

were observed as in the preceding experiment: ethyl benzyl ether 63%, **2** 59%, **3** 5.3%. The neutral product structure was confirmed by ir analysis of the crude product distillate, bp 98–180° (1 atm), after acid washing and drying over calcium chloride. Gc characterization showed only a single peak for this material; its ir spectrum for a carbon disulfide solution with peaks at 3020 w, 2960 m, 2860 s, 1365 m, 1345 m, 1300 vw, 1265 vw, 1250 vw, 1200 w, 1165 w, 1145 w, 1110–1100 s\*, 1070 m, 1030 w, 1015 w, 905 vw, 890 vw, 850 vw, 735 s, and 695 s cm<sup>-1</sup>, was identical with that of the previously synthesized ether.

**Rearrangement Product Ratios from the *n*-Butyllithium Reactions with *N,N*-Dimethylbenzylaminium (1) Halides.**—In this series of reactions, 15 ml of 1.5 *M* (23 mmol) *n*-butyllithium in hexane was rapidly added to a vigorously stirred suspension

of 20 mmol of 1 halide in 85 ml of anhydrous ethyl ether. After 24 hr stirring at room temperature, 25 ml of water was added. The organic phase which separated was dried over potassium carbonate and analyzed directly at 168° on the GE-SF96 column. In no case was a peak or shoulder on an adjacent peak evident for an *o*-xylyl product. Therefore, the relative yields of rearrangement of  $\alpha$ - and  $\beta$ -phenethyl products **4** and **5** were calculated directly from the areas of their respective gc peaks.

**Registry No.**—**1** chloride, 3204-68-0; **1** bromide, 23145-45-1; **1** iodide, 25458-36-0; **5**, 28059-49-6; **7**, 28059-50-9; KOH, 1310-58-3; NaOEt, 141-52-6; MeLi, 917-54-4; C<sub>6</sub>H<sub>5</sub>Li, 591-51-5; *n*-BuLi, 109-72-8.

## Benzynes Addition to *N,N*-Dimethylbenzylamine<sup>1a</sup>

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*N*-Methyl-*N*-( $\alpha$ -phenethyl)aniline (**1**) was obtained as the principal amine addition-rearrangement product when benzyne was generated by the attack of organolithium compounds on fluoro-, chloro-, or bromobenzene in *N,N*-dimethylbenzylamine. Small amounts of *N*-methyl-*N*-benzylamine (**2**) and *N*-methyl-*N*-( $\beta$ -phenethyl)aniline (**3**) were also formed. Considerable variation in yields were observed with base and halobenzene variation. Fluorobenzene reaction with the metalated product from room temperature reaction of *N,N*-dimethylbenzylamine gave the same principal product plus a small amount of *N,N*-dimethyl-*o*-phenylbenzylamine (**4**). Proton magnetic resonance studies of the fluorobenzene, *n*-butyllithium, dimethylbenzylamine reaction show stimulated emission and enhanced adsorption in the chemical shift for the benzylic protons of the product. These data are interpreted as evidence for an ortho betaine from benzyne-amine addition which undergoes a proton shift to a benzyl ylide and subsequent free-radical pair methyl migration to the major product.

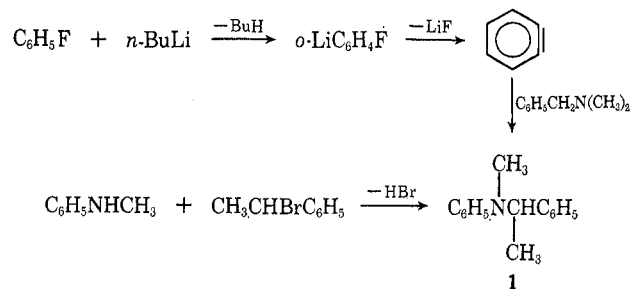
Although extensive studies of benzyne reactions have been reported,<sup>2,3</sup> relatively little work has been directed toward the addition of neutral, lone pair, electron donors to the active aromatic sites.<sup>4,5</sup> Several examples of this type of reaction involving tertiary aliphatic amine additions have been carried out by Wittig and coworkers<sup>6–9</sup> and by Hellmann's group<sup>10–13</sup> using Grignard generated benzyne, while benzyne *vs.* displacement reactions of strong bases on halobenzenes have been characterized with aniline derivatives.<sup>14,15</sup>

Since this last method, the action of organolithium compounds on monohalobenzenes, provides a method

of generating intermediates comparable to those of several quaternary ammonium salt rearrangements, we have carried out this study on the addition of benzyne to *N,N*-dimethylbenzylamine. Where feasible, this work paralleled the organolithium rearrangements of the *N,N*-dimethyl-*N*-benzylaminium ion.<sup>16</sup>

### Results and Discussion

The principal addition-rearrangement product, *N*-methyl-*N*-( $\alpha$ -phenethyl)aniline (**1**), was obtained in 35% yield from the reaction of *n*-butyllithium and fluorobenzene in a 1:3:1 v/v solution of *N,N*-dimethylbenzylamine, anhydrous ether, and *n*-hexane. Identification of this product was based on the identity of proton magnetic resonance (pmr) and infrared (ir)



spectra for material from a preparative scale reaction<sup>17</sup> and for the authentic compound synthesized by the reaction<sup>18</sup> of *N*-methylaniline and  $\alpha$ -bromoethylbenzene. The formation of **1** was smooth reaching three-

(1) (a) This investigation was supported by U. S. Public Health Service Grant GM-09136 from the National Institute of General Medical Sciences and was presented in part before the Division of Organic Chemistry, 145th National Meeting of the American Chemical Society, New York, N. Y., Sept 1963, Abstracts, 5Q. (b) To whom reprint requests should be sent, Marshall University. (c) Fulbright student, State University of New York at Stony Brook, 1962–1964.

