

**Trityl Bromide.**—Trityl bromide was prepared by the method previously reported.<sup>27</sup> The colorless solid melted at 145–147°.

***N*-Tritylpyridinium Bromide.** The solution of 5.2 g (0.016 mol) of trityl bromide and 7.1 g (0.09 mol) of pyridine in 50 ml of acetonitrile was stirred for 24 hr and then the solvent and excess pyridine were removed under vacuum. After washing with pentane, a slightly tan solid was recovered in 40% yield, mp 137–139° dec (lit.<sup>27</sup> mp 139° dec).

**Reaction of *N*-Tritylpyridinium Bromide with Pyridinium Chloride.**—The mixture of solution of 2.00 g (0.005 mol) of *N*-tritylpyridinium bromide and 1.50 g (0.013 mol) of pyridinium chloride in 50 ml of dry acetonitrile was stirred at room temperature for 10 min and the solvent was evaporated under reduced pressure. The residue was extracted with 50 ml of dry petroleum ether and then the solvent was removed under reduced pressure. The white solid, recovered in 80% yield, melted at 111–112° and proved to be trityl chloride by mixture melting point measurement and infrared spectroscopy.

**$\alpha$ -Substituted Pyridinium Compounds.**—2,6-Dimethyl-*N*-pyridinium iodide was obtained by passing dry hydrogen iodide into the benzene solution of 2,6-dimethylpyridine, mp 185°. 2,6-Dimethyl-*N*-methylpyridinium iodide was synthesized from 2,6-dimethylpyridine with methyl iodide by refluxing. The product was recrystallized from ethanol, mp 239–240°.

(27) W. E. Backmann, "Organic Syntheses," Coll. Vol. 3, Wiley, New York, N. Y., p 841.

*Anal.* Calcd for C<sub>8</sub>H<sub>12</sub>NI: C, 38.6; H, 4.82; N, 5.63; I, 51.0. Found: C, 38.4; H, 4.83; N, 5.77; I, 51.1.

2,6-Di-*tert*-butylpyridine was prepared by the method of Brown and Kanner,<sup>28</sup> bp 61–62° (1 mm), the chloroaurate, mp 188° (lit.<sup>28</sup> 184.5°).

*Anal.* Calcd for C<sub>18</sub>H<sub>22</sub>NAuCl<sub>4</sub>: C, 29.4; H, 4.15; Cl, 26.7; N, 2.64. Found: C, 29.9; H, 4.29; Cl, 26.4; N, 3.08.

2,6-Di-*tert*-butyl-*N*-pyridinium iodide was synthesized by passing dry hydrogen iodide into the benzene solution of 2,6-di-*tert*-butylpyridine, mp 196–197°.

**Registry No.**—Triphenylmethyl chloride, 76-83-5; pyridine, 110-86-1; I, 26156-82-1; I perchlorate, 26156-83-2; I fluoroborate, 26156-84-3; pyridinium chloride, 628-13-7; *N*-methylpyridinium iodide, 930-73-4; *N*-benzylpyridinium chloride, 2876-13-3; *N*-benzhydrylpyridinium chloride, 26156-88-7; III, 7206-97-5;  $\gamma$ -picoline, 108-89-4; *N*- $\gamma$ -picolinium chloride, 14401-93-5; *N*-trityl- $\gamma$ -picolinium perchlorate, 26154-09-6.

**Acknowledgment.**—The authors gratefully acknowledge numerous stimulating discussions with Professor C. G. Swain.

(28) H. C. Brown and B. Kanner, *J. Amer. Chem. Soc.*, **88**, 986 (1966).

## Bromine-Lithium Exchange of *p*-Bromo-*N,N*-dimethylaniline with *n*-Butyllithium

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Received February 20, 1970

A product study of the reaction between *p*-bromo-*N,N*-dimethylaniline (1) and *n*-butyllithium (2) was made. Yields as high as 91% of *p*-(*N,N*-dimethylamino)phenyllithium (3) were obtained at 25° with a contact time of 30 hr. Several amines arising from nitrogen, ring, and chain alkylation were found at all temperatures. A dimeric amine, *N,N,N',N'*-tetramethyl-*p*-benzidine (9), was isolated from runs at high temperature. *N*-Methyl alkylation of 3 with 2 and 1-iodobutane failed. Ring carbon alkylation with 1-iodobutane gave the expected product, *p*-(*n*-butyl)-*N,N*-dimethylaniline (8).

The halogen-lithium exchange reaction between organolithium compounds and organic halides, mainly bromides and iodides, first discovered by the schools of Gilman<sup>1b</sup> and Wittig<sup>2</sup> has received wide synthetic application. Mechanistic studies have also been carried out in order to unveil the details of the reaction.<sup>3</sup>

Our interest in halogen-lithium exchange reactions and in the chemistry of tertiary amines has led us to re-investigate the reaction between *p*-bromo-*N,N*-dimethylaniline (1) and *n*-butyllithium (2) in the inert solvent *n*-hexane. The reaction is known to yield *p*-(*N,N*-dimethylamino)phenyllithium (3), which was derivatized with carbon dioxide and eventually identified as the methyl ether.<sup>4</sup> Since 1 is also used for a color test of aliphatic organolithium compounds,<sup>5</sup> it was of interest to know the spectrum of products arising from the exchange reaction as well as their dependence on reaction conditions.

