6-Chloro-3-trimethylsilyl-2-dimethylsilabenzimidazoline (14a), 6-Chloro-1-trimethylsilyl-2-dimethylsilabenzimidazoline (14b), and 6-Chloro-1,3-bis(trimethylsilyl)-2-dimethylsilabenzimidazoline (16). A solution of (8.6 g, 0.03 mol) **6a** in 50 ml of tetrahydrofuran was allowed to react with 9.4 ml (0.015 mol) of *n*-butyllithium. After protonation with pyrrole, the product was distilled at 133–134° (0.5 Torr), 7.7 g (85%) being collected. Glpc analysis showed three peaks, two eluting very close to each other. Preparative glpc was used to separate the components into two portions; the two peaks (55% of the total) eluting next to each other were found to be a 54:46 mixture of isomers **14a** and **14b** respectively, mp 28–34°.

Anal. Calcd for $C_{11}H_{19}ClN_2Si_2$: C, 48.77; H, 7.07; N, 10.35; Si, 20.73. Found: C, 49.04; H, 7.11; N, 10.43; Si, 20.47.

The component with the longest retention time was identified as **16** by nmr and ir analysis, mp 85.0–86.5°.

Anal. Calcd for $C_{14}H_{27}ClN_2Si_3$: C, 49.01; H, 7.93; N, 8.17; Si, 24.56. Found: C, 47.95; H, 7.67; N, 8.19; Si, 25.11.

6-Chloro-1-methyl-3-trimethylsilyl-2-dimethylsilylbenzimidazoline (15). *n*-Butyllithium (9.4 ml, 0.015 mol) was added to a solution of 6.0 g (0.02 mol) of **8b** in 50 ml of tetrahydrofuran. After treating with 1.34 g (0.02 mol) of pyrrole the product was distilled at 138–140° (1.4 Torr), 5.1 g (85%) being collected; glpc analysis indicated 77% **15**, a waxy solid, and 23% starting material.

Anal. Calcd for $C_{12}H_{21}ClN_2Si_2$: C, 50.58; H, 7.42; Cl, 12.46; N, 9.83; Si, 19.71. Found: C, 50.96; H, 7.67; Cl, 11.98; N, 9.83; Si, 19.46.

New Anionic Rearrangements. XI.[1] Anionic Rearrangement of Arylhydrazines[2,3]

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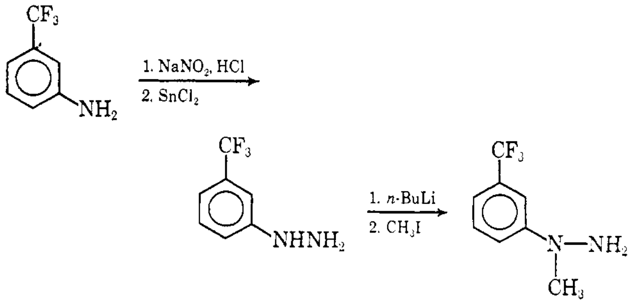
Abstract: 1,2-Anionic rearrangement of aryl groups from one nitrogen atom to another takes place in 1,1-diaryl and 1-aryl-1-methylhydrazines when the latter are converted to dianions. No migration of aryl groups takes place in arylhydrazine monoanions. The kinetics of rearrangement of 1,1-diphenylhydrazine and 1,1-di-*p*-tolylhydrazine dianions was studied by nmr spectroscopy. The reaction is intramolecular and first order in dianion; the rearrangement step is rate limiting, although deprotonation to the dianion is also slow. A 1,4-N → N anionic rearrangement of phenyl in N-methyl-N-phenyl-*o*-phenylenediamine dianion is also described.

Aryl groups have frequently been studied as migrating substituents in anionic rearrangements. For instance, aryl groups migrate from one carbon atom to another in the 1,2-anionic rearrangement of substituted ethanes.[4,5] After discovery of the very rapid 1,2-anionic rearrangement of organosilyl hydrazines,[6] it was of interest to find out whether aromatic groups would also undergo migration in arylhydrazine anions.

The compounds chosen for study were 1,1-diphenylhydrazine (**1**), 1,1-di-*p*-tolylhydrazine (**3**), 1-methyl-1-phenylhydrazine (**5**), and 1-methyl-1-*m*-trifluoromethylphenylhydrazine (**7**). Compounds **1** and **5** were obtained commercially, and **3** was prepared by a standard method.[7] To synthesize the new compound **7**, *m*-aminobenzotrifluoride was diazotized and reduced to form *m*-trifluoromethylphenylhydrazine, which was methylated using *n*-butyllithium and methyl iodide.

Treatment of the four hydrazines with 1 equiv of an alkyllithium compound converted them to their monoanions, **1a**, **3a**, **5a**, and **7a**, by rapid proton transfer. In striking contrast to the organosilyl hydrazine monoanions, which rearrange rapidly even at −80°, no rearrangement whatsoever was observed for the arylhydrazine monoanions. Even long heating at 110° did not lead to migration of the aryl groups (at still higher temperatures decomposition resulted).