(2) For reviews of aryne chemistry, see E. F. Jenny, M. C. Caserio, and J. D. Roberts, *Experientia*, **14**, 349 (1958); R. Huisgen and J. Sauer, *Angew. Chem.*, **72**, 91 (1960); R. Huisgen, "Organometallic Chemistry," H. Zeiss, Ed., Reinhold, New York, N. Y., 1960, pp 75–87; J. F. Bunnett, *J. Chem. Educ.*, **38**, 278 (1961); H. Heaney, *Chem. Rev.*, **62**, 81 (1962); G. Wittig, *Angew. Chem., Int. Ed. Engl.*, **4**, 731 (1965).

(3) R. W. Hoffman, "Dehydrobenzene and Cycloalkynes," Academic Press, New York, N. Y., 1967.

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(10) H. Hellmann and W. Unseld, *Justus Liebig's Ann. Chem.*, **631**, 82 (1960).

(11) H. Hellmann and W. Unseld, *ibid.*, **631**, 89 (1960).

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(15) H. Heaney and T. J. Ward, *Chem. Commun.*, 810 (1969).

(16) A. R. Lepley and A. G. Giumanini, *J. Org. Chem.*, **36**, 1217 (1971).

(17) A. G. Giumanini and A. R. Lepley, *Bull. Chem. Soc. Jap.*, **42**, 2359 (1969).

(18) A. H. Wagg, T. S. Stevens, and D. M. Ostle, *J. Chem. Soc.*, 4057 (1958).

fourths of the maximum yield after 9 hr at constant temperature. Changes in base or halobenzene (Table I) all resulted in decreased yields of 1. Phenyl-

TABLE I

*N*-METHYL-*N*-( $\alpha$ -PHENETHYL)ANILINE (1) PRODUCED IN THE ADDITION OF DIMETHYLBENZYLAMINE<sup>a</sup> TO BENZYNE

Benzyne source	Yield of 1, %
1 <i>o</i> -NH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CO <sub>2</sub> H + 1 <i>n</i> -BuONO	3
1 C <sub>6</sub> H <sub>5</sub> Br + 2 C <sub>6</sub> H <sub>5</sub> Li	4
1 C <sub>6</sub> H <sub>5</sub> Cl + 2 C <sub>6</sub> H <sub>5</sub> Li	10
1 C <sub>6</sub> H <sub>5</sub> Cl + 1 <i>n</i> -BuLi	14
1 C <sub>6</sub> H <sub>5</sub> Cl + 2 <i>n</i> -BuLi	18
1 <i>o</i> -FC <sub>6</sub> H <sub>4</sub> Br + 1 Mg	21 <sup>b</sup>
1 C <sub>6</sub> H <sub>5</sub> F + 2 <i>n</i> -BuLi	33

<sup>a</sup> Six- to eightfold excess used. <sup>b</sup> Equimolar amount of amine, ref 10.

lithium and chlorobenzene gave approximately one-half the production of 1 as was formed with *n*-butyllithium and the same halobenzene. Fluoro-, chloro-, and bromobenzene, in that order, gave decreasing amounts of 1. The *in situ* generation of benzyne<sup>19</sup> from anthranilic acid and *n*-butyl nitrite gave a maximum yield of 3% 1 on reaction with dimethylbenzylamine. An equal amount of *N*-methyl-*N*-benzylamine (2) was formed in the latter reaction.

This same material, 2, was also detected in small amounts, 1.0 and 0.2% yields, respectively, from chloro- and fluorobenzene reactions with *n*-butyllithium in dimethylbenzylamine. *N*-Methyl-*N*-( $\beta$ -phenethyl)aniline (3) was formed in 1.0 and 0.5% in these same reactions. In general, the reactions were slower and yields of secondary productions, 2 and 3, were higher with changes in the halobenzene from fluoro to chloro to bromo. The pmr (Table II) and gas chromatographic (Table III) data for these compounds and a number of related isomeric compounds were used in confirming structures.

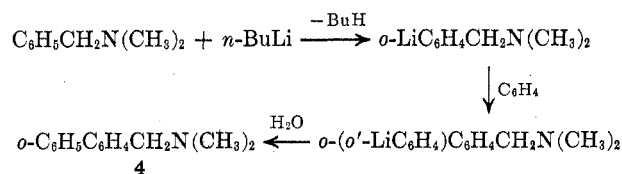
Since the amine reactant in these studies has been reported<sup>20</sup> to rapidly convert to species lithiated in the  $\alpha$  and ortho positions, *N,N*-dimethylbenzylamine was treated with *n*-butyllithium for 24 hr at room temperature before addition of fluorobenzene. In this case, 1 was the principal product, 17%, and small amounts of three other compounds were detected. Compounds with the gc and organoleptic characteristics of benzaldehyde and *N,N*-dimethylaniline were present in trace amounts relative to the starting amine. The third compound, *N,N*-dimethyl-*o*-phenylbenzylamine (4), was formed in 1.0% yield.

Benzyne is generated by the action of a strong base on a haloaromatic compound in two steps:<sup>2</sup> (1) ortho proton abstraction by the base, and (2) loss of metal halide from the metalated haloaromatic formed in step 1. Although the equilibrium characteristics of the first step have been studied,<sup>21</sup> the use of *n*-butyl- or phenyllithium effectively eliminated reversibility in the metalation reaction. Benzyne formation or re-

action with this species thus became the subsequent routes in conversion of the ortho halo metal compound. The halide reactivity order F > Cl > Br for benzyne formation was the same as that previously observed.<sup>2,3</sup>

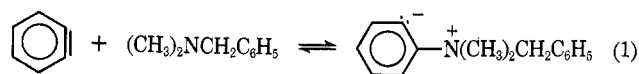
The benzyne generated acts as an electrophilic reagent in subsequent reactions. The base itself can react with benzyne if present in an excess if step 1 is rate controlling. Although biphenyl and/or metalated diphenyl were present in the phenyllithium solution used, additional amounts of this material may also have been formed by a side reaction of phenyllithium with benzyne. *n*-Butylbenzene was not sought in the current experiments; however, it has been reported<sup>2</sup> when benzyne is generated with *n*-butyllithium. Other related species could form from the addition of the ortho halo metal intermediate to benzyne.