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(1) (a) This work is taken in part from the doctorate thesis of G. L., 1969–1970. (b) H. Gilman and A. L. Jacoby, *J. Org. Chem.*, **3**, 108 (1939).

(2) G. Wittig, U. Pockels, and H. Dröge, *Chem. Ber.*, **71**, 1903 (1938).

(3) (a) D. E. Applequist and D. F. O'Brien, *J. Amer. Chem. Soc.*, **85**, 743 (1963). (b) H. J. S. Winkler and H. Winkler, *ibid.*, **88**, 964, 969 (1966).

(c) A. R. Lepley, *Chem. Commun.*, 64 (1969).

(4) H. Gilman and I. Banner, *J. Amer. Chem. Soc.*, **62**, 344 (1940).

(5) H. Gilman and J. Swiss, *ibid.*, **62**, 1847 (1940).

## Results and Discussion

Glc quantitative determination<sup>6</sup> showed that *N,N*-dimethylaniline was obtained in 91% yield by quenching with water the reaction mixture from the interaction of 1 with a 60% excess of 2 at 0°. Quenching with D<sub>2</sub>O (Table II, run 6) gave *p*-deuterio-*N,N*-dimethylaniline (5),<sup>7</sup> whose mass spectrum (*M*<sup>+</sup> 122, Table I) was consistent with nuclear deuteration (*m/e* at 78), but was not distinct from that of *o*-deuterio-*N,N*-dimethylaniline, which was prepared by direct metalation of *N,N*-dimethylaniline with *n*-butyllithium,<sup>8</sup> followed by quenching with deuterium oxide. The pmr spectrum of 5, however, besides revealing no significant *m*-deuteration and an isotopic purity of ~80%, showed a distinct A<sub>2</sub>B<sub>2</sub> quartet in the aromatic region and the ir spectrum confirmed the position of deuteration with the characteristic *o-o-p* bending absorption of aromatic hydrogen at 12.15  $\mu$  as well as the expected pattern<sup>9</sup> at 5–6  $\mu$ . Table II shows all the

(6) Essential glc data are collected in Table I and conditions are reported in the Experimental Section.

(7) G. Fraenkel and J. P. Kim, *J. Amer. Chem. Soc.*, **88**, 4203 (1966).

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

(9) R. T. Conley, "Infrared Spectroscopy," Allyn and Bacon, Boston, Mass., 1966, p 118.

TABLE I  
MASS SPECTROMETRY<sup>a</sup> AND GLC RETENTION TIME RATIOS ( $\rho$ ) AT 150° OF TERTIARY AMINES RELATED WITH THE EXCHANGE REACTION OF *p*-BROMO-*N,N*-DIMETHYLANILINE (1) WITH *n*-BUTYLLITHIUM (2)

Compd	Molecular formula	Ten highest ions ( <i>m/e</i> ) <sup>c</sup> (relative abundance)										$\rho^d$
		120	121	77	51	42	105	39	104	50	91	
<i>N,N</i> -Dimethylaniline (4) <sup>b</sup>	C <sub>8</sub> H <sub>11</sub> N	100	<u>68</u>	33		17	17	14	14	11	8	0.40
		100	80	28	18	17	16	15	14	14	14	
<i>p-d-N,N</i> -Dimethylaniline (5)	C <sub>8</sub> H <sub>10</sub> DN	121	<u>122</u>	78	120	106	105	52	51	42	123	0.40
		100	80	28	18	17	16	15	14	14	14	
<i>o-d-N,N</i> -Dimethylaniline <sup>e</sup>	C <sub>8</sub> H <sub>10</sub> DN	121	<u>122</u>	123	120	78	106	42	52	51	105	0.40
		100	94	32	29	27	19	17	17	16	16	
<i>N</i> -( <i>n</i> -Butyl)- <i>N</i> -methylaniline (6) <sup>b</sup>	C <sub>11</sub> H <sub>17</sub> N	120	77	<u>104</u>	51	42	39	105	121	<u>163</u>	91	0.73
		100	34	17	16	13	12	12	10	7	7	
<i>N</i> -( <i>n</i> -Pentyl)- <i>N</i> -methylaniline (7) <sup>b</sup>	C <sub>12</sub> H <sub>19</sub> N	120	77	<u>104</u>	51	105	39	121	42	41	91	1.000
		100	41	19	18	16	12	11	11	9	9	
<i>p</i> -( <i>n</i> -Butyl)- <i>N,N</i> -dimethylaniline (8)	C <sub>12</sub> H <sub>19</sub> N	134	118	<u>177</u>	135	91	77	39	65	146	51	1.17
		100	33	28	23	15	13	8	8	7	6	
<i>p</i> -Bromo- <i>N,N</i> -dimethylaniline (1) <sup>b</sup>	C <sub>8</sub> H <sub>10</sub> BrN	200	199	198	201	118	77	50	75	63	51	1.92
		100	94	93	91	33	25	25	18	18	18	
<i>p</i> -( <i>n</i> -Butyl)- <i>N</i> -( <i>n</i> -butyl)- <i>N</i> -methylaniline (11)	C <sub>15</sub> H <sub>25</sub> N	176	118	41	42	120	91	34	177	133	77	2.25
		100	86	53	45	42	36	30	29	27	26	
<i>p</i> -( <i>n</i> -Butyl)- <i>N</i> -( <i>n</i> -pentyl)- <i>N</i> -methylaniline (12)	C <sub>16</sub> H <sub>27</sub> N	176	118	41	43	120	39	133	190	132	146	3.15
		100	58	39	38	37	28	26	22	22	22	
<i>p</i> -Bromo- <i>N</i> -( <i>n</i> -pentyl)- <i>N</i> -methylaniline (14)	C <sub>12</sub> H <sub>18</sub> BrN	198	200	119	118	<u>256</u>	42	258	41	185	39	1.52 <sup>f</sup>
		100	100	18	17	13	12	12	12	9	8	
<i>N,N,N',N'</i> -Tetramethyl- <i>p</i> -benzidine (9) <sup>b</sup>	C <sub>16</sub> H <sub>20</sub> N <sub>2</sub>	240	225	241	119	224	152	239	120	119	209	1.52 <sup>f</sup>
		100	44	20	18	16	11	10	10	8	7	

