and 0.771 and their respective yields were 19.0 and 71.0% based on active lithium content after reflux.

The ether solution was repeatedly extracted with 2 *N* HCl which removed the second gc component. During the first hydrochloric acid extraction a crystalline solid, mp 183–186° dec, separated. It was filtered and dried and had infrared peaks at 2.95 m, 3.18 m, 3.48 m, 3.80 s, 3.90 s, 4.00 m, 4.09 m, 6.21 w, 6.61 m, 6.78 m, 6.85 m, 7.10 w, 7.40 w, 7.58 w, 7.70 m, 7.90 s*, 8.21 s*, 8.50–8.60 s, 8.70 s, 9.00 s, 9.79 w, 10.06 w, 10.21 s, 10.46 m, 10.68 s, 11.10 w, 10.85 s, 13.40 m, and 14.12 s μ. The pmr of the salt was run in deuterium oxide using the water singlet at 4.81 ppm (relative to TMS) as a conversion standard to δ_{TMS}. A 15% solution of the salt had methyl on nitrogen singlet resonance at 3.33 ppm and an aromatic multiplet centered at 7.90 ppm. The relative peak areas by integration were 6:4, respectively.

Anal. Calcd for $C_{11}H_{12}ClF_6NO$: C, 40.09; H, 3.71; Cl, 10.98; F, 35.38; N, 4.34. Found: C, 39.83; H, 3.99; Cl, 10.42; F, 35.02; N, 4.49.

The salt gave only the second gc component on treatment with dilute sodium hydroxide solution.

The ether solution from above and the hydrochloric acid extracts were worked up separately.

The ether solution was washed well with water, dried over anhdrous sodium sulfate, and distilled, bp 70° (0.3 mm), giving a pale yellow oil. This compound corresponds to the first gc component, has a characteristic pleasant smell, crystallized on standing to a bright pale yellow solid, mp 46–48°, and had infrared bands at 2.9–3.0 m, 3.4 m, 5.45 m, 5.58 m, 6.22 m, 6.50 s, 6.72 m, 6.88 m, 6.98 m, 7.05 m, 7.70 s, 7.95 s*, 8.2 s, 8.40–8.45 s, 8.71–8.80 m, 8.90 s, 9.05 m, 9.65 m, 10.30 s, 10.42 m, 10.62 m, 10.81 s, 11.30 w, 12.74 w, 12.91 w, 13.10 m, 13.50 w, and 14.08 s μ.

Anal. Calcd for $C_{11}H_{11}F_6NO$: C, 46.10; H, 3.84; N, 4.88; F, 39.79. Found: C, 45.73; H, 3.82; N, 4.93; F, 39.27.

On the basis of the elemental analysis, infrared spectrum and pmr spectrum (Table II), this compound was assigned the structure *m*-dimethylaminophenylbis(trifluoromethyl)carbinol.

The hydrochloric acid solution was washed once with ether, cooled in ice, made alkaline with sodium hydroxide solution, and extracted with ether. The ether extracts were washed with water, dried over anhydrous sodium sulfate, filtered, and evaporated. A pale brown crystalline solid with a pleasant odor was obtained. This material corresponds to the second gc component, was soluble in concentrated sodium hydroxide solutions but extractable with ether, recrystallized from ligroin, mp 73–75°, and had infrared bands at 3.1–3.2 m, 3.45 m, 6.21 m, 6.60 m, 6.80 m, 6.85 m, 6.95 w, 7.18 m, 7.82 s, 8.15 s, 8.26 s, 8.40 s*, 8.60 m, 8.78 s, 9.00 s, 9.55 w, 9.86 w, 10.37 m, 10.55 m, 10.70 s, 12.01 m, 12.15 m, 13.02 w, 13.55 w, and 14.18 m μ.

Anal. Calcd for $C_{11}H_{11}F_6NO$: C, 46.10; H, 3.84; N, 4.88; F, 39.79. Found: C, 46.16; H, 3.79; N, 5.17; F, 39.75.