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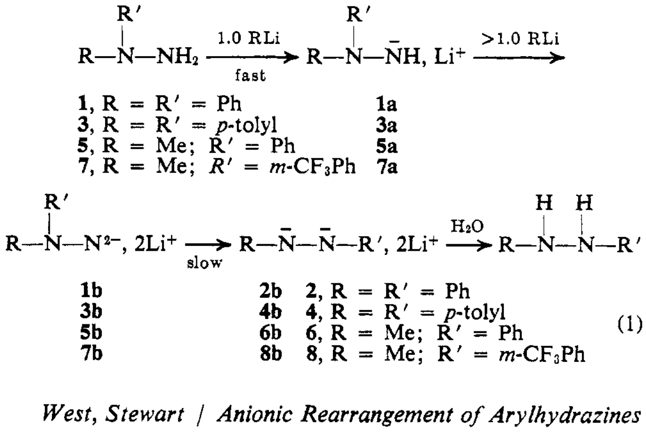
Anionic rearrangement of arylhydrazines did take place, however, when they were converted to their dian-



$$\mathrm{R{-}\overset{R'}{\underset{|}{N}}{-}NH_2} \xrightarrow[\text{fast}]{1.0\ \mathrm{RLi}} \mathrm{R{-}\overset{R'}{\underset{|}{N}}{-}\bar{N}H,\ Li^+} \xrightarrow{>1.0\ \mathrm{RLi}}$$

1, R = R′ = Ph **1a**
3, R = R′ = *p*-tolyl **3a**
5, R = Me; R′ = Ph **5a**
7, R = Me; *R′* = *m*-CF_3Ph **7a**

$$\mathrm{R{-}\overset{R'}{\underset{|}{N}}{-}N^{2-},\ 2Li^+} \xrightarrow[\text{slow}]{} \mathrm{R{-}\bar{N}{-}\bar{N}{-}R',\ 2Li^+} \xrightarrow{\mathrm{H_2O}} \mathrm{R{-}\overset{H}{\underset{|}{N}}{-}\overset{H}{\underset{|}{N}}{-}R'} \tag{1}$$

1b **2b** **2**, R = R′ = Ph
3b **4b** **4**, R = R′ = *p*-tolyl
5b **6b** **6**, R = Me; R′ = Ph
7b **8b** **8**, R = Me; R′ = *m*-CF_3Ph

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[1] Previous paper in this series: H. F. Stewart, D. G. Koepsell, and R. West, *J. Amer. Chem. Soc.*, **92**, 846 (1970).

[2] For a preliminary communication on this topic see R. West, H. F. Stewart, and G. R. Husk, *ibid.*, **89**, 5050 (1967).

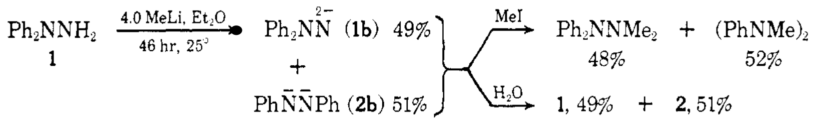
[3] Research sponsored by Air Force Office of Scientific Research, (SRC), OAR, USAF Grant No. AF-AFOSR 1061-66.

[4] (a) E. Grovenstein, *J. Amer. Chem. Soc.*, **79**, 4985 (1957); (b) E. Grovenstein and G. Wentworth, *ibid.*, **89**, 1852 (1967).

[5] (a) H. E. Zimmerman and F. J. Smentowski, *ibid.*, **79**, 5455 (1957); (b) H. E. Zimmerman and A. Zweig, *ibid.*, **83**, 1196 (1961).

[6] (a) R. E. Bailey and R. West, *ibid.*, **86**, 5369 (1964); (b) R. West, M. Ishikawa, and R. E. Bailey, *ibid.*, **88**, 4648 (1966); (c) R. West, M. Ishikawa, and R. E. Bailey, *ibid.*, **89**, 4068 (1967); (d) R. West, M. Ishikawa, and R. E. Bailey, *ibid.*, **89**, 4072 (1967); (e) R. West and M. Ishikawa, *ibid.*, **89**, 4981 (1967).

[7] O. F. Bennett, J. Bornstein, S. A. Leone, and W. F. Sullivan, *ibid.*, **79**, 1745 (1957).



ions.[8] When **1**, **3**, **5**, or **7** are treated with more than 1 equiv of alkyllithium, a second, slower proton transfer takes place to give the dianions **1b**, **3b**, **5b**, and **7b**, which slowly rearranged to the more stable isomers **2b**, **4b**, **6b**, and **8b**, respectively.

Rearrangements of the hydrazide dianions could be followed either by quenching of the reaction solution after a given time and analysis of the quenched mixture by gas chromatography or nmr spectroscopy, or (more conveniently) by following the rearrangement itself by nmr spectroscopy. The results from quenching with water or with methyl iodide, and from direct nmr spectroscopy were remarkably consistent, probably because the quenching reactions were much faster than the rearrangement itself and so froze the reaction composition.

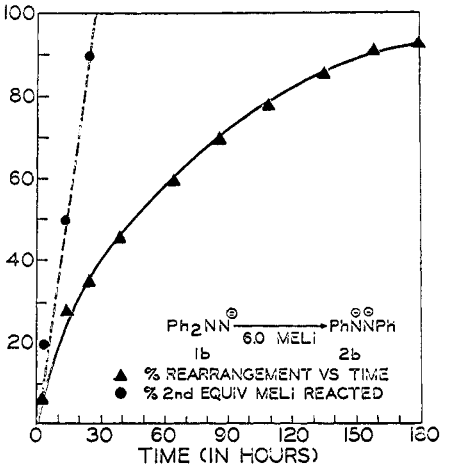


Figure 1. The rearrangement of 1,1-diphenylhydrazine **1**, 0.267 *M*, in diethyl ether containing 6.0 equiv of methyllithium at 25°.

Direct nmr spectroscopy of the reaction mixture also allowed observation of the formation of the dianion. The disappearance of the methyllithium resonance at −1.93 ppm provided a convenient measure of the extent of deprotonation. The first deprotonation step from the free hydrazine to the monoanion is rapid, going to completion within the time of sample preparation (*ca.* 10 min). Deprotonation of mono- to dianions is slow at 25°, requiring several hours for completion. However, the rearrangement itself is even slower, so that dianion formation was normally complete before very much rearrangement had taken place (Figure 1).