<sup>a</sup> For experimental conditions see Experimental Section. <sup>b</sup> Spectra of the compound from an independent synthesis. The spectrum of the actual compound from the reaction corresponded to this fragmentation pattern. <sup>c</sup> Parent peaks are underlined. <sup>d</sup> See Experimental Section for glc conditions. <sup>e</sup> Spectrum of the iterative metalation-deuteration mixture described in the Experimental Section. <sup>f</sup> At 250°, using diphenylamine as standard.

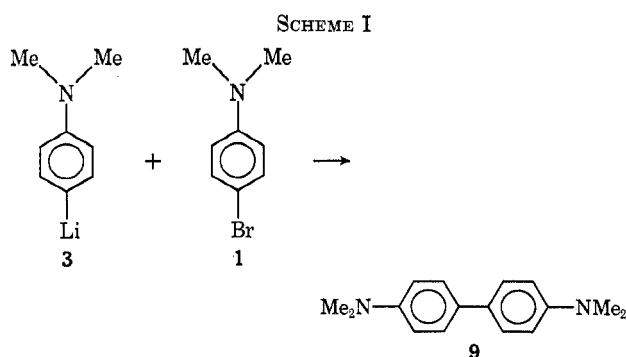
TABLE II  
REACTION OF *p*-BROMO-*N,N*-DIMETHYLANILINE (1) WITH *n*-BUTYLLITHIUM (2). PRODUCT DISTRIBUTION<sup>a</sup>

Run	1, mmol	2, mmol	Ratio, 2:1	Temp, °C	Reaction time, hr	Products (% yield) <sup>b</sup>				
						<i>p</i> -Bromo- <i>N,N</i> -dimethylaniline 1	<i>N,N</i> -Dimethylaniline 4	<i>N</i> -( <i>n</i> -Butyl)- <i>N</i> -methylaniline		
							6	7	8	
1 <sup>c</sup>	25	50	2.0	48	27	... <sup>d</sup>	>47.0	... <sup>d</sup>	... <sup>d</sup>	... <sup>d</sup>
2	25	100	4.0	62 ± 2	3	0.0	53.0	... <sup>d</sup>	6.2	12.0
3 <sup>e</sup>	5	16	3.2	75 ± 2	3	0.0	76.0	... <sup>d</sup>	10.9	8.8
4 <sup>e</sup>	5	16	3.2	2 ± 1	3	... <sup>d</sup>	35.7	... <sup>d</sup>	... <sup>d</sup>	... <sup>d</sup>
5	5	16	3.2	25 ± 1	30	0.0	91.0	1.2	4.2	3.3
6 <sup>e,f</sup>	25	55	2.2	32	15	0.0	38.5	1.5	4.6	6.2

<sup>a</sup> Runs were carried out in nitrogen atmosphere unless stated otherwise. Butyllithium concentration in hexane was between 1.4 and 1.6 *N*. <sup>b</sup> Yields were determined by glc using 1 as internal standard. <sup>c</sup> Dropwise addition of 2 during 15 min. In all other runs 2 was added in one lot at room temperature. <sup>d</sup> The product was present in undetermined yield. <sup>e</sup> Not in nitrogen atmosphere. <sup>f</sup> Quenching with deuterium oxide. Upon distillation, *p*-deuterio-*N,N*-dimethylaniline was obtained in 36% yield.

pertinent results relative to the reaction of 1 with 2. Glc at higher temperature<sup>6</sup> of the water-quenched exchange mixture revealed the presence of at least three other products, adequately separated to obtain their mass spectra and allow their quantitative evaluation by means of an added standard. The new amines were *N*-(*n*-butyl)-*N*-methylaniline (6), *N*-(*n*-pentyl)-*N*-methylaniline (7), and *p*-(*n*-butyl)-*N,N*-dimethylaniline (8), as initially revealed by their retention time ratios and enhancing with authentic materials and definitively ascertained on the basis of the recorded mass spectra (Table I). Vacuum distillation of the more volatile products (runs 2 and 3) left a dark oil from which was isolated *N,N,N',N'*-tetramethyl-*p*-benzidine (9).