On the basis of the elemental analysis, infrared spectrum, and pmr spectrum (Table II), this compound was assigned the structure of *o*-dimethylaminophenylbis(trifluoromethyl)carbinol.

Benzyne Addition to Dialkylanilines[1a,b]

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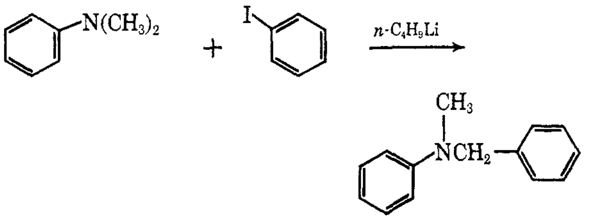
Received March 10, 1966

Benzyne generated by the action of *n*-butyllithium on fluoro- and chlorobenzene has been treated with dialkylanilines. Reaction with dimethylaniline gave N-methyldiphenylamine, N-ethyldiphenylamine, and *o*-(dimethylamino)biphenyl. The analogous compounds, N-(2-butyl)diphenylamine and *o*-(diethylamino)biphenyl, were identified in benzyne reaction with diethylaniline. The *o*-(dialkylamino)biphenyls were formed by reaction of benzyne with the *ortho*-metallation product of the dialkylanilines. Slow benzyne generation or elevated temperatures favor formation of this product. The diphenylamines were rearrangement or elimination products from an intermediate betaine formed by benzyne addition of the unshared nitrogen electrons. The formation of N-benzyl-N-methylaniline by α substitution was not observed.

The recent use of iodobenzene in the α substitution of dimethylaniline,[2] eq 1, suggests as alternative possibilities that (a) a benzyne intermediate may participate in the α-substitution reaction, or (b) the α-substitution reaction may furnish a method of differentiating between benzyne and nonbenzyne intermediates in aromatic dehydrohalogenation reactions. The iodo group which participates in α alkylation was found to be the least effective halide in biphenyl formation from phenyllithium and halobenzenes,[3] a reaction later shown to follow a benzyne mechanism.[4,5] Iodobenzene was also the least reactive halobenzene in the reactions with lithium piperidide to give N-phenylpiperidine.[6]



(1)

Both of these reactions are hypothetically additions of an organo metallic or carbanion to the benzyne intermediate. A more sensitive method of differentiating between benzyne and alternative mechanisms, such as double displacement, would be to use a less reactive benzyne trap. The benzyne addition of tertiary amines might be such a reaction.

Several products were observed in the benzyne reaction with triethylamine. Wittig and Benz[7] identified the major product as N,N-diethylaniline and a minor component as N-(2-butyl)-N-ethylaniline.[8] The mechanism in this reaction, as in other tertiary amine reactions with benzyne,[9,10] proceeds *via* addition of the nonbonding electrons on nitrogen to the active benzyne site. Only one of the unoccupied aromatic positions is

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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; (b) this investigation was supported by Public Health Service Grant GM-09136, from the National Institute of General Medical Sciences; (c) 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).

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

[4] R. Huisgen, "Organometallic Chemistry," H. Zeiss, Ed., Reinhold Publishing Corp., New York, N. Y., 1960, p 75.

[5] H. Heaney, *Chem. Rev.*, **62**, 81 (1962).

[6] R. Huisgen and J. Sauer, *Chem. Ber.*, **93**, 192 (1959).

[7] G. Wittig and E. Benz, *ibid.*, **92**, 1999 (1959).

[8] This compound was earlier erroneously identified as *o*-N,N-triethylaniline: G. Wittig and W. Merkle, *ibid.*, **76**, 109 (1943). The correction in identification was overlooked in a recent review.[5]

[9] H. Hellman and W. Unseld, *Ann.*, **631**, 82, 95 (1960); H. Hellmann and G. W. Scheytt, *ibid.*, **642**, 22 (1961).