To follow the actual N→N migration in the diarylhydrazine dianions, the nmr spectrum in the aryl region was studied. Sample spectra for the **1b**–**2b** rearranging system are shown in Figure 2. The anions both give resonances in the region from 6.3 to 7.0 ppm, but only the 1,1-dianion has peaks in the 7.0–7.3 ppm region, and only the rearranged dianion **2b** has resonances at 5.8–6.2 ppm. The ratio of downfield to upfield protons could therefore be used as a measure of the relative concentrations of **1b** and **2b**. For the rearrangement of **3b** to **4b**, it was more convenient to follow the methyl resonances of the *p*-tolyl groups, which were sharp singlets at 2.22 and 2.06 ppm, respectively, in diethyl ether solution.

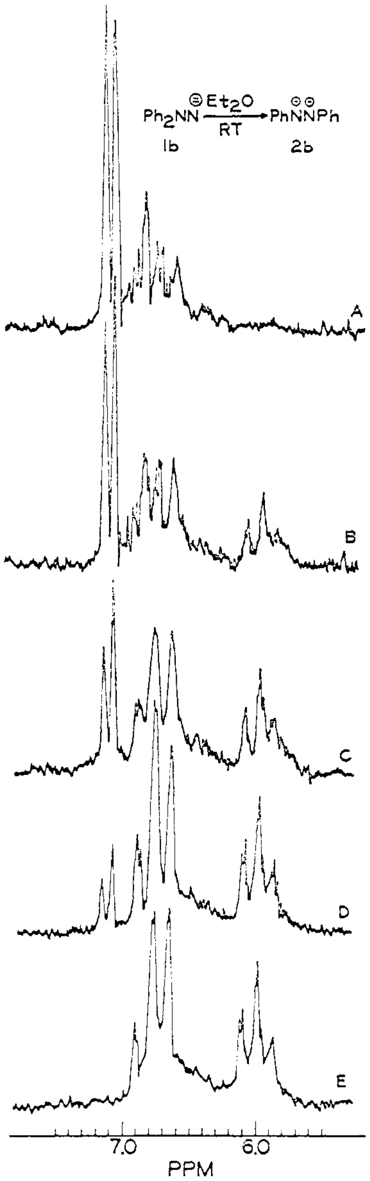


Figure 2. Nmr spectrum in the aryl region for the dianion **1b** rearranging to **2b**. Initial concentrations were 0.267 *M* **1** and 10.4 equiv of methyllithium in diethyl ether at 25°. Times (hr): A, 2; B, 32; C, 60; D, 143; E, >250.

Data for the rearrangement of **1b** and **3b** are given in Tables I and II, respectively. Plots of the logarithm of dianion concentration *vs.* time gave excellent straight lines up to more than 90% rearrangement, indicating that the migration is first order in dianion and that reverse reaction is negligible. A sample plot is shown in Figure 3. The rate of rearrangement of **1b** is indepen-

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[8] By dianions we shall mean generally the dilithium derivatives of the hydrazines. It is of course recognized that there may be some covalent contribution to the N–Li bond. The dianionic rearrangement was first observed accidentally when an excess of alkyllithium was inadvertently added to a sample of **1**.

Table I. Rearrangement of 1,1-Diphenylhydrazine Dianion (**1b**) at 25° in Diethyl Ether

$^{a}k = 4.7 \times 10^{-3}$ hr^{-1} [c]			$k = 4.9 \times 10^{-3}$ hr^{-1} [d]			$k = 5.4 \times 10^{-3}$ hr^{-1} [e]			$k = 5.1 \times 10^{-3}$ hr^{-1} [f]		
Time, hr	% **1b**	Log **1b**	Time, hr	% **1b**	Log **1b**	Time, hr	% **1b**	Log **1b**	Time, hr	% **1b**	Log **1b**
2	100	2.00	1	98	1.992	2	94	1.974	1	95	1.978
4	97	1.986	12	87	1.940	13	72	1.857	12	82	1.914
7	81	1.909	34	64	1.806	24	65	1.812	32	61	1.786
8	79	1.898	60	50	1.700	38	54	1.732	60	49	1.690
18	72	1.857	90	39	1.591	64	40	1.602	90	35	1.544
42	56	1.748	119	28	1.446	85	30	1.477	119	27	1.432
54	47	1.672	143	19	1.278	109	21	1.322	143	18	1.256
79	38	1.580	212	14	1.146	134	17	1.231	212	9	0.950
99[b]	32	1.505	>250	0		159	11	1.041	250	0	
						181	9	0.954			

[a] Slopes were determined by the least-squares method. [b] Solid **2b** started separating from solution after this time. [c] 3.5 equiv of MeLi; 0.536 *M* **1**. [d] 3.5 equiv of MeLi; 0.267 *M* **1**. [e] 6.5 equiv of MeLi; 0.267 *M* **1**. [f] 10.4 equiv of MeLi; 0.267 *M* **1**.

Table II. Rearrangement of 1,1-Di-*p*-tolylhydrazine Dianion (**3b**) 0.267 *M* in Diethyl Ether

Time, hr	% **3b**
2	96
13	92
24	75
38	57
63	38
85	25
109	14
133	8
181	<2

dent of methyllithium concentration (except perhaps at very high CH_3Li concentrations), and the rate constant is independent of hydrazine concentration, having the value 5.1 ± 0.3 × 10^{-3} hr^{-1} at 25° in diethyl ether (Table I).[9] Rearrangement of **3b** is slightly *faster* than that of **1b**, the rate constant being 8.0 × 10^{-3} hr^{-1} under the same conditions (Table II).