It is likely that 9 was formed by direct substitution (Scheme I); aryl bromides are known to undergo such reaction with aryllithiums under similar conditions.<sup>10</sup>



Indeed, gas chromatography-mass spectrometry of the higher boiling amines which were formed in small amounts in the exchange reactions at higher tempera-

(10) L. Friedman and J. F. Chlebowski, *J. Amer. Chem. Soc.*, **91**, 4864 (1969).

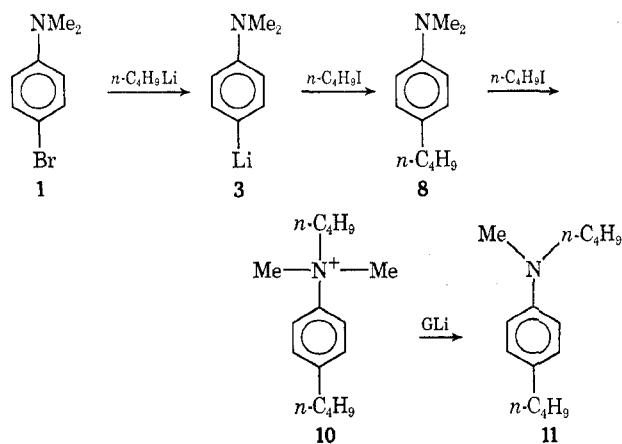
TABLE III  
 REACTIONS OF *p*-(*N,N*-DIMETHYLAMINO)PHENYL LITHIUM (3) AND RELATED EXPERIMENTS<sup>a</sup>

Run	Reactants exchange system <sup>c</sup>		Temp, °C	Time, hr	Coreactant <sup>e</sup> (mmol)	Temp, °C	Time, hr	Products, % yield <sup>b</sup>				
	1, mmol	2, mmol						1	4	6	7	8
1 <sup>e</sup>	25	55	24	24	1-Iodobutane (30)	24	100	0.0	25.0	... <sup>d</sup>	1.7	15.7
2	25	52	15	27	1-Iodobutane (26)	Reflux	24	... <sup>d</sup>	... <sup>d</sup>	... <sup>d</sup>	... <sup>d</sup>	30.0 <sup>f</sup>
3	25	48	70	4	1-Iodobutane (30)	Reflux	5.5	0.0	6.5	... <sup>d</sup>	0.4	32.5
4	25	50	65	4.5	1-Iodobutane (51) 2 (25)	-15 up to +15	4.5	0.0	37.0	... <sup>d</sup>	6.05	11.0
5	5	22.5	25	24	1-Iodobutane (12.5) Et <sub>2</sub> O (5 ml)	0	3	0.0	40.0	... <sup>d</sup>	4.5	4.4
6 <sup>g</sup>	1 (5)				1-Iodobutane (10) 2 (20)	-8 up to +18	24	14.9	23.0	Trace	2.5	1.2
7 <sup>h</sup>	Final unquenched reaction mixture from run 6				2 (80)	20	24	0.0	... <sup>d</sup>	... <sup>d</sup>	... <sup>d</sup>	... <sup>d</sup>

<sup>a,b</sup> See footnotes *a* and *b* of Table II. <sup>c</sup> Butyllithium and coreactant were added in one lot. <sup>d,e</sup> See footnotes *d* and *e* of Table II. <sup>f</sup> Yield in distilled product corrected for impurities. <sup>g</sup> Also ~6% of *p*-bromo-*N*-(*n*-pentyl)-*N*-methylaniline (14). <sup>h</sup> The final reaction mixture showed an increased ratio 7:8 and the disappearance of 14.

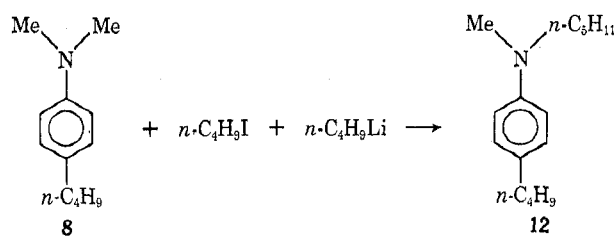
tures did not reveal any *N,N,N',N'*-tetramethyl-3,4'-diaminobiphenyl in the complex mixture, suggesting that a benzyne reaction is not a major pathway, although the substituent effect on the addition of a carbanion to a 1-dimethylamino-3,4-benzyne is not known.<sup>11</sup> Oxidation of 3 could perhaps lead to 9,<sup>12</sup> but there was no difference between reactions in air and in a pure nitrogen atmosphere.