Metalation of *N,N*-dimethylbenzylamine occurs in the ortho position.<sup>20</sup> The benzyne adduct of this metalated species gives 4, an isomer of 1, on reaction



with water. Neither 4 nor benzhydryldimethylamine (5), a potential product *via* methylene metalation of dimethylbenzylamine, was observed in direct reactions of an organolithium reagent with halobenzene in amine. However, when the amine was allowed to react with *n*-butyllithium prior to fluorobenzene addition, a small amount of 4 was observed. These observations may be interpreted in any of several fashions; either metalation of the amine was relatively slow under the reaction conditions and/or amounts of metalated amine were very small and/or the addition of these metalated species to benzyne is relatively inefficient. The first of these possibilities is favored, although not necessarily to the exclusion of the others by the premetalation reaction results and by the observed very slow change in integrated nmr proton ratios for mixtures of the tertiary amine and *n*-butyllithium.

The equilibrium addition<sup>22</sup> of the less basic, neutral nitrogen lone pair to benzyne (eq 1) is favored by



high amine concentrations. Since low aryne concentrations mitigate against further benzyne addition to the betaine, S<sub>N</sub>i-sigmatropic shifts<sup>23</sup> of the betaine are proposed to account for final aniline-containing products in the aprotic media. A pseudo-Sommelet [3,3] shift of the betaine to an *exo*-methylenecyclohexadiene

(22) Evidence for equilibrium is the formation of products attributable to benzyne generation in base attack on quaternary anilinium salts: F. Weygand, A. Schroll, and H. Daniel, *Chem. Ber.*, **97**, 857 (1964); A. G. Giumanini, *Chem. Ind. (London)*, 1140 (1967).

(23) Although no stereochemistry distinguishing between the inversion of a nucleophilic displacement and the retention of a sigmatropic shift is possible in these reactions, we have used the more descriptive reaction orders as defined by A. R. Lepley and A. G. Giumanini in "Mechanisms of Molecular Migration," Vol. 3, B. S. Thyagarajan, Ed., Interscience, New York, N. Y., 1970.

(19) Method of L. Friedman and F. M. Logullo, *J. Amer. Chem. Soc.*, **85**, 1549 (1963); *J. Org. Chem.*, **34**, 3089 (1969).

(20) W. H. Puterbaugh and C. R. Hauser, *J. Amer. Chem. Soc.*, **85**, 2467 (1963).

(21) J. F. Bunnett and D. A. R. Happer, *J. Org. Chem.*, **31**, 2369 (1966).

TABLE II  
PROTON MAGNETIC RESONANCE SPECTRA OF REACTION PRODUCTS RELATED TO THE BENZYNE ADDITION TO  
DIMETHYLBENZYLAMINE AND TO THE REARRANGEMENT OF DIMETHYLBENZYLANILINIUM SALTS<sup>a</sup>

Compd	Chemical shift <sup>b</sup>											
	C	NC	CH <sub>2</sub>	Ar	NAr	C, Ar	NC, Ar	CH <sub>2</sub>	Ar, Ar	NAr, Ar	CH	H
<i>N,N</i> -Dimethylaniline					2.78 s (6)							6.60 m (3), 7.08 m (2)
<i>N,N</i> -Dimethylbenzhydrol-amine (5)	2.11 s (6)											7.23 m (10)
<i>N,N</i> -Dimethylbenzylamine	2.13 s (6)						3.31 s (2)				4.00 s (1)	7.20 m (5)
<i>N,N</i> -Dimethyl- <i>o</i> -benzyl-aniline (7)					2.57 s (6)				4.01 s (2)			7.01 m (9)
<i>N,N</i> -Dimethyl- <i>o</i> -phenyl-amine (4)	2.08 s (6)						3.23 s (2)					7.29 m (9)
<i>N</i> -Ethyl- <i>N</i> -benzylamine	1.12 t (3)							3.35 q (2)		4.34 s (2)		6.67 m (3), 7.16 m (7)
<i>N</i> -Methyl- <i>N</i> -benzyl-aniline (2)					2.86 s (3)					4.36 s (2)		6.63 m (3), 7.15 m (7)
<i>N</i> -Methyl- <i>N</i> -benzyl- <i>o</i> -toluidine (6)					2.34 s (3)	2.50 s (3)				3.92 s (2)		6.99 m (4), 7.23 m (5)
<i>N</i> -Methyldibenzyl-amine (10)	2.08 s (3)						3.41 s (4)					7.22 m (10)
<i>N</i> -Methyl- <i>N</i> -( $\alpha$ -phenethyl)aniline (1)	1.46 d (3)				2.56 s (3)						5.03 q (1)	6.71 m (3), 7.18 m (7)
<i>N</i> -Methyl- <i>N</i> -( $\beta$ -phenethyl)aniline (3)					2.74 s (3) <sup>c</sup>	2.77 m (2) <sup>c,d</sup>		3.44 m (2) <sup>d</sup>				6.60 m (3), 7.11 m (7)
<i>N</i> -Methyl- <i>N</i> -( <i>o</i> -xylyl)-aniline					2.21 s (3)	2.86 s (3)				4.32 s (2)		6.62 m (3), 7.03 m (6)

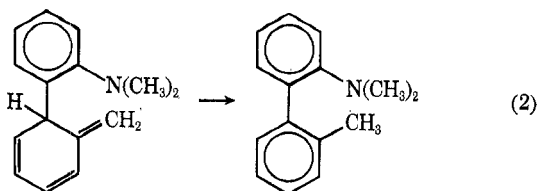
<sup>a</sup> Reference 16. <sup>b</sup> All peaks are relative to tetramethylsilane as  $\delta$  values in parts per million (ppm); splitting, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet; J values are 7.0  $\pm$  0.1 cps unless otherwise indicated; values in parentheses are relative integrated peak ratios in compound. <sup>c</sup> Overlapping singlet and multiplet, center of multiplet determined from integral and singlet peak maximum. <sup>d</sup> Centers of respective parts of A<sub>2</sub>X<sub>2</sub> multiplet.