In order to establish the inter- or intramolecular nature of the rearrangement, a mixing experiment was performed. A mixture of **1** and **3** was treated with excess methyllithium and allowed to rearrange for 115 hr, then hydrolyzed. Analysis of the hydrolyzed mixture showed 70% rearrangement to a mixture of **2** and **4**, with no detectable crossover product such as 1-phenyl-2-*p*-tolylhydrazine. Thus the rearrangement appears to be fully intramolecular, like the silylhydrazine rearrangements studied earlier.[6]

Rearrangement of the dilithium salt of **1b** was also carried out at room temperature in pentane and dimethylsulfoxide; the rate of rearrangement was not studied in detail, but was not markedly altered. The amount of rearrangement after a given time was increased about threefold when the reaction was carried out in cyclohexane at 65°. Rearrangement was also somewhat more rapid when dimsylsodium in dimethyl sulfoxide was used as the base. Differences in ion pairing when sodium is the counterion could explain the increased rate. However, dimsylsodium was ineffective in causing rearrangement of **3** or **5**, perhaps because it is too weak a base to remove the second proton from these hydrazines.

Compared to rearrangements of **1** and **3**, those of **5** and **7** were much less clean, with decomposition always accompanying the aryl migration. Kinetic investigations were not attempted, but the amount of **5** and **6** was determined after various lengths of time by nmr and gas chromatographic analysis of hydrolyzed samples. Data for the reaction are given in Table III.

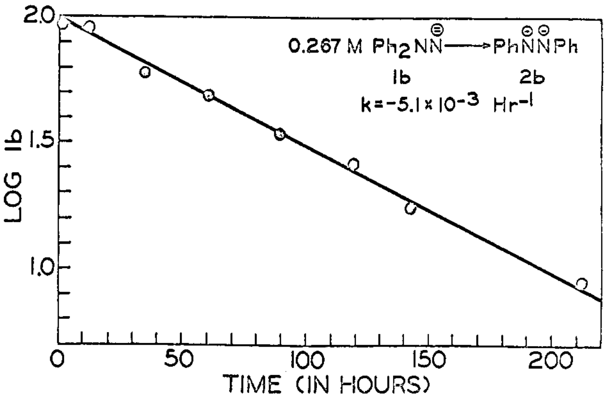

Figure 3. Typical plot of the logarithm of concentration of **1b** in moles/liter *vs.* time. Methyllithium:**1** ratio in this experiment was 10.4:1. (At lower CH_3Li ratios deprotonation is rate limiting in early stages, and the first few points deviate somewhat from the linear relationship shown.)

High concentrations at alkyllithium and long reaction times lead to decomposition mainly to aniline, which must arise from the rearranged dianion **6b**. The rearrangement of **7** was detected only by nmr of the hydrolyzed solution. Rearrangement of **7b** was studied only qualitatively but does not seem to be greatly different from that for **5b**.

Table III. Rearrangement of 1-Methyl-1-phenylhydrazine (**5**) in Diethyl Ether

Ratio CH_3Li:**5**	Time, hr	Temp, °C	% rearr[a]	Other products[b]
1.0	21	23–28	0.0	None
1.0	38	65[c]	0.0	None
1.0	44	100–112[d]	0.0	Trace MA
2.5	22	23–28	35	10% A, 8% MA
	40	23–28	46	21% A, 8% MA
4.0	20	23–28	43	44% A, 8% MA
	41	23–28	57	59% A, 17% MA

[a] Determined by nmr ratio of *Me*-N for **5** and **6**. [b] Glpc area percentages, A = aniline, MA = methylaniline. [c] Solvent tetrahydrofuran. [d] Solvent bis(2-methoxyethyl) ether.

The dianion of 1,1-dimethylhydrazine was also investigated; it undergoes no rearrangement on long

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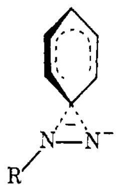
[9] This corresponds to a half-time of 68 hr for rearrangement of **1b** under the conditions given.

heating to 100° with excess base. Apparently it is the aryl group which migrates in **5b** and **7b**. The hydrazine dianion rearrangement thus resembles the anionic rearrangement of ethanes in that aryl groups will migrate but alkyl groups will not.[4,5]

Mechanism. The arylhydrazine monoanions **1a, 3a, 5a,** and **7a** do not rearrange, even though the rearranged anions in which the negative charge could be delocalized onto the aromatic ring should be more stable. The activation energy for aryl migration in the monoanions must be so great that rearrangement is not observed. In the dianions, the driving force for rearrangement must be very much greater than in the monoanions, because the large repulsion of the two negative charges on the same nitrogen is relieved in the rearranged dianions. Nevertheless, rearrangement of arylhydrazine dianions is surprisingly slow, being much slower than that for arylethane monoanions.[4]

The results of kinetic and mixing experiments suggest that the hydrazine dianion rearrangement proceeds through a bridged transition state **9** in which the aryl group is at some point bonded equally to both nitrogen atoms, and the negative charge may be partially delocalized onto the migrating ring. Similar transition states have been proposed for aryl migration in the ethane rearrangement.[5] The silylhydrazine rearrangement is also thought to involve a bridged transition state **10**. The fact that silicon can easily become pentacoordinate must greatly lower the energy of **10** and account for the remarkable speed of silylhydrazine rearrangements.