When 3 was treated with 1-iodobutane, the major product was the *para*-substituted amine 8, whose structure was confirmed by pmr spectroscopy (A<sub>2</sub>B<sub>2</sub> quartet for 4 H, singlet for 6 H, triplet for 2 H and the *n*-propyl characteristic pattern all in the expected locations). The reaction was best effected at reflux temperature and the most important side product was *p*-(*n*-butyl)-*N*-(*n*-butyl)-*N*-methylaniline (11), identified by mass spectroscopy and most probably arising from quaternarization of 8 by 1-iodobutane, followed by methyl displacement.



Another amine, well separated under the glc conditions used, was identified as *p*-(*n*-butyl)-*N*-(*n*-pentyl)-*N*-methylaniline (12) on the basis of its mass spectrum, showing a molecular ion at *m/e* 233 and ions from both propyl and butyl cleavage. Since *N*-(*n*-pentyl)-*N*-methylaniline (7) does not exhibit propyl elimination,

this amine cannot be *N,N*-di(*n*-pentyl)aniline, a product which would arise from double lateral alkylation of *N,N*-dimethylaniline: it was formed most likely by the action of 1-iodobutane and leftover *n*-butyllithium on *p*-(*n*-butyl)-*N,N*-dimethylaniline (8). A pathway sim-



ilar to that outlined above for 11 should hypothetically also be operative for 6. The exchange reaction produces 1-bromobutane which can react either with any organometallic species (*i.e.*, with *n*-butyllithium to give *n*-octane or 3 to yield 8) or with the nitrogen of 3 (or 1) to give a quaternary ion which is eventually transformed to 6 by *n*-butyllithium.

*N*-(*n*-Pentyl)-*N*-methylaniline (7) is a product of lateral alkylation<sup>13</sup> of *N,N*-dimethylaniline. But it is quite unlikely that large amounts of the latter compound are formed under these conditions. It was therefore anticipated that 3 could undergo lateral alkylation. To test this hypothesis, 3 was treated with excess *n*-butyllithium and 1-iodobutane under the conditions for lateral alkylation. Since the amount of 7 did not increase (Table III, run 4), 3 did not undergo lateral alkylation. Also, the reaction of 1-iodobutane with *n*-butyllithium mainly to yield *n*-octane in these conditions is faster than any other. This could be due to the insolubility<sup>14</sup> of 3 in the reaction mixture; the necessary<sup>15</sup> amine-organolithium complex could not be formed, thus preventing further reaction. In this line of thought, we solubilized 3 by the addition of ether, but, again, lateral butylation did not occur to a larger extent (Table III, run 5). Evidently 3 is unable to coordinate *n*-butyllithium, perhaps because of de-

(11) R. W. Hoffman, "Dehydrobenzene and Cycloalkenes," Academic Press, New York, N. Y., 1967, pp 106-150.

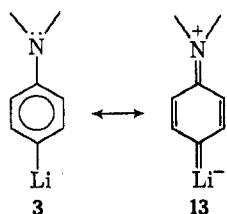
(12) G. A. Razuvayev, E. V. Mitrofanova, and G. G. Petukhov, *Zh. Obshch. Khim.*, **31**, 2343 (1961); A. R. Lepley, V. C. Dohm, and A. G. Giumanini, *J. Org. Chem.*, **34**, 3042 (1969).

(13) A. R. Lepley and A. G. Giumanini, *Chem. Ind. (London)*, 1035 (1965).

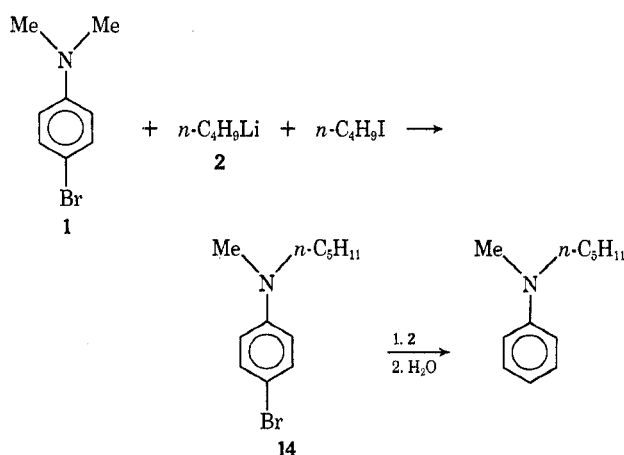
(14) A. R. Lepley and A. G. Giumanini, *J. Org. Chem.*, **31**, 2055 (1966).