TABLE III

Compd	Retention ratio by column		
	20% 20M Carbowax plus 5% KOH <sup>a</sup>	20% GE-SF96 <sup>b</sup> 168°C	20% Apiezon H <sup>c</sup> 200°C <sup>d</sup>
<i>N,N</i> -Dimethyl- <i>o</i> -phenylbenzylamine (4)	0.896	1.00	0.855
<i>N,N</i> -Dimethylbenzhydrolamine <sup>e</sup> (5)	1.00	1.00	1.00
<i>N,N</i> -Dimethyl- <i>o</i> -benzylamine (7)	1.29	1.22	1.08
<i>N</i> -Methyl- <i>N</i> -benzyl- <i>o</i> -toluidine <sup>f</sup> (6)	1.34	1.29	1.20
<i>N</i> -Methyldibenzylamine (10)	1.37	1.28	1.28
<i>N</i> -Methyl- <i>N</i> -benzylamine (2)	2.17	1.45	1.65
<i>N</i> -Ethyl- <i>N</i> -benzylamine		1.73	
<i>N</i> -Methyl- <i>N</i> -( $\alpha$ -phenethyl)aniline (1)	2.21	1.76	1.86
<i>N</i> -Methyl- <i>N</i> -( <i>o</i> -xylyl)aniline	2.91	2.18	1.88
<i>N</i> -Methyl- <i>N</i> -( $\beta$ -phenethyl)aniline (3)	3.13	2.29	2.02

<sup>a</sup> 0.25 in.  $\times$  12 ft column, 190°C, 150 ml/min He flow; ratios are  $\pm$ 0.01. <sup>b</sup> 0.25 in.  $\times$  5 ft column. <sup>c</sup> 72 ml/min He flow; ratios are  $\pm$ 0.01. <sup>d</sup> 26 ml/min He flow; ratios are  $\pm$ 0.02. <sup>e</sup> 1/8 in.  $\times$  5 ft column, 195°C, 30 ml/min N<sub>2</sub> flow; ratios are  $\pm$ 0.005. <sup>f</sup> Retention ratio standard. <sup>g</sup> Used as internal standard for quantitative analysis.

and subsequent [1,3] proton migration would form the biphenyl product of eq 2, but no product was



detected with the properties of this compound. [1,3] shifts from betaine nitrogen to the ortho aniline position by methyl or benzyl groups would produce *N*-methyl-*N*-benzyl-*o*-toluidine (6) or *N,N*-dimethyl-*o*-benzylaniline (7), respectively. Although such a direct in-



ternal displacement of an ethyl group in the benzyne addition of triethylamine was suggested,<sup>6</sup> it was later shown<sup>9</sup> that the product observed came from an  $\alpha$  rearrangement. Absence of 6 and 7 in the current reactions supports the forbidden nature of [1,3] processes since the intermolecular displacement products *N,N*-dimethylaniline and 2 were observed.

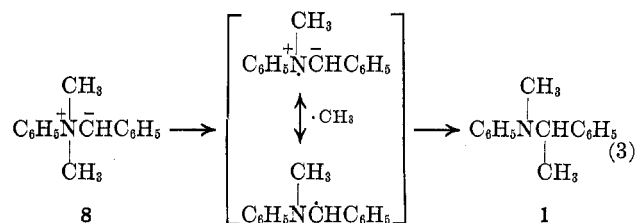
Proton migrations [1,4] from either benzyl or methyl groups of the betaine give the respective ylides 8 and 9. The subsequent conversion of 8 and 9 to 1



and 2 is the same as discussed for rearrangements of the *N,N*-dimethyl-*N*-benzylanilinium ion.<sup>16</sup> The ammonium salt rearrangement to 1 was favored by low strength in the attacking base. In the betaine, the proton-abstracting power of the ortho anion is probably less than that of any of the organolithium bases studied. The benzyl proton migration, favored by phenyllithium attack on the salt, was even more viable with the ortho betaine. The contrast of phenyllithium and butyllithium as benzyne-generating agents indicates that the stronger base was rapidly consumed so that internal benzyl proton migration was betaine controlled. The slower phenyllithium generation of benzyne thus provided a stronger base which was still present to modulate the methyl ylide formation and increase the relative production of the  $\beta$ -phenethyl product, 3. Although ylides are generated by comparable bases from two different starting points, the Stevens rearrangement *via*  $\alpha$  methyl migration from 8 to form 1 predominates in both cases. Therefore, it is possible to extrapolate the following detailed evidence from the benzene reaction to the quaternary salt rearrangement.

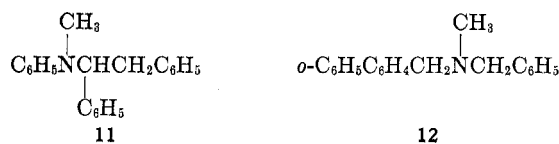
The definition of the pathway from 8 to 1 is based on proton magnetic resonance (pmr) measurements during the benzyne addition reaction. When reaction is complete within 30 min, the pmr spectrum of the reaction mixture gives a -0.9:-4.9:5.6:1.1 peak intensity ratio for the methyne quartet of 1 at  $\delta$  5.01 ppm. Since the intensity ratio differs from the normal 0.9:3.0:3.0:1.1 observed in pure 1 (Table II), chemically

induced dynamic nuclear polarization (CIDNP)<sup>24</sup> giving a multiplet effect<sup>25</sup> was evident.<sup>26</sup> CIDNP multiplet effects with downfield emission and upfield absorption occur when singlet radical pairs are direct product precursors.<sup>27</sup> Thus a radical pair compatible with homolytic cleavage of the single bond must precede 1. The caged singlet state, however, does not produce a multiplet effect except when some spin sorting takes place by conversion to a triplet pair and subsequent separation of the radical pair. A loss of  $\cdot\text{CH}_3$  from the cage of eq 3 would give 2 if the re-



maining radical abstracted hydrogen; the related dimers were not sought. Absence of CIDNP effects in 2 do not effect this interpretation since multiplet effects are self-cancelling in singlets.<sup>28</sup> If the ratio of 1:2, > 30:<1, indicates the amount of 1 contributing to the multiplet effect, then (a) trapping within the cage of eq 3 is very efficient; (b) most of the production of 1 is by some other route; or (c) major amounts of dimeric and other unidentified materials are present. While we have not yet distinguished between these possibilities, we favor a. However, we can demonstrate that the conditions for CIDNP measurements do not greatly change the reaction chemistry.