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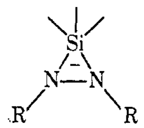

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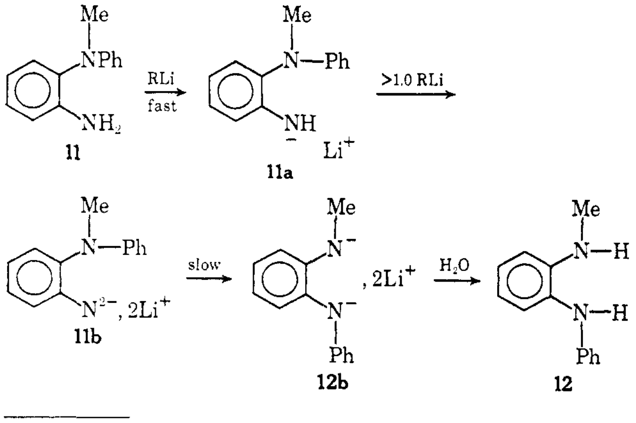
1,4-Anionic Rearrangement of Phenyl Group. Reactions involving anionic rearrangements to remote sites (Smiles rearrangements) are well known,[10] but aryl or alkyl migration from nitrogen to nitrogen has not previously been observed. Recently we have shown that organosilyl moieties will migrate 1,4 or 1,5 in N–N anionic rearrangement.[1,11] It was therefore of interest to study similar aryl migration. A suitable substrate is N-methyl-N-phenyl-*o*-phenylenediamine, **11**, prepared by methylation of N-phenyl-*o*-phenylenediamine. Reaction with 1 equiv of alkyllithium leads to a monoanion **11a** which does not rearrange. Additional base converts **11a** to the dianion **11b**, which does rearrange to the more stable isomer **12b**. The latter can be protonated to the rearranged diamine **12**. Although this 1,4-anionic rearrangement has not been studied in detail, results to date indicate that it is quite analogous to the 1,2-anionic rearrangement of arylhydrazines.



Experimental Section

Proton nmr spectra were determined with a Varian A-60A or HA-100 spectrometer equipped with variable temperature probes and proton decoupling equipment; chemical shifts were obtained by internal referencing with cyclohexane in ether solution. In cases where the diethyl ether resonance interfered with the compound peaks, dioxane was used as the solvent and reference. Ir spectra were obtained on a Perkin-Elmer 457 grating spectrophotometer. Analytical and preparative gas chromatography were carried out using a Barber-Coleman 5340 TC chromatograph equipped with a Model 5000 temperature-programming unit. Preparative and analytical work was done using a 1/4 in. × 10 ft aluminum column packed with a 25% D.C.-200 Gum (Dow Corning Corp.) on 40–60 mesh Chromosorb W, and a helium flow rate of 100 cc/min. Temperature control was critical, because thermal decomposition of the hydrazines was generally observed when the injector and/or column exceeded 275°. The detectors were kept at 300°. All boiling points and melting points were uncorrected. Analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

Materials. All chemicals were reagent grade materials. Solvents such as cyclohexane, benzene, and diethyl ether were further purified by refluxing over sodium or lithium aluminum hydride followed by fractional distillation from these drying agents just before use. Dioxane and dimethyl sulfoxide were distilled from calcium hydride and stored over Linde 4A molecular sieves. 1,2-Diphenylhydrazine (**2**), 1-methyl-1-phenylhydrazine (**7**), methyl iodide, *p*-toluidine, N-phenyl-*o*-phenylenediamine, *m*-aminobenzotrifluoride, and 1,1-diphenylhydrazine (**1**) (as the hydrochloride) were obtained from Aldrich Chemical Co. The hydrochloride was converted to the free compound by extraction with aqueous potassium hydroxide, extraction with ether and distillation. *n*-Butyllithium (hexane solution), *t*-butyllithium (pentane solution), and methyllithium (diethyl ether solution) were obtained from Foote Mineral Co. The concentration of the latter compound was determined by establishing the mole ratio of diethyl ether to methyllithium, using nmr analysis. The alkyllithium concentration of the other bases was determined by titration.[12]

***m*-Trifluoromethylphenylhydrazine.** The procedure of Bennett, Bornstein, Leone, and Sullivan[7] was followed. Concentrated hydrochloric acid (250 ml) was added to *m*-aminobenzotrifluoride (65 g, 0.4 mol) and the resulting white suspension was cooled to 0°. Sodium nitrite (27.6 g, 0.4 mol) in 125 ml of water, precooled to 0°, was slowly added to the solution of the amine hydrochloride. The temperature of the reaction was maintained at 0° ± 3° using a salt–ice bath. The diazonium salt solution was then treated with a chilled solution of stannous chloride dihydrate (200 g, 0.89 mol) in 200 ml of concentrated hydrochloric acid. After the addition was complete the mixture was stirred at 0° for 1 hr. A cream colored solid which formed was collected by filtration, pressed dry, and taken up in a 25% solution of sodium hydroxide (200 ml). The aqueous solution was extracted with three 300-ml portions of diethyl ether. The ether extracts were combined, and dried (KOH pellets) for 12 hr. The solvent was removed by vacuum stripping and the residue distilled giving 41.2 g (64%) of product, bp 80–84° (6.0 Torr) [lit.[7] bp 80–83° (9.0 Torr)].

1-Methyl-1-*m*-trifluoromethylphenylhydrazine (7). A solution of *m*-trifluoromethylphenylhydrazine (7.6 g, 0.043 mol) in 25 ml of diethyl ether was treated with 27 ml of *n*-butyllithium 1.6 *M* in hexane (0.043 mol) at 0°. After 35 min, 6.67 g (0.047 mol) of methyl iodide was added followed by 25 ml of chilled tetrahydrofuran. Stirring was continued for 24 hr at room temperature and then solvent was removed by vacuum distillation. The residue was distilled yielding 8.1 g (98%) of colorless liquid **7**, bp 84° (0.4

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[10] J. F. Bunnett and R. E. Zahler, *Chem. Rev.*, **49**, 362 (1951).

[11] R. West, M. Ishikawa, and S. Murai, *J. Amer. Chem. Soc.*, **90**, 727 (1968).

[12] H. Gilman and A. H. Hauben, *ibid.*, **66**, 1515 (1944).