[10] H. Hellman and W. Unseld, *ibid.*, **631**, 85 (1960).

normally substituted in the reaction products except when methylene diamines were used.[10]

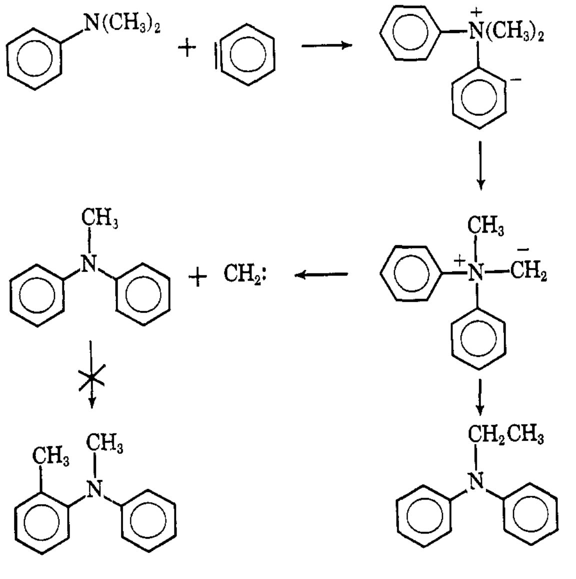
Since the α alkylation of dimethylaniline involves C–H, rather than N reaction, and since such insertion has not been previously reported in benzyne reactions, we have attempted in this study to determine the monomeric addition products of benzyne and N,N-dimethylaniline.

Results and Discussion

Benzyne generation for these studies was carried out paralleling the α-substitution reactions.[2] Fluoro- or chlorobenzene, dimethyl- or diethylaniline, and *n*-butyllithium solution were mixed. The *ortho* metallaion of the halobenzene produced the *o*-haloanion which can form benzyne by loss of halide ion.[11]

If now dimethylaniline reacts with the benzyne in a fashion analogous to that of triethylamine,[7] a betaine intermediate should form (Scheme I). The betaine in turn can undergo intramolecular proton transfer to the methyl ylide[12] in which (a) methyl group migration should give N-ethyldiphenylamine, or (b) singlet carbene loss should give N-methyldiphenylamine. *o*-Carbene insertion in this last compound or methyl migration in the original betaine would be required to form *o*-N-dimethyldiphenylamine.[13] A second *o*-amine product might be formed by the metallation of the starting amine[3,14] followed by benzyne addition to the organometallic. The reaction quenching procedure would give *o*-(dimethylamino)biphenyl from this lithium compound.

SCHEME I



The four compounds predicted were obtained and their properties determined for comparison with the benzyne reaction products. N-Ethyldiphenylamine was prepared by the action of potassium N-ethylanilide on bromobenzene at reflux.[15] The room temperature reaction of lithium *o*-N-dimethylanilide and fluorobenzene gave *o*-N-dimethyldiphenylamine. *o*-(Dimethylamino)biphenyl was formed from *o*-aminobiphenyl and dimethyl sulfate.[16] N-Methyldiphenylamine was commercially available. The gas chromatographic (gc) retention ratios (Table I), infrared spectra, and proton magnetic resonance (pmr) spectra (Table II) of these compounds were compared with those of the products from the benzyne reactions with dimethylaniline.