In order to accelerate the reaction from 9-24 hr to <30 min, concentrations and temperature were increased and catalyst was added to speed metalation by depolymerization of the *n*-butyllithium hexamer.<sup>29</sup> The elimination of diluents, heating to 60°, and addition of very small amounts of *N,N,N,N*-tetramethylethylenediamine (TMEDA) are adequate to give a strong *e/a* multiplet in the *N,N*-dimethylbenzylamine reaction. The quantitative variation in the reaction of *N*-methyldibenzylamine (10) with fluorobenzene and *n*-butyllithium and the resulting effect on yields of *N*-methyl-*N*-(1,2-diphenylethyl)aniline (11) and *N*-methyl-*N*-benzyl-*o*-phenylbenzylamine (12) are shown



in Table IV.<sup>30</sup> CIDNP effect pmr spectra were attained from both the methyne and methylene protons of 11<sup>26</sup> but only when 11 was formed in high yields and reaction completion was rapid. Since comparable results are obtained both in slow and fast reactions and the catalyst is known to accelerate the first reaction

(24) For a recent review, see H. R. Ward, *Accounts Chem. Res.*, **4**, in press.

(25) A. R. Lepley, *J. Amer. Chem. Soc.*, **91**, 749 (1969).

(26) A. R. Lepley, *ibid.*, **91**, 1237 (1969); *Chem. Commun.*, 1460 (1969).

(27) G. L. Closs and L. E. Closs, *J. Amer. Chem. Soc.*, **91**, 4550 (1969).

(28) Decoupling experiments on the pmr multiplet effect spectra in RLi + R'I reactions confirm this conclusion: A. R. Lepley, unpublished work.

(29) J. M. Mallan and R. L. Bebb, *Chem. Rev.*, **69**, 693 (1969).

(30) A. R. Lepley and P. M. Cook, unpublished work.

TABLE IV  
EFFECT OF REAGENTS ON PRODUCT DISTRIBUTIONS IN  
BENZYLNE ADDITION TO *N*-METHYLDIBENZYLAMINE (10)

Molar ratio <i>n</i> -BuLi <sup>a</sup> :10:C <sub>6</sub> H <sub>5</sub> F	Time, hr	% yield	
		11	12
1:1:1	24	8.3	6.0
1:5:1	24	24.9	4.0
1:1:1 <sup>b</sup>	0.5	1.8	3.6
1:5:1 <sup>b</sup>	0.5	24.6 <sup>c</sup>	2.8

<sup>a</sup> *n*-BuLi (1.5 *M*) in hexane. <sup>b</sup> Plus 0.01 mol ratio TMEDA.  
<sup>c</sup> CIDNP in pmr spectrum during reaction.

step, the subsequent steps are essentially unchanged under CIDNP conditions.

The generalized radical pair pathway of eq 3 offers a reasonable explanation for the observations. These and the related results discussed for ammonium salts<sup>16</sup> furnish a strong basis for future tests of rearrangement mechanisms.

### Experimental Section<sup>31</sup>

**Gas Chromatography (Table II).**—Separations were accomplished on an Aerograph A-90P using the nonpolar substrate GE-SF96. The polar 20M Carbowax plus KOH column was used on an F & M Model 500. Several compounds, inadequately separated on the preceding columns, were characterized on an Apiezon H column using an Aerograph A-600 with flame ionization detector. Quantitative analyses were carried out on the Carbowax and GE-SF96 columns.

**Chemicals.**—Bromo-, chloro-, and fluorobenzene,  $\alpha$ -chlorotoluene,  $\alpha$ -bromo-*o*-xylene, ( $\alpha$ -bromoethyl)benzene, *N*-methyl-*o*-toluidine, *N*-methylaniline, *N*-methyl-*N*-benzylaniline, *N*-ethyl-*N*-benzylaniline, *n*-butyl nitrite, and anthranilic acid were purchased from Eastman. *N,N*-Dimethylbenzylamine and *N*-methyldibenzylamine (10) were obtained from Miles Chemical. *o*-Nitrobenzyl chloride and aminodiphenylmethane were from Aldrich, and *o*-aminobiphenyl was a Pfister product. Foote Mineral Co. 15% *n*-butyllithium in hexane and 20% phenyllithium in 3:1 v/v benzene-ether were titrated to determine active lithium content<sup>32</sup> before use. *N*-Methyl-*N*-( $\beta$ -phenethyl)aniline (3)<sup>16</sup> and *n*-pentylbenzene<sup>33</sup> were available from related studies.

**2-Cyanobiphenyl.**—*o*-Aminobiphenyl (100 g, 0.59 mol) was mixed with 150 ml (1.8 mol) of concentrated hydrochloric acid. The salt slurry formed was cooled to 0° by addition of crushed ice and an ice-cold solution of 42 g (0.61 mol) of sodium nitrite in 100 ml of water was added at such a rate that the temperature did not rise above 5°. The mixture was neutralized with solid sodium carbonate. Cuprous cyanide<sup>35</sup> (65 g, 0.75 mol) was suspended in 450 ml of water and 82 g (1.25 mol) of potassium cyanide was added to effect solution. The cyanide solution was cooled to 0° by addition of ice, mixed with 200 ml of toluene, and slowly added to the diazonium solution with vigorous stirring while maintaining the temperature below 5°. The tarry mixture was allowed to gradually warm to room temperature and then was heated to 50°. On cooling the oily layer was separated. Toluene extracts were combined with the previous organic layer and washed with dilute (6 *F*) hydrochloric acid, sodium bicarbonate solution, and then water, dried with sodium sulfate, and distilled. The product, 45 g, 43% yield, was obtained as a colorless oil boiling at 170–171° (15 mm) [lit.<sup>36</sup> 163° (14 mm)],  $n_D^{25}$  1.6147. The infrared spectrum had bands at 3030 w, 2220 w,

1590 w, 1555 vw, 1470 m, 1445 w, 1425 w, 1265 vw, 1185 vw, 1160 vw, 1075 vw, 1010 w, 920 vw, 845 vw, 780 w, 762 s, 738 s, and 700 s<sup>\*</sup> cm<sup>-1</sup>.