Torr); nmr (cyclohexane) δ, 3.46 (S, 2, *NH*$_2$), 2.82 (S, 3, *Me*-N), and 6.75–7.33 ppm (M, 4.2, *Ar*-N).

Anal. Calcd for $C_7H_9F_3N_2$: C, 50.53; H, 4.77; N, 14.73; F, 29.97. Found: C, 51.27; H, 5.01; N, 14.76; F, 28.98.

N,N-Di-*p*-tolylamine. *p*-Toluidine (40.0 g, 0.374 mol) and *p*-toluidine hydrochloride (48.4 g, 0.338 mol) were heated in a thick-walled glass ampoule for 37 hr at 240–250°. When cooled the contents of the ampoule were extracted with dilute hydrochloric acid (100 ml) and three times with 100-ml portions of diethyl ether. The ethereal extracts were combined, dried ($MgSO_4$), and concentrated. The residue was recrystallized twice from aqueous ethanol, giving 56 g (85%) of product, mp 75–79° [lit.[13] mp 79°].

N-Nitrosodi-*p*-tolylamine. Di-*p*-tolylamine (30.0 g, 0.15 mol) was put into solution with ethanol (200 ml) and allowed to react with concentrated hydrochloric acid (35 ml). Sodium nitrite (22.5 g, 0.306 mol) in a 1:1 ethanol–water mixture (100 ml) was added to the hydrochloride. Orange crystals formed immediately and after the solution was cooled to −30°, the crystals were collected by filtration. The crystalline product was recrystallized in ethanol–water, affording golden yellow needles, mp 101–103° [lit.[14] mp 102–103° (dec)].

1,1-Di-*p*-tolylhydrazine (3). The procedure followed was that of Poirier and Bennington.[15] A solution of lithium aluminum hydride (4.18 g, 0.11 mol) in 100 ml of diethyl ether, was added to a solution of N-nitrosodi-*p*-tolylamine (23.1 g, 0.102 mol) in 150 ml of diethyl ether over 1 hr at 10°. After stirring for an additional 1.5 hr at room temperature, 100 ml of wet ether was added followed immediately by 200 ml of a 30% solution of potassium sodium tartrate. The aqueous layer was extracted with three 100-ml portions of diethyl ether. The ethereal solution was dried (KOH pellets) and concentrated. Silver-white platelets, 16 g (80%), were obtained after recrystallization from cold ether, mp 89–91°, hydrochloride mp 145–146° [lit.[15] mp 147°]; nmr (cyclohexane) δ 2.33 (s, 5.8, *Me*Ar), 3.59 (S, 4.0, *NH*$_2$), and 6.61 ppm (S, 8.7, *Ar*).

N-Methyl-N-phenyl-*o*-phenylenediamine (11). N-Phenyl-*o*-phenylenediamine (10.7 g, 0.058 mol) in 60 ml of diethyl ether was treated with 1.58 *M* methyllithium (42.0 ml, 0.063 mol) at room temperature. After 18 hr the solution was cooled to 0° and 6.0 g of methyl bromide (0.063 mol) was added. The reaction was warmed to 23° over 5 hr and then stirred at 23–25° for 22 hr. The mixture was extracted with water; the ethereal solution was separated, dried (Na_2SO_4), concentrated, and the residue distilled, giving 9.3 g (82%) of light yellow liquid, bp 165–173° (2.5 Torr) [lit.[16] bp 142° (1.0 Torr)]: nmr (acetone) δ 3.08 (S, 3.0, *Me*), 4.25 (S broad, 2.0, *NH*$_2$) and 6.47–7.31 ppm (M, 9.0, *Ar*).

Anionic Rearrangements

Two general rearrangement methods were used during this investigation, atmospheric pressure and sealed tube. Atmospheric pressure reactions were analyzed by quenching the reaction mixture and establishing the identification and ratio of the isomeric derivatives. Sealed tube reactions were analyzed by nmr, observing the ratio of isomeric dianions present in solution. The two methods were compared several times and agreement was always within ±2%.

General Method. Atmospheric Pressure. The reaction apparatus consisted of a small two-necked, round-bottomed flask, fitted with a condenser set for reflux, nitrogen inlet tube, Teflon-covered magnet and a rubber serum stopper. The assembled apparatus was dried by passing a stream of nitrogen through it while heating with a heat gun. Nitrogen exit was made *via* a needle in the serum stopper. The substrate and solvent were injected into the reaction vessel, followed by the slow addition of alkyllithium while the reaction solution was being rapidly stirred. During the reaction period samples were removed using syringe technique and transferred into another reaction vessel containing the derivatizing agent water or methyl iodide. The solvent layer was separated, dried (Na_2SO_4), and concentrated by evaporation under a nitrogen stream. The dried, concentrated solvent solution (diethyl ether in most cases) was used for nmr and glpc analysis. The identity of various reaction components was always confirmed by isolation of pure species or by comparing glpc retention times and nmr spectra with authentic samples.

Anionic Resarrangements of 1,1-Diphenylhydrazine (1). Atmospheric Pressure. In a typical experiment, **1** (0.736 g, 4.0 mmol) was allowed to react with 1.7 *M* methyllithium (1.8 ml, 32 mmol) at room temperature for 140 hr. The solution was light yellow to orange during the reaction. The reaction mixture was quenched by adding it to 50 ml of water. The ethereal layer was separated, dried (Na_2SO_4), and concentrated. The residue was recrystallized from ethanol–water giving 0.60 g (86%) of **2** as light orange crystals, mp 126–129° [lit.[17] mp 126°]. The ir spectra were identical with those of an authentic sample of 1,2-diphenylhydrazine (**2**).

