaction was then refluxed. The mixture was quenched 14 hr after iodobenzene addition; the yield determined for N-(*n*-pentyl)methylaniline was 5.5%, and N-benzyl methylaniline, 7%. In a second experiment, a solution of 7.5 ml (60 mmoles) of dimethylaniline and 25 ml of 1.6 *N* (40 mmoles) *n*-butyllithium was heated to reflux for 24 hr. Iodobenzene (4.4 ml, 40 mmoles) was added at −10° and the reaction at room temperature was followed by gc. Product formation was exceedingly slow, after 7 days 3% of N-benzylmethylaniline was observed. In addition, 2% biphenyl and 3% of mixed *o*-(dimethylamino)biphenyl and N-methyldiphenylamine[3] were formed.

Reaction of Dimethylaniline, Iodobenzene, and Phenyllithium.—N,N-Dimethylaniline (12.2 ml, 0.1 mole), 2.2 ml (20 mmoles) of iodobenzene, and 18.5 ml of 2.16 *N* (40 mmoles) phenyllithium in benzene–ether were treated as described in the general procedure. The reaction was followed by gc. After 4 days, the mixture was quenched. Gc analysis showed peaks at retention ratios of 0.86, 1.40, and 2.65 with respect to N-benzhydryldimethylamine. The first of these peaks 1.7% yield, may be *o*-(dimethylamino)biphenyl or N-methyldiphenylamine.[3] The second component, 1.8% yield, was identical with N-benzylmethylaniline from the reaction of dimethylaniline, iodobenzene, and *n*-butyllithium. The retention ratio and infrared of the third component, 5% yield, were the same as those of commercial *o*-terphenyl.

Reaction of Dimethylaniline, 1-Iodobutane, and Phenyllithium.—N,N-Dimethylaniline (12.2 ml, 0.1 mole), 2.3 ml (20 mmoles) 1-iodobutane, and 18.5 ml of 2.16 *N* (40 mmoles) phenyllithium in benzene–ether were treated as described in the general procedure. The reaction was followed for 24 hr by gc. A single product peak with retention ratio 1.40 relative to N-benzhydryldimethylamine was observed. Maximum yield, 9%, of the product N-benzylmethylaniline was obtained after 3.25 hr.

Reactions of Dimethylaniline, 1-Iodobutane, and *n*-Butyllithium.—N,N-Dimethylaniline (12.2 ml, 0.10 mole), 2.3 ml (20 mmoles) of 1-iodobutane, and 25 ml of 1.6 *N* (40 mmoles) *n*-butyllithium were treated as described in the general procedure. Reaction mixtures were sampled at frequent intervals, Figure 1. In all reactions, the gc had only one new peak with a retention ratio of 1.296 with respect to N-*n*-butylethylaniline (*cf.* Table I). The product was identical with the first gc product component from iodobenzene reactions, N-(n-pentyl)methylaniline. Maximum yield, 33%, was attained after 2.5 hr. In a parallel reaction with 4.5 ml (40 mmoles) of 1-iodobutane, 27% N-(*n*-pentyl)methylaniline was obtained after 2.5 hr.

The reaction was also run with the addition of 15 ml of either sodium dried *n*-pentane or anhydrous diethyl ether using the original reagent quantities described. The product yield after 2.5 hr was 22% in pentane and 11% in ether.

Reactions of N,N-Diethylaniline, 1-Iodobutane, and *n*-Butyllithium.—N,N-Diethylaniline (15 ml, 0.1 mole), 2.3 ml (20 mmoles) of 1-iodobutane, and 26 ml of 1.6 *N* (40 mmoles) *n*-butyllithium were treated as described in the general procedure. Reaction mixtures were sampled at 0.5, 1.0, 1.5, 2.0, 3, 4, and 24 hr or quenched after 5.5 or 24 hr. In all cases, the gc showed only one new peak with retention ratio of 0.695 with respect to N-benzhydryldimethylamine (*cf.* Table I). The infrared and pmr spectra on material isolated by preparative gc were identical with the spectra of N-(2-hexyl)ethylaniline. Maximum yield of product, 29 ± 1%, was obtained after 4 hr.

Acknowledgment.—This work was supported in part by U. S. Public Health Service Grant GM-09136 from the National Institute of General Medical Sciences. The authors wish to thank Armida B. Giumanini and Dr. Wajid A. Khan for aid in instrumental analysis.