***N,N*-Dimethyl-*o*-phenylbenzylamine (4).**—2-Cyanobiphenyl (44 g, 0.25 mol) in 200 ml of anhydrous ether was reduced with a suspension of lithium aluminum hydride<sup>37</sup> in 500 ml of anhydrous ether. After removing excess hydride with 20% NaOH and water, and decanting, the ether was stripped from the solution to give crude primary amine.<sup>38</sup> Formic acid (90% solution, 1.25 mol) and then 0.55 mol of formaldehyde<sup>39</sup> were added with cooling to the crude amine. The mixture was refluxed for 16 hr. Hydrochloric acid (12 *N*, 0.44 mol) was added and the mixture was vacuum evaporated to half its volume. The solution was made strongly basic by slow addition of solid sodium hydroxide and was then extracted with ether. The ether layer was dried over solid potassium hydroxide. Distillation of the ether solution gave 26 g, 50% yield, of the gas chromatographically pure product, bp 162–164° (21 mm),  $n_D^{25}$  1.5759,  $d_4^{20}$  1.003. The infrared spectrum had bands at 3060 w, 2940 m, 2820 m, 2770 s, 1685 vw, 1590 w, 1475 m, 1450 m, 1360 m, 1300 vw, 1282 vw, 1260–1245 w, 1173 w, 1147 vw, 1097 w, 1075 vw, 1045 m, 1030 m, 1011 m, 946 vw, 915 vw, 880 vw, 852 w, 776 m, 754 s<sup>\*</sup>, 724 w, and 703 s cm<sup>-1</sup>.

*Anal.* Calcd for C<sub>15</sub>H<sub>17</sub>N: C, 85.26; H, 8.11; N, 6.63. Found: C, 85.43; H, 8.05; N, 6.45.

***o*-Nitrodiphenylmethane.**—Aluminum chloride (51 g, 0.38 mol) was slowly added at 0° with vigorous stirring to an anhydrous solution of 39 g (0.23 mol) of *o*-nitrobenzyl chloride<sup>40</sup> in 500 ml of benzene and reacted as previously described.<sup>41</sup> After washing and drying, vacuum distillation gave 21 g, 43% yield, of the product boiling at 204–207° (21 mm) [lit.<sup>41</sup> 183–184° (10 mm)]. The product had infrared peaks at 3070 w, 2930 vw, 2857 vw, 1608 w, 1530 s<sup>\*</sup>, 1495 m, 1452 w, 1355 s, 1183 vw, 1112 w, 1078 vw, 1033 vw, 1019 vw, 864 w, 819 vw, 790 w, 745–735 m, and 704 m cm<sup>-1</sup>.

***o*-Benzylaniline.**—Five grams of 10% palladium on powdered charcoal was added to a stirred boiling solution of 20 g (94 mmol) of *o*-nitrodiphenylmethane in 400 ml of 95% ethanol. Hydrazine hydrate (37 ml) was slowly added and the solution was refluxed until evolution of gas ceased. The solution was filtered and distilled giving 13.5 g, 79% yield, of product, bp 171–172° (12 mm) [lit.<sup>41</sup> 172–173° (13 mm)], with infrared peaks at 3450 w, 3370 m, 3225 w, 3020 m, 2910 w, 2850 vw, 1620 s<sup>\*</sup>, 1510 s, 1485 s, 1450 m, 1275 m, 1180 w, 1075 w, 1040 w, 838 w, 783 w, 754 s, 731 s, and 698 s cm<sup>-1</sup>.

***N,N*-Dimethyl-*o*-benzylaniline (7).**—*o*-Benzylaniline (4.5 g, 24 mmol) was mixed with 6.8 g (49 mmol) of trimethyl phosphate and heated gently in a 1-l. flask until a fine mist appeared. The heat was removed until the initial reaction ceased and then the solution was gently refluxed for 2 hr. A solution of 20 g of sodium hydroxide in 150 ml of water was slowly added to the cooled reaction mixture. Then 200 ml of water was added and the amine was extracted with ether. The ether solution was dried over sodium hydroxide pellets, decanted, and vacuum distilled to give 1.8 g, 35% yield, of the tertiary amine, bp 93–95° (0.01 mm),  $n_D^{25}$  1.5799.

*Anal.* Calcd for C<sub>15</sub>H<sub>17</sub>N: C, 85.26; H, 8.11; N, 6.63. Found: C, 85.11; H, 8.23; N, 6.80.

The product had infrared peaks at 3020 m, 2940 m, 2860 w, 2830 w, 2780 w, 1675 w, 1600 m, 1490 s<sup>\*</sup>, 1450 s, 1315 w, 1180 w, 1157 w, 1094 w, 1064 w, 1050 w, 1034 w, 950 w, 769 m, 750 m, 731 m, and 700 s cm<sup>-1</sup>.

***N*-Methyl-*N*-benzyl-*o*-toluidine (6).**<sup>42</sup>—*N*-Methyl-*o*-toluidine (22 ml, 166 mmol) and 19 ml (166 mmol) of  $\alpha$ -chlorotoluene were heated at 100° for 5 hr. The crystalline product was triturated with four 50-ml portions of ether and the remaining solid was mixed with 50 ml of 6 *N* sodium hydroxide. The oil which resulted was extracted with ether. The ether layer was washed with 6 *N* sodium hydroxide and water, dried over anhydrous silica gel, decanted, and distilled. A 57% yield, 20 g, of product

(31) (a) Analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. (b) Physical constants were measured and are reported as previously described: A. R. Lepley, V. C. Dohm, and A. G. Giumanini, *J. Org. Chem.*, **34**, 3042 (1969); A. R. Lepley and R. H. Becker, *Tetrahedron*, **21**, 2865 (1965).