In similar experiments to the above, different amounts of methyllithium were allowed to react with **1** and samples were taken and hydrolyzed at several time intervals. The per cent rearrangement was determined by the integration ratios of the N–H resonance in ether solution: resonance for **1** δ 3.8 ppm and **2** δ 5.8 ppm. The data from several experiments are summarized in Table IV. The apparent dependence of reaction rate on concentration at CH_3Li:**1** mole ratios above 2.0 probably reflects both differences in the deprotonation rate and loss of base through slight hydrolysis and oxidation, which are unavoidable in the atmospheric pressure experiments.

Table IV. Rearrangement of 1,1-Diphenylhydrazine (**1**) at 30° in Diethyl Ether

Molar ratio CH_3Li:**1**	Reaction time, hr	% rearrangement
1.0	90	0
1.5	90	5
1.8	90	11
2.0	44	29
	90	43
3.0	20	28
	44	42
	90	61
8.0	25	70
	44	82
	71	>95

General Method. Sealed Tube Rearrangements. The same general procedure was used for all the anionic rearrangement reactions done in sealed tubes. A thin-walled nmr tube was fitted with a small rubber serum stopper wired securely in place with copper wire. Two hypodermic needles, one the inlet for high purity, dry nitrogen, the other the exit, were inserted through the stopper. With a rapid nitrogen flow, the tube was heated to >150° with a heat gun.

After the tube cooled to room temperature, the exit needle was removed. Usually 0.3–0.7 mmol (0.05–0.10 g) of hydrazine substrate was added to the tube which was then cooled to −80° with solid carbon dioxide before 1.0–3.6 mmol (1.5–2.25 ml) of 1.6 *M* meth-

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(13) G. deLaire, Ch. Girard, and P. Chapoteaut, *Ann.*, **140**, 346 (1866).

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(15) R. H. Poirier and F. Bennington, *J. Amer. Chem. Soc.*, **74**, 3192 (1952).

(16) W. F. Short and C. I. Broderick, British Patent 738,013 (1955).

(17) P. Jacobson and A. Hugershaff, *Chem. Ber.*, **36**, 3841 (1903).

yllithium was added. The solution was *carefully mixed* while warming to room temperature. Ether was either added, or evaporated *via* nitrogen sweep, to maintain the desired hydrazine concentration. The reaction solutions were homogeneous and varied in color from light yellow to light green. The tubes were carefully sealed just below the serum stopper.

The progress of the rearrangement was followed by monitoring changes in the nmr spectra of the hydrazide dianions. The nmr spectra of the dianions of **1b** and **2b** are shown in Figure 2. **1b** has a group of fairly sharp peaks centered at 7.0 ± 0.4 ppm, and **2b** appears as two groups of triplets, one centered at 6.8 ± 0.2 ppm (J = 7.8 Hz) and one shifted upfield, centered at 6.0 ± 0.2 ppm (J = 7.0 Hz). These two groups of peaks are in a ratio of 3:2, respectively.[18] The spectrum formed by rearrangement was the same as that obtained if **2** was allowed to react with methyllithium in diethyl ether. Using these spectra it was possible to monitor the rearrangement by integration of the phenyl peaks and establishing the ratio of downfield peaks (all the **1b** protons plus the *meta* and one *ortho* proton of **2b**) to the upfield peaks (*para* and one *ortho* proton of **2b**). The downfield/upfield ratio once established could be fitted to a standard curve (% **2b** *vs.* downfield/upfield, which was obtained by calculating the various theoretical downfield to upfield ratios from corresponding percentages of **1b** and **2b**) and the per cent **2b** obtained directly. The accuracy of this method was tested many times by hydrolyzing a sample which had been analyzed for the dianions by nmr. In every example the two methods agreed within ±2%. The separation of the **2b** peaks are temperature, solvent, and concentration dependent, so the method was not usable when solvents other than diethyl ether were used.

The rearrangement of **3b** was easily followed using sealed tube technique by observing the disappearance of the *Me*Ar peak at 2.22 ppm for **3b** and the formation of a new *Me*Ar peak at 2.06 ppm for **4b**.[19] Data from these rearrangements are given in Table II.

Attempted Rearrangement of Monoanion (1a). The monoanion of **1** was formed by treating **1** (1.472 g, 8.0 mmol) with 1.7 *M* methyllithium (4.7 ml, 8.0 mmol) at room temperature. Bis(2-methoxyethyl) ether (20 ml) was added and the reaction was heated to reflux. The excess ether was removed and the solution was heated at reflux (110–112°) for 26 hr before being hydrolyzed. The ether layer was separated, dried (Na_2SO_4), and concentrated. Nmr and glpc analysis shows no rearrangement to **2**. The only products detected were **1** and a trace of diphenylamine.

Rearrangement of 1,1-Diphenylhydrazine Dianion (1b) in Cyclohexane. The dianion of 1,1-diphenylhydrazine, **1b**, was formed by the reaction of **1** (0.736 g, 4.0 mmol) with 1.7 *M* methyllithium (4.7 ml, 8.0 mmol) in 15 ml of diethyl ether for 24 hr at room temperature. An nmr of this anionic solution showed no methyllithium resonance at −1.91 ppm and no N–H resonance for **1** at 3.8 ppm. The ether was removed by distillation and replaced with cyclohexane (15 ml). The reaction solution became a bright green and after 22 hr at 65–70° the solution was still green but contained a yellow precipitant. The solution was hydrolyzed in the standard manner and the nmr analysis indicated 45% rearrangement to **2**.