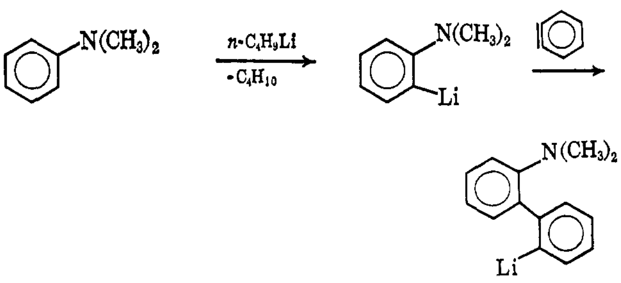


TABLE I

GAS CHROMATOGRAPHIC RETENTION RATIOS[a] OF REACTANTS, PRODUCTS, AND STANDARDS IN THE BENZYNE ADDITION TO DIALKYLANILINES

Compound	Retention ratios Calibration	Reaction products from $C_6H_5N(CH_3)_2$	 $C_6H_5N(C_2H_5)_2$
N-(*n*-Butyl)-N-methylaniline	0.360[b]		
Biphenyl	0.415		
N-Methyldiphenylamine	0.86	0.86	
o-(Dimethylamino)biphenyl	0.88		
Diphenylamine	0.94		
o-N-Dimethyldiphenylamine	0.95		
N-Benzhydryldimethylamine	1.00[c]		
N-Ethyldiphenylamine	1.03	1.03	1.03[d]
o-(Diethylamino)biphenyl	1.27		1.27
N-Benzyl-N-methylaniline	1.40		
N-(*n*-Butyl)diphenylamine	1.87		
o-Terphenyl	2.65		
N-(*n*-Pentyl)diphenylamine	2.67		

[a] 0.25 in. × 10 ft column of 20% GE-SF96 on 40–60 mesh Chromosorb W, 170 cc/min of He flow, 185°; ratios are ±0.005. [b] Standard for quantitative analysis. [c] Standard for retention ratio; retention time, 14.6 ± 0.7 min; peak width at half-height, 1.07 ± 0.05 min. [d] Major component was not N-ethyldiphenylamine.

The gc from the reaction mixture of dimethylaniline, fluorobenzene, and *n*-butyllithium (Table I), indicated that *o*-N-dimethyldiphenylamine was not present in detectable amounts. The major gc component had a retention ratio and infrared spectrum comparable with N-methyldiphenylamine. Elemental analysis seemed to confirm this identification but pmr on material from preparative gc had a persistent singlet absorption at 2.49 ppm in addition to the 3.25 methyl singlet for N-methyldiphenylamine. The extraneous pmr singlet was compatible with *o*-(dimethylamino)biphenyl which has a slightly greater retention ratio. If *o*-(dimethylamino)biphenyl was present in a much smaller amount than N-methyldiphenylamine, as indicated by the pmr peak areas, the overlapping gc peaks would have the appearance and retention ratio observed.

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[11] J. A. Zoltewicz and J. F. Bunnett, *J. Am. Chem. Soc.*, **87**, 2640 (1965).

[12] *Cf.* the action of phenyllithium on trimethylanilinium bromide, F. Weygand, A. Schroll, and H. Daniel, *Chem. Ber.*, **97**, 857 (1964).

[13] This product was considered improbable on the basis of ref 7, but could not be totally neglected; *cf.* ref 8.

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

[15] *Cf.* F. Scardiglia and J. D. Roberts, *J. Org. Chem.*, **23**, 629 (1958).

[16] D. P. Evans and R. Williams, *J. Chem. Soc.*, 1199 (1939).

TABLE II

PROTON NUCLEAR MAGNETIC RESONANCE SPECTRA OF REACTION PRODUCTS AND OTHER COMPOUNDS RELATED TO THE BENZYNE ADDITION TO DIALKYLANILINES

	Chemical shift[a]				
	CH_3		CH_2		
Compound	C	NAr	C, NAr	Ar, NAr	HAr
N-Benzyl-N-methylaniline		2.86 s (3)		4.36 s (2)	6.89 m (10)
N-Methyldiphenylamine		3.22 s (3)			7.09 m (10)
o-(Dimethylamino)biphenyl		2.49 s (6)			7.28 m (9)
N-Ethyldiphenylamine	1.18 t (3)		3.82 q (2)		6.96 m (10)
o-(Diethylamino)biphenyl	0.87 t (6)		2.85 q (4)		7.20 m (9)
Reactions					
Fluorobenzene, *n*-butyllithium, plus dimethylaniline					
Gc peak 1		2.49 s (1) 3.25 s (1)			7.15 m (5.2)
Diethylaniline					
Gc peak 1	1.11 m (3.5)[b]	2.53 m (1)[b]			7.25 m (4.5)
Gc peak 2	0.87 t (6)		2.85 q (4)		7.21 m (9)