(15) A. G. Giumanini, W. A. Khan, and A. R. Lepley, *Chim. Ind. (Milan)*, **49**, 1340 (1967).

creased basicity of the nitrogen lone pair, which may be delocalized according to "structure" 13 in what amounts

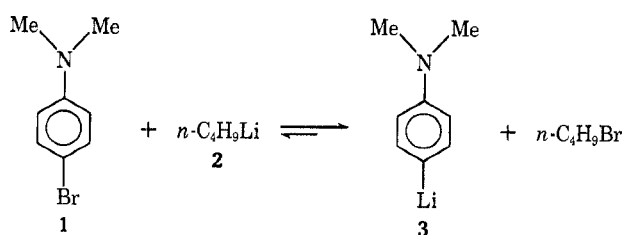


to internal solvation. But 1 was found to dissolve in *n*-hexane containing *n*-butyllithium (it is insoluble in *n*-hexane alone) and the complex formed to react smoothly with 1-iodobutane to yield 14 (Table III, run 6): it appears that it is the complex 1-2 which is laterally alkylated to 14 by the 1-bromobutane formed in the exchange. Indeed, 14 was completely converted to 7 by subsequent treatment with *n*-butyllithium (Table III, run 7).



### Conclusions

The exchange equilibrium of the reaction lies largely to the right in agreement with the relative group basic-



ities of *p*-(*N,N*-dimethylamino)phenyl and *n*-butyl "anions."<sup>3a</sup> Possibly, it is further drawn into the preferred direction by the rapid reaction of 1-bromobutane with *n*-butyllithium to give octane for the most part. Lower temperatures favor high yields of 3, but side reactions take place at any temperature to give alkylated amines in significant amounts especially at high temperatures, which also cause the formation of dimeric products.<sup>16</sup>

Some *o*-metalated *N,N*-dimethylaniline, evidenced by the pmr spectrum of a distilled sample of the exchange reaction mixture quenched with deuterium oxide, has probably to be related to direct metalation

(16) Very small amounts of "dimeric" amines are contained in the higher boiling fractions from exchange runs at elevated temperatures. These compounds may derive from benzyne and free-radical coupling reactions.

of small amounts of 4 formed from 3 and any potential proton donor (*e.g.*, 1-bromobutane) followed by direct *o*-metalation by *n*-butyllithium.

This work has therefore pointed out that the apparently simple<sup>4</sup> halogen-metal interchange studied may be accompanied by a number of side reactions, which depend on experimental conditions and become very important at high temperatures.

### Experimental Section

**Materials.**—*p*-Bromo-*N,N*-dimethylaniline (1) was obtained from BDH and used without further purification. *n*-Butyllithium (2) was prepared in *n*-hexane from 1-chlorobutane (Carlo Erba) as previously described<sup>17</sup> (1.4–1.6 *N*). 1-Iodobutane was obtained from Fluka. Amines 6 and 7 were available from previous work.<sup>11,12</sup>

**Mass Spectra.**—Mass spectra were recorded with a Perkin-Elmer 270 gas chromatograph-mass spectrometer at 70 eV and a chamber temperature of 220–260°. Table I contains all essential data on compounds of interest to this work.

**Gas Chromatography.**—A Perkin-Elmer 900 gas chromatograph using a flame ionization detector was used. Best results were obtained with a 2-m column packed with 5% FFAP supported on 80–100 mesh Chromosorb W. Compound 1 was used as internal standard for quantitative determinations; calibration factors were determined with authentic materials. Convenient temperatures were in the range 120–250°. Table I contains all glc data of compounds related to this work. Neutral compounds formed in the exchange reactions did not interfere with the quantitative determination of the resulting amines or the starting material.

**Pmr and ir spectra** were recorded respectively with a Varian DP 60 in carbon tetrachloride and with a Beckman IR 5 (neat or KBr pellet for solid materials) spectrometer.

**Melting points** were determined by a Kofler apparatus and are not corrected.

**Reaction of *p*-Bromo-*N,N*-dimethylaniline (1) with *n*-Butyllithium (2).** **General Procedure.**<sup>18</sup>—The amine (25 mmol) and *n*-butyllithium (2) (50 mmol) were stirred during 27 hr under nitrogen atmosphere in a tightly sealed erlenmeyer flask at 48°. The mixture was cooled to room temperature and carefully quenched with water (10 ml). The amines may be extracted with hydrochloric acid and liberated with sodium hydroxide and then distilled. It was found that there was no interference from neutral materials to the quantitative and qualitative determination of amines; therefore this determination was often carried out directly on the quenched hexane solution. The exclusion of air from the reaction was also found not necessary to obtain yields as good as 91% of *N,N*-dimethylaniline (4). Exchange reaction results are collected in Table III. *N,N,N',N'*-Tetramethyl-*p*-benzidine (9) was separated from high temperature reactions as follows: the amine fraction from acid-base separation of the reaction mixture was distilled at ~13 Torr up to a temperature of 200° (external oil bath). The residue<sup>16</sup> partially solidified at room temperature to a slightly brown crystalline solid, which had the same glc retention time of authentic 9 (see infrared data and Table I). Two recrystallizations from ethanol gave an ochre compound, mp 190–194° (lit.<sup>7</sup> 198°); mixture melting point gave no depression.