(32) H. Gilman and F. K. Cartledge, *J. Organometal. Chem.*, **2**, 447 (1964); D. E. Applequist and D. F. O'Brien, *J. Amer. Chem. Soc.*, **85**, 743 (1963); H. Gilman and A. H. Haubein, *ibid.*, **66**, 1515 (1944).

(33) A. R. Lepley and A. G. Giumanini, *J. Org. Chem.*, **32**, 1706 (1967).

(34) Cf. H. T. Clarke and R. R. Read, *Org. Syn.*, **1**, 514 (1941).

(35) H. J. Barber, *J. Chem. Soc.*, 79 (1943).

(36) J. von Braun and G. Manz, *Justus Liebig's Ann. Chem.*, **468**, 258 (1929).

(37) General nitrile reduction method of L. Amundsen and L. Nelson, *J. Amer. Chem. Soc.*, **73**, 242 (1951).

(38) This primary amine has previously been prepared by other methods: T. A. Geissman and R. W. Tess, *ibid.*, **62**, 514 (1940); cf. ref 36.

(39) General methylation method of H. T. Clark, H. B. Gillespie, and S. Z. Weisshaus, *ibid.*, **55**, 4571 (1933).

(40) Recrystallized from petroleum ether, (bp 35–60°), prior to use, mp 48–49°.

(41) P. Carré, *C. R. Acad. Sci.*, **148**, 101 (1909).

(42) E. Wedekind and F. Oberheide, *Ber.*, **37**, 3898 (1904).

was obtained boiling at 158–159° (12 mm) [lit.<sup>42</sup> 167° (13 mm)],  $n_D^{20}$  1.5742,  $d_4^{20}$  1.019. The infrared spectrum had bands at 3060 w, 2970 w, 2870 w, 2825 w, 1610 m, 1495 s\*, 1460 m, 1368 m, 1334 w, 1300 vw, 1230 m, 1177 w, 1123 w, 1099 m, 1078 w, 1058 w, 1033 w, 990 vw, 910 vw, 818 vw, 768 s, 750 w, 726 s, and 699 m  $\text{cm}^{-1}$ .

**N-Methyl-N-( $\alpha$ -phenethyl)aniline (1).**—N-Methylaniline (25 ml, 0.23 mol) was added to an excess (50 ml, 0.35 mol) of  $\alpha$ -bromoethylbenzene. After the initial reaction subsided, the mixture was heated for 2 hr on a steam bath. The mixture, which solidified on cooling, was washed with cold acetone which left a readily filtered, white crystalline powder. The solid was dissolved in water and solid potassium hydroxide was added until strongly basic. The insoluble oily amine was extracted with ether, and the ether solution was dried over potassium hydroxide, decanted, and distilled. A 49% yield, 24 g, of product was obtained boiling at 188–189° (23 mm) [lit. 158–165° (7 mm),<sup>18</sup> 166–168° (14 mm)<sup>43</sup>],  $n_D^{20}$  1.5946 [lit.<sup>43</sup>  $n_D^{20}$  1.5967],  $d_4^{20}$  1.033. Infrared analysis showed bands at 3030 w, 2970 w, 2870 w, 2800 vw, 1605 s, 1510 s\*, 1450 m, 1370 m, 1315 m, 1208 w, 1185 w, 1162 vw, 1103 m, 1031 m, 997 w, 909 vw, 787 w, 751 s, 723 w, and 965 s  $\text{cm}^{-1}$ .

**N-Methyl-N-(*o*-xylyl)aniline.**<sup>44</sup>—N-Methylaniline (18 ml, 166 mmol) and 22 ml (166 mmol) of  $\alpha$ -bromo-*o*-xylene were treated as in the preparation of N-methyl-N-benzyl-*o*-toluidine. A 40% yield, 14 g, of product was obtained which boiled at 165–170° (13 mm) [lit.<sup>44</sup> 200° (35 mm)],  $n_D^{20}$  1.5998,  $d_4^{20}$  1.057, with infrared peaks at 3060 w, 2940 m, 1610 s, 1515 s\*, 1470 m, 1385 m, 1355 m, 1265 m, 1222 m, 1213 m, 1162 w, 1125 w, 1108 w, 1055 vw, 1040 w, 1008 w, 994 w, 957 w, 930 w, 868 vw, 751 s, and 694 m  $\text{cm}^{-1}$ .

**N,N-Dimethylbenzhydramine (5).**— $\alpha$ -Aminodiphenylmethane (47 ml, 0.27 mol) was mixed with 50 ml of 36% formaldehyde and 52 ml of 95% formic acid. Reaction and work-up were as in the preparation of 4. Evaporation of the final dried ether solution gave a crude solid, mp 55, which when recrystallized from absolute ethanol gave 21 g, 37% yield, of white crystalline product, mp 69–70° (lit.<sup>46</sup> 68.5–70.5°).

**Benzyne Additions of Benzylidimethylamine. General Procedure Using Organolithium Compounds.**—The halobenzene (20 mmol) was added to a rapidly stirred mixture of 40 mmol of the organolithium compound, 20 ml of N,N-dimethylbenzylamine, and 80 ml of anhydrous ether under a dry nitrogen atmosphere. After 24 hr at room temperature, 15 ml of water and then 100 ml of 6 N hydrochloric acid were added. The aqueous layer was separated and made strongly alkaline with solid sodium hydroxide. The products were recovered by ether extraction of the basic aqueous solution. The ether was evaporated and basic products were determined by gc.

The back extraction procedure was shown to be generally unnecessary by gc. Satisfactory gc analysis were obtained merely by adding water to the reaction mixture and separating the ether layer which contains the products. This procedure was used for yield vs. time studies as described in the following examples.