[a] All peaks are relative to tetramethylsilane in parts per million; splitting: s = singlet, t = triplet, q = quartet, m = multiplet; all J values are 7.0 ± 0.1 cps; values in parentheses are relative integrated peak ratios. [b] Includes CH_3, CH_2, and CH groups.

The amounts of these two components varied from reaction to reaction. In particular when benzyne generation was slower as is the case with chlorobenzene,[3,4,6] the relative amount of *o*-dimethylaminophenyllithium which forms in the metallation reaction would be greater. The relative amount of *o*-(dimethylamino)biphenyl in the gc peak increased as anticipated.

$$C_6H_5N(CH_3)_2 + C_6H_5X \xrightarrow[32°,\ 3\ \text{days}]{n\text{-}C_4H_9Li}$$

$$\begin{array}{ccccc} (C_6H_5)_2NCH_3 & + & o\text{-}C_6H_5C_6H_4N(CH_3)_2 & + & (C_6H_5)_2NC_2H_5 \\ 12.0\% & & 2.0\% & & 1.4\% \\ 3.0\% & & 1.5\% & & \ldots \end{array}$$

$$X = F, Cl$$

A second gc component was observed in the fluorobenzene reaction with dimethylaniline. Although the quantity of this material was quite small, the retention ratio and data from other reactions[7] indicated that this compound was probably N-ethyldiphenylamine. The yield from quantitative gc was calculated as N-ethyldiphenylamine. Support for this assignment also came from the benzyne reaction with diethylaniline.

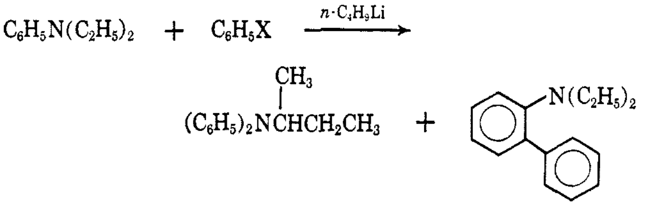
If one replaces the methyl groups on nitrogen with ethyl groups, the products by analogous steps from the intermediate betaine would be N-ethyldiphenylamine and N-(2-butyl)diphenylamine. *o*-(Diethylamino)biphenyl would be formed by benzyne addition of the *ortho*-metallation product of diethylaniline. We were unable to prepare N-(2-butyl)diphenylamine, but determined the retention ratio for the *n*-butyl isomer, Table I, from the α-alkylation reaction of N-methyldiphenylamine with 1-iodopropane and *n*-butyllithium.

$$CH_3N(C_6H_5)_2 + n\text{-}C_3H_7I + n\text{-}C_4H_9Li \longrightarrow$$

$$\begin{array}{ccc} n\text{-}C_4H_9N(C_6H_5)_2 & + & n\text{-}C_5H_{11}N(C_6H_5)_2 \\ 8\% & & 10\% \end{array}$$

Triethyl phosphate was used for the preparation of *o*-(diethylamino)biphenyl from *o*-aminobiphenyl.

Two product peaks were observed in the gc of the benzyne reaction with diethylaniline. The retention ratio corresponded to N-ethyldiphenylamine and *o*-(diethylamino)biphenyl, Table I. The latter product was confirmed by infrared and pmr spectra and molecular weight determination. The same data for the first gc peak indicated that the compound or mixture was not principally N-ethyldiphenylamine. The molecular weight of 218 was close to that of *o*-(diethylamino)biphenyl and the pmr indicated a 1:1 ratio of aromatic to aliphatic protons. Only one proton was on an alkyl carbon attached to nitrogen and the characteristic methyl and methylene splittings of an ethyl group were absent. The first gc component was, therefore, principally N-(2-butyl)diphenylamine. It was not possible to determine the amount, if any, of N-ethyldiphenylamine by pmr but the molecular weight measurement indicated that the ethyl compound did not exceed one-quarter of the material in the gc peak.