***p*-(*n*-Butyl)-*N,N*-dimethylaniline (8).**—1 (25 mmol) was stirred with *n*-butyllithium (52 mmol) during 27 hr at 15°. The mixture was taken to reflux temperature and 1-iodobutane (25 mmol) was added during 5 min and reflux then continued for 24 hr. Work-up of the mixture gave 5.73 g of amines, which were distilled under vacuum to yield 33% of 8, bp 84°, 0.8 Torr.<sup>19</sup> Another preparation in which the lithium-bromine interchange was performed at 60° during 3 hr and at 75° for an additional hour, followed by 5.5 hour reflux with 1-iodobutane, gave 32.5% yield (glc). When the exchange was performed in optimal conditions (91% yield) but followed by 100 hr stirring

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

(18) In addition to the papers of Gilman's group (ref 4 and 5), another recent paper appeared describing the preparation of 3: G. Hallas and D. R. Waring, *Chem. Ind. (London)*, 620 (1969).

(19) Lit.<sup>6</sup> 185° at 2 Torr. This value seems to be in error.

at 24° with 1-iodobutane, only 15.7% (glc) of the new amine was obtained. Small impurities of *N*-(*n*-butyl)-*N*-methylaniline (6), *N*-(*n*-pentyl)-*N*-methylaniline (7), and *p*-(*n*-butyl)-*N*-(*n*-butyl)-*N*-methylaniline (11) were detected in the reaction mixture by glc: ir 3.44 s, 3.52 s, 3.60 m, 6.20 s, 6.61 s, 6.80 m, 7.45 m, 8.18 w, 8.41 w, 8.62 m, 8.85 w, 9.45 w, 10.57 w, and 12.42  $\mu$  m; pmr  $\delta$  0.92 (3 H), 1.61 (4 H), 2.48 (2 H), 2.80 (6 H), and 6.78 (4 H, A<sub>2</sub>B<sub>2</sub>, q).

**Attempted Lateral Alkylation of 3.**—(1) In two parallel experiments, 3 was prepared. In one the reaction mixture from the exchange and hydrolysis was analyzed (4, 53%; 7, 6.2%; 8, 12%); the other was treated with 25 mmol 2 and 51.5 mmol 1-iodobutane at -15° and the mixture stirred during 4 hr, allowing it to warm up to 15°. Glc analysis gave 4 (37.0%), 7 (6.05%), and 8 (11.0%). No lateral alkylation of 3 was achieved by the standard alkyllithium-alkyl iodide technique. (2) To 3 from 5 mmol of 1 and 22.5 mmol of 2 (24 hr, 25°) was added 5 ml of anhydrous ether and, at 0°, 12.5 mmol of 1-iodobutane. The temperature was allowed to go up to 20° during 3 hr. The quenched reaction mixture was analyzed (glc): 3 (40%), 7 (4.5%), and 8 (4.4%). No lateral alkylation was therefore achieved by the addition of 1-iodobutane.

**Lateral Alkylation of *p*-Bromo-*N,N*-dimethylaniline (1). Lithium-Bromine Exchange of *p*-Bromo-*N*-(*n*-pentyl)-*N*-methylaniline (14) with *n*-Butyllithium (12).**—*p*-Bromo-*N,N*-dimethylaniline (1) (5 mmol) and *n*-butyllithium (2) (20 mmol) were mixed at -10° and, as soon as a homogeneous solution formed, 1-iodobutane (10 mmol) was added. After stirring for 1 hr at -8°, the solution was gradually warmed up to 18° in 23 hr. The quenched reaction mixture contained (glc) 4 (23%), 7 (2.55%), 8 (1.2%), 1 (14.9%) and 14 (6%). The dry hexane mixture was then stirred 24 hr with excess *n*-butyllithium at room temperature and quenched as usual. Both brominated amines disappeared completely while the 7 to 8 ratio increased from 2.13 to 3.1.

***p*-Deuterio-*N,N*-dimethylaniline (5).**—This compound could be easily obtained by adding deuterium oxide to the exchange mixture and distilling the product:<sup>20</sup> ir 3.27 m, 3.33 m, 3.50 s,

3.60 s, 4.44 w, 4.84 w, 5.33 w, 5.70 w, 5.86 vw, 6.29 s, 6.70 s, 6.97 s, 7.45 s, 8.22 s, 8.42 s, 8.86 m, 9.45 s, 9.78 m, 10.23 s, 10.62 s, 11.61 w, 12.19 s, 13.37 w, 13.63 m, 13.94 m, and 14.52  $\mu$  w; pmr (neat)  $\delta$  2.65 (6 H, s), 6.85 (4.28 H, A<sub>2</sub>B<sub>2</sub>, q). This spectrum is in agreement with that reported in the literature.<sup>6</sup>

***o*-Deuterio-*N,N*-dimethylaniline.**—This compound, with possible traces<sup>17</sup> of *m*-deuterio substitution, and in admixture with *o,o'*-dideuterioaniline and unreacted *N,N*-dimethylaniline (4) may be obtained by repetitive metalation with refluxing *n*-butyllithium (2) followed by quenching with deuterium oxide. A sample in our hands contained (4 iterations) 18% unreacted material, 53% monodeuterioaniline and 29% dideuterioaniline, as was determined by mass spectrometry.