**Reaction of Chlorobenzene with *n*-Butyllithium in N,N-Dimethylbenzylamine.**—*n*-Butyllithium (15 ml of 1.5 M, 23 mmol) in hexane was rapidly added to a solution of 1.9 ml (20 mmol) of chlorobenzene, 80 ml of anhydrous ether, and 20 ml (135 mmol) of N,N-dimethylbenzylamine and reacted as described in the general procedure. The solution immediately became bright yellow and 1 hr later a white precipitate began to form. Gc of the separated amines at 200° on GE-SF96 indicated the presence of three peaks with relative areas of 6, 87, and 7%. The first and third peaks had retention ratios of 0.86 and 1.24 with respect to the second. The principal component (second peak) was comparable to the material obtained in the large scale reaction with fluorobenzene.<sup>17</sup> The absolute yield of this compound, N-methyl-N-( $\alpha$ -phenethyl)aniline (1), was 14%. The third peak was found to be compatible with assignment of N-methyl-N-( $\beta$ -phenethyl)aniline (3) by peak enhancement.

Stilbene was not detected in the neutral extracts of this or other halobenzene reactions.

The replacement of chlorobenzene with a comparable quantity of fluorobenzene gave a basic extract with the same three gc peaks in the relative ratio 0.5:98:1.5%.

**Reactions Conditions Giving CIDNP.**—The anhydrous tertiary amine, 0.25 cc of N,N-dimethylbenzylamine (or 10 for reactions producing CIDNP in 11), was added to 0.625 cc of 1.5 M *n*-butyllithium in hexane inside an over-dried, thin-wall, 5-mm nmr tube. The solution rapidly changes color to yellow orange and a small amount of precipitate formed. The external lock pmr spectrometer was tuned on the sample at 40° using the  $-\text{CH}_2\text{Li}$  group at  $\delta$  -0.8 ppm. The sample was removed and the probe was heated to 60°. Fluorobenzene (150  $\mu\text{l}$ ) was added to the solution at ambient temperature, rapidly followed by 6  $\mu\text{l}$  of TMEDA. The tube was quickly but firmly capped, thoroughly shaken, and inserted in the nmr probe. Spectra were recorded within 15 sec of mixing and scans repeated for 5 to 10 min.

**Reaction of Fluorobenzene with Lithiated N,N-Dimethylbenzylamine.**—The addition of 70 ml of 1.5 M (115 mmol) *n*-butyllithium in hexane to 17 ml (115 mmol) of N,N-dimethylbenzylamine gave a bright orange solution for the slightly exothermic reaction. After 24 hr at room temperature, large colorless crystals separated from the solution. Fluorobenzene (9.4 ml, 100 mmol) was then added dropwise with rapid stirring. Water (25 ml) was carefully added after an additional 24 hr. Two gc peaks for products were observed at 168° on GE-SF96. The first of these had a gc retention ratio of 0.57 with respect to the second. Preparative gc gave a material for the second peak with refractive index of  $n_D^{20}$  1.5948 and an ir spectrum identical with that of 1, 17.3% yield. Distillation gave a fraction boiling at 125–138° (1 mm) which had a pmr spectrum identical with the  $\alpha$ -phenethyl compound except for a trace peak at  $\delta$  2.08 ppm. This pmr peak was due to the first of the high boiling gc peaks, for which the ir spectrum on a preparative gc sample was comparable with that of 4, 1.0% yield.

A low boiling fraction [ $<40^\circ$  (1 mm)] for the distillation showed two trace peaks in gc analysis at 122° on GE-SF96.<sup>16</sup> The ir spectra of preparative gc samples were comparable with those of commercial benzaldehyde and N,N-dimethylaniline.

**Reactions of N,N-Dimethylbenzylamine, Butyl Nitrite, and Anthranilic Acid.**—N,N-Dimethylbenzylamine (20 ml, 135 mmol) in 25 ml of methylene chloride was mixed with a solution of 4.6 ml (40 mmol) of *n*-butyl nitrite. This solution was heated to reflux and a solution of 5.5 g (40 mmol) of anthranilic acid in 30 ml of methylene chloride and 5 ml of dimethylbenzylamine was added with stirring over 30 min. The gc peak with a retention ratio of 1.75 on GE-SF96 at 168° slowly increased to a maximum of 3% yield (calculated as 1) after 2–3 hr.

A similar reaction used 100 ml of benzene as the solvent and 11 ml (0.1 mol) of *n*-butyl nitrite added in four equal portions at 30-min intervals to the refluxing solution. A mixture of 55 ml (0.4 mol) of dimethylbenzylamine and 13.7 g (0.1 mol) of anthranilic acid in 80 ml of benzene was added dropwise over a 2-hr period. After addition was complete, the mixture was cooled and extracted with 20% potassium hydroxide solution and then with concentrated hydrochloric acid. The acid extracts were made basic with 20% potassium hydroxide solution and the amines were removed by ether extraction. Evaporation of the ether solution and gc of the remaining oil showed peaks of retention ratio 1.45 and 1.76 with the relative areas 7:6, respectively. The total yield of both components was <6%.

**Registry No.**—1, 6299-04-3; 2, 614-30-2; 3, 28059-49-6; 4, 20292-22-2; 5, 5336-72-1; 6, 28059-58-7; 7, 28059-59-8; 10, 102-05-6; benzyne, 462-80-6; 2-cyanobiphenyl, 24973-49-7; *o*-nitrodiphenylmethane, 5840-40-4; *o*-benzylaniline, 28059-64-5; N-methyl-N-(*o*-xylyl)aniline, 28059-65-6; N,N-dimethylaniline, 121-69-7; N,N-dimethylbenzylamine, 103-83-3; N-ethyl-N-benzylaniline, 92-59-1.

(43) D. A. Archer, H. Booth, and P. C. Crisp, *J. Chem. Soc.*, 249 (1964).

(44) J. von Braun, *Ber.*, **43**, 1355 (1910).

(45) M. Sommelet, *C. R. Acad. Sci.*, **175**, 1149 (1922).