The variation in product yields was observed at ambient and reflux for the diethylaniline reaction with benzyne from fluoro- and chlorobenzene, Table III. As previously noted the slower benzyne generation from chlorobenzene favored the reaction with the metallated diethylaniline. A temperature increase had a similar effect. In addition, since the excess *n*-butyllithium was destroyed in the metallation process, the loss of benzyne through reaction with *n*-butyllithium[4,5] decreased, and total yield of observed products increased. Steric hindrance in betaine formation undoubtedly contributed to the decrease in diethylaniline reactivity compared with that of dimethylaniline.

TABLE III

REACTION OF DIETHYLANILINE WITH BENZYNE GENERATED FROM FLUORO- OR CHLOROBENZENE AND *n*-BUTYLLITHIUM

			% yield	
X	Time, hr	Temp, °C	$(C_6H_5)_2N\underset{\substack{\mid \\ CH_3}}{C}HCH_2CH_3$[a]	$o\text{-}C_6H_5C_6H_4N(C_2H_5)_2$
F	72	32	1.9	1.7
F	4	Reflux	1.9	3.7
Cl	72	32	0.1	0.7
Cl	21	Reflux	...	13

[a] May include N-ethyldiphenylamine.

The products observed for benzyne addition to dimethyl- and diethylaniline indicate a competition between betaine formation and metallated species reaction. The betaines underwent both alkyl group elimination and rearrangement. The relative amounts of these processes were strongly dependent on the alkyl group, methyl favored elimination, and ethyl rearrangement. Since iodobenzene gives a totally different product, N-benzyl-N-methylaniline, when treated with dimethylaniline and *n*-butyllithium,[2] the iodobenzene reaction must not take place through a benzyne intermediate. Previous investigators[3,6] have observed differences in rates for the "benzyne" reactions from halobenzenes, but the same products were always found. These products may have been formed by mechanisms other than benzyne addition. The current study indicates that a distinct difference in reaction mechanisms may be possible in "benzyne" generation if less-reactive benzyne traps are used.

Experimental Section[17]

Physical Constants.—Proton magnetic resonance (pmr) spectra were measured on a Varian A-60 nmr spectrometer as 20% by volume solutions in carbon tetrachloride with approximately 1% tetramethylsilane as an internal standard as previously described.[18] Infrared measurements were made on the pure liquids or on potassium bromide disks of the solids, using a Perkin-Elmer Infracord spectrophotometer, Model 137. 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). Molecular weights were measured using a Microlab vapor pressure osmometer. Commercial N-methyldiphenylamine (formula wt 183.4 g/mole) was used as a standard for calibration. Measurements were made in benzene at 37°.

Gas Chromatography.—Retention ratios and product yields were determined using an internal standard method.[19] An F & M Model 500 gas chromatography was used as previously described[20] using a 0.25 in. × 10 ft column of 20% GD-SF96 on 40–60 mesh Chromosorb W. The flow rate was maintained between 160 and 170 cc/min of helium for analyses at 185°.