***N,N,N',N'*-Tetramethyl-*p*-benzidine (9).**—This compound was prepared according to a method described in the literature,<sup>21</sup> by adding 20 mmol of potassium permanganate in 100 ml of 2 *N* sulfuric acid to a well-stirred solution of 0.1 mol of *N,N*-dimethylaniline in 60 ml of 2 *N* sulfuric acid at room temperature during 15 min. Work-up as indicated,<sup>21</sup> followed by treatment with base, extraction with ether-alcohol, evaporation of the solvent, and recrystallization from ethanol, gave slightly ochre needles: mp 194–198° (lit.<sup>21</sup> 198°); ir (KBr) 3.42 w, 6.17 s, 6.63 s, 6.92 m, 7.37 s, 8.13 m, 8.33 s, 8.50 m, 9.48 w, 10.54 w, and 12.36  $\mu$  s; pmr (CS<sub>2</sub>-CCl<sub>4</sub>)  $\delta$  6.77 (8 H, A<sub>2</sub>B<sub>2</sub>, q) and 2.94 (12 H, s); mass spectrum (vaporized from the solid inlet system at ~90°) mol wt, 240. The same compound was obtained in low yield from the interaction of *p*-benzidine with dimethyl sulfate (3 hr at 100°).

**Registry No.**—1, 586-77-6; 2, 109-72-8; 4, 121-69-7; 5, 19125-73-6; 6, 3416-49-7; 7, 3299-39-6; 8, 13330-29-5; 9, 366-29-0; 11, 25906-38-1; 12, 25906-36-9; 14, 25906-39-2; *o-d-N,N*-dimethylaniline, 24214-95-7.

**Acknowledgments.**—We wish to express our gratitude to Mrs. Armida B. Giumanini for recording the mass and pmr spectra and to Professor U. Pallotta of the Institute of Industrial Agriculture of this University for kindly allowing us to use some of his laboratory facilities.

(21) R. Willstaetter and R. Pummerer, *Chem. Ber.*, **37**, 3733 (1904).

## Schmidt Reaction of 2,4,6-Cyclooctatrien-1-one

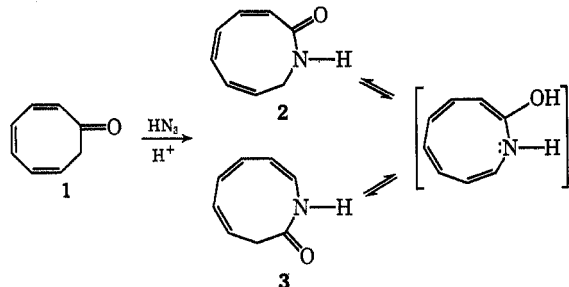
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Received November 17, 1969

The Schmidt reaction of 2,4,6-cyclooctatrien-1-one in concentrated sulfuric acid produced 8,9-dihydrophthalimidine (4), which could have formed only from the migration of the methylene group. The other isomeric product, 3a,9a-dihydroindolone, which would have required the migration of the vinyl group, was not observed. On the other hand, the same reaction in trifluoroacetic acid produced 5*H*-tetrazolo[1,5-*a*]azonine (5) and its valence isomer 5a,9a-dihydro-5*H*-tetrazolo[5,1-*a*]isoindole (6) as the main products, with a small amount of 4.

The Schmidt reaction of 2,4,6-cyclooctatrien-1-one (1) is expected to produce 2,9-dihydro-2-oxoazonine (2) and 2,3-dihydro-2-oxoazonine (3) from the migration of



(1) (a) This is publication number 23-69 from Colorado State University. (b) T. J. Katz, *J. Amer. Chem. Soc.*, **82**, 3784 (1960).

alkyl and vinyl groups, respectively. Both 2 and 3 are tautomers of 2-hydroxyazonine, a 10- $\pi$  electron system which could show aromatic properties. Azoneine and its analogs, oxonin and thionin, are of theoretical interest due to the possibility of their being 10- $\pi$  aromatic systems isoelectronic with cyclooctatetraene dianion<sup>1b</sup> and cyclononatetraene anion,<sup>2</sup> both of which are 10- $\pi$  aromatic systems. 4,5:6,7-Dibenzoxonin and 4,5:6,7-dibenzothionin have been prepared and shown to exist in nonaromatic buckled conformations.<sup>3</sup> The urethan

(2) (a) E. A. LaLancette and R. E. Benson, *ibid.*, **85**, 2853 (1963); **87**, 1941 (1965). (b) T. J. Katz and P. J. Garratt, *ibid.*, **85**, 2852 (1963); **86**, 5194 (1964).

(3) A. P. Bindra, J. A. Elix, P. J. Garratt, and R. H. Mitchell, *ibid.*, **90**, 7372 (1968).