Chemicals.—Bromobenzene, N-ethylaniline, and mono-free diethylaniline were obtained from Matheson and *o*-aminobiphenyl from Pfister. *n*-Butyllithium (Foote Mineral, 15% in hexane) was analyzed by the double titration method for active lithium content.[21]

o-**(Dimethylamino)biphenyl**—*o*-Aminobiphenyl (25 g, 141 mmoles), 15 ml of dimethyl sulfate (0.16 mole), and 7 g of sodium hydroxide in 25 ml of water were treated as previously described.[16] Gc of the crude product indicated large amounts of unreacted starting amine. The crude product was refluxed for 2 hr with 30 ml of dimethyl sulfate and 14 g of sodium hydroxide in 50 ml of water. After cooling, the organic phase was separated and the aqueous layer was extracted with ether. Organic layers were combined, dried over anhydrous sodium sulfate, decanted, and distilled. The product, 19.2 g, 67%, had a bp 94° (0.5 mm) [lit.[16] 145° (11 mm)] and refractive indices of $n^{20}\mathrm{D}$ 1.6057, $n^{25}\mathrm{D}$ 1.6035, and $n^{30}\mathrm{D}$ 1.6007. The infrared spectrum had bands at 3.30 w, 3.41 m, 3.53 m, 3.61 m, 6.27 m, 6.67 m, 6.73 s, 6.90 m, 7.01 m, 7.58 m, 7.96 w, 8.38 w, 8.62 m, 8.74 w, 9.00 w, 9.31 vw, 9.46 m, 9.88 w, 10.53 m, 10.93 vw, 12.88 m, 13.10 m, 13.49 s*, and 14.25 s μ.

o,**N-Dimethyldiphenylamine.**—*o*,N-Dimethylaniline (24.2 g, 200 mmoles) was dissolved in 80 ml of anhydrous ether and 200 ml of 1.6 *N* *n*-butyllithium in hexane was slowly added with stirring while cooling at or below −10°. Fluorobenzene (19.2 g, 200 mmoles) was added to the mixture after warming to 10°. After 2 days at room temperature, 50 ml of methanol was slowly added with cooling; then 200 ml of water was added. The organic phase was separated, dried over anhydrous sodium sulfate, and distilled. The fraction, 1.38 g, boiling at 85–103° (0.15 mm) was 85% (3.3% over-all, gc) of product. *o*,N-Dimethyldiphenylamine had a gc retention ratio of 0.792 with respect to *o*-(diethylamino)biphenyl (equiv 0.95, Table I). The infrared spectrum of the preparative gc-purified product had bands at 3.31 w, 3.44 w, 6.28 s, 6.68 s*, 6.92 w, 7.44 m, 7.70 w, 7.98 w, 8.43 vw, 8.79 w, 8.98 w, 9.35 vw, 9.1–9.2 vw, 10.08 vw, 11.42 vw, 12.63 vw, 12.98 w, 13.32 s, 13.70 m, and 14.42 m μ.

o-**(Diethylamino)biphenyl.**—*o*-Aminobiphenyl, 17 g, and triethyl phosphate, 22 g, were heated gently to initiate reaction. When the initial reaction subsided the mixture was refluxed for 7 hr. After cooling to 50°, a solution of 18 g of sodium hydroxide in 65 ml of water was added and the mixture was again refluxed for 1 hr. The oil that separated on cooling was decanted from the crystalline phosphates. The solid material was dissolved in 100 ml of water and extracted with several portions of ether. The ether layers were combined with the original oil and the ether was vacuum evaporated. Acetic anhydride, 25 ml, was added and allowed to stand at room temperature for 1 week. The solution, containing the amine, was made strongly acid with 6 *N* hydrochloric acid and was extracted with two 15-ml portions of ether. Solid sodium hydroxide was added slowly with cooling to the water layer until strongly basic. The oil which separated was removed by several ether extractions. The ether extracts from the basic solution were dried over anhydrous magnesium sulfate and distilled. The product (9.3 g, 38% yield) boiled at 106–108° (0.3 mm), and had refractive indices of $n^{20}\mathrm{D}$ 1.5973, $n^{25}\mathrm{D}$ 1.5773, and $n^{30}\mathrm{D}$ 1.5784.

Anal. Calcd for $C_{14}H_{19}N$: C, 85.28; H, 8.50; N, 6.23. Found: C, 85.33; H, 8.52; N, 6.32.

The infrared spectrum had bands at 3.28 w, 3.36 m, 3.41 w, 3.57 w, 6.02 vw, 6.28 w, 6.68 m, 6.75 s, 6.91 w, 6.98 m, 7.26 m, 7.54 w, 7.70 w, 7.95 m, 8.07 m, 8.48 m, 8.72 vw, 9.00 w, 9.31 w, 9.48 w, 9.68 vw, 9.89 w, 10.95 vw, 11.1 vw, 12.7 vw, 13.02 m, 13.20 m, 13.47 s*, and 14.29 s μ.

N-Ethyldiphenylamine.—Potassium metal, 5.1 g, was added to 40 ml of dry N-ethylaniline and allowed to react at reflux for 14 hr. Bromobenzene, 16 ml, was then added and reflux was continued for 1 hr. The mixture was cooled, 50 ml of water was cautiously added with cooling and stirring, and the mixture was extracted with several portions of ether. Combination of the ether layers, drying over anhydrous sodium sulfate, and distillation gave 10 g (30% yield) of the product: bp 143–145° (5 mm); $n^{25}\mathrm{D}$ 1.6040 [lit.[22] 147° (10 mm), $n^{20}\mathrm{D}$ 1.6095]; infrared bands at 3.30 w, 3.38 w, 3.42 w, 3.50 w, 6.28 s, 6.68 s*, 6.91 w, 7.29 m, 7.41 w, 7.63 w, 7.92 m, 8.04 m, 8.42 w, 8.67 w, 8.82 w, 9.08 w, 9.30 w, 9.69 w, 10.05 w, 12.7 w, 13.32 s, and 14.4 s μ.

N-(*n*-Butyl)diphenylamine and N-(*n*-Pentyl)diphenylamine.—1-Iodopropane (3.4 g, 20 mmoles) was added at −10° to a stirred solution of 10 ml (60 mmoles) of N-methyldiphenylamine and 13 ml of 1.6 N *n*-butyllithium (20 mmoles) in hexane. The reaction mixture was allowed to warm slowly to room temperature (1 hr) and then stirred at this temperature for 2 hr. The reaction was quenched with ice and the organic layer was analyzed by gc. *o*-Diethylaminobiphenyl was used as the standard. N-(*n*-Butyl)diphenylamine with a retention ratio of 1.47 with respect to the standard (equiv 1.87, Table I) was formed in 8.0% yield. N-(*n*-Pentyl)diphenylamine, 2.10 *vs.* standard (equiv 2.67, Table I), was obtained in 9.8% yield. The starting N-methyldiphenylamine had a retention ratio of 0.69 with respect to this standard.

General Procedure for Benzyne Reactions.—*n*-Butyllithium (50 ml of 1.6 *N* in hexane) was added rapidly to a mixture of 150 mmoles of N,N-dimethyl- or N,N-diethylaniline and 50 mmoles of fluoro- or chlorobenzene. Room temperature reactions were stoppered and stirred at 25–33° for the specified period. Other solutions were placed under a condenser with drying tube and refluxed. Samples, 2 ml, were withdrawn from time to time and quenched with 1 ml of distilled water, and 1 ml of a standard solution of N-(*n*-butyl)-N-methylaniline was added. After thorough mixing a sample, 50–100 μl, was injected into the gc. Retention ratios and yields were calculated from the chromatograms. Proton nmr using methyl group singlet integrals was used to determine relative amounts of *o*-(dimethyl-

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

(18) A. R. Lepley and R. H. Becker, *Tetrahedron*, **21**, 2365 (1965).

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

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

(21) H. Gilman and A. H. Haubein, *ibid.*, **66**, 1515 (1944).

(22) B. P. Lugovkin and B. A. Arbuzov, *Zh. Obshch Khim.*, **22**, 2041 (1952); *Chem. Abstr.*, **47**, 9284*b* (1953).

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), $n^{25}\text{D}$ 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).