Rearrangement of 1 with Other Bases. Dimsylsodium. In a typical reaction sodium hydride 52% in mineral oil (1.95 g, 0.04 mol) was added to a solution of **1** (1.84 g, 0.01 mol) in 30 ml of dimethyl sulfoxide at room temperature with stirring. After 22 hr the solution was black and had become viscous. When water (5.0 ml) was added a vigorous reaction resulted with gas evolution. The reaction mixture was added to ice-water and diethyl ether was added to aid layer separation. The ether layer was dried (Na_2SO_4) and concentrated. Nmr analysis showed that 85% rearrangement to **2** had occurred. The ether was removed and the residue was recrystallized from ethanol–water, yielding 0.76 g of pure **2**. The results from several similar experiments are summarized in Table V. Similar experiments with **3** and **5** gave no rearrangement after 48 hr.

Table V. Dimsylsodium as a Base for the Rearrangement of **1** at Room Temperature

Equiv of dimsylsodium	Reaction time, hr	% rearrangement
0.5	72	0.0
0.8	48	0.0
1.5	54	67
2.1	54	62
4.0	22	85

Dimsyllithium was evaluated as the base by treating 1.5 *M* methyllithium (8.3 ml, 0.0125 mol) with a solution of **1** (0.921 g, 0.005 mol) in 25 ml of dimethyl sulfoxide. The reaction mixture was stirred at room temperature for 54 hr and then hydrolyzed. Nmr analysis showed 17% rearrangement to **2**.

***t*-Butyllithium** was investigated as a base by adding 1.24 *M* *t*-butyllithium (16.1 ml, 0.02 mol) to a heterogenous mixture of **1** (1.84 g, 0.01 mol) in 15 ml of pentane. The reaction mixture was stirred at room temperature for 50 hr before being hydrolyzed. After work-up nmr analysis indicated 15% rearrangement to **2**.

Rearrangement of 1,1-Di-*p*-tolylhydrazine (3). Atmospheric Pressure. Methyllithium (1.6 *M*) (33.0 ml, 0.053 mol) was added to a solution of **3** (2.8 g, 0.0132 mol) in ether (15 ml) at room temperature. A clear light yellow solution was formed. After stirring for 145 hr at 25° the reaction mixture was added to water (10 ml). The ethereal layer was separated, dried (Na_2SO_4), and concentrated. The solid residue was recrystallized from ethanol–water, yielding 2.0 g (70%) of **4**, mp 132–133° (lit.[19] 133–134°); nmr (cyclohexane) δ 2.14 (S, 6, CH_3-Ar), 5.10 (S, 2, N-*H*); 6.56 (d, 4, J = 8 Hz, *Ar*), and 6.85 ppm (d, 4, J = 8 Hz, *Ar*).

Rearrangement of 1-Methyl-1-phenylhydrazine (5). Atmospheric Pressure. As an example of the experi-

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(18) Detailed analysis of the spectra of **2b** showed the downfield peaks to be the combination of the *meta* protons and one *ortho* proton; and the upfield resonance, the *para* proton and the other *ortho* proton. At 37° (the temperature of the nmr probe), the *ortho* protons were nonequivalent on the nmr time scale. If the sample was heated in the nmr probe to 75°, the broad doublets for the *ortho* protons merge together and form one doublet between the up and downfield peaks. Similar observations were made if the solvent used was tetrahydrofuran or if the cation of **2b** was sodium. This interesting phenomenon of nonequivalent *ortho* protons in **2b** and other amine anions is currently under investigation.

(19) The chemical shifts were taken relative to the CH_2 quartet of ether at 3.58 ppm.

ments tabulated in Table III 1.7 *M* methyllithium (10.6 ml, 0.018 mol) was added to a solution of 1.0 g of **5** (0.008 mol) in 15 ml of diethyl ether. After stirring at room temperature for various times, a sample of the reaction mixture was hydrolyzed. The ratio of **5** to 1-methyl-2-phenylhydrazine (**6**) was determined by integrating the N*Me* nmr resonance for **5** at 2.88 ± 0.05 ppm and **6**, 2.45 ± 0.03 ppm in diethyl ether. (The positions of these peaks were somewhat dependent on the concentration of the substrate.) Decomposition products such as N-methylaniline δ 2.65 ± 0.03 ppm (*Me*N) and aniline δ 3.9 ppm (NH_2) were also determined. These decomposition products were identified after preparative gas chromatography. Gas chromatography also provided a check on the percentages of aniline and N-methylaniline, but we were unable to separate **5** and **6** by this method.

Rearrangement of 1-Methyl-1-*m*-trifluoromethylphenylhydrazine. Atmospheric Pressure. Methyllithium, 1.6 *M* in diethyl ether (37.0 ml, 0.06 mol) was slowly added to a solution of **7** (1.9 g, 0.01 mol) in diethyl ether (5 ml). The first sample was taken and hydrolyzed after stirring at room temperature for 29 hr. The hydrolyzed sample was processed in the usual manner and analyzed by nmr. Assuming a new resonance at 2.20 ppm to be the *Me*N of 1-methyl-2-*m*-trifluoromethylphenylhydrazine (**8**) 45% rearrangement had occurred. Further reaction of the original sample caused gross decomposition of the hydrazine isomers.

Mixing Experiment Rearrangement of 1 and 3. **1** (0.51 g, 0.0028 mol) and **3** (1.27 g, 0.006 mol) were mixed and treated with 1.6 *M* methyllithium (32.0 ml, 0.0512 mol). The reaction was stirred at room temperature for 115 hr before being hydrolyzed in 100 ml of water. The diethyl ether layer was separated, dried (Na_2SO_4), and concentrated by vacuum stripping on a rotating evaporator. The yellow crystalline residue weighed 1.78 g (100%). A small sample of these crystals was put into diethyl ether solution and analyzed by glpc. Three peaks were detected in a ratio of 30:23:47. Internal glpc standards showed these to be **1** plus **2**, **3**, and **4**, respectively. The products were separated by preparative gas chromatography and the assignments of **3** and **4** were confirmed by comparison with authentic materials. The first peak was shown by nmr to contain 30% **1** and 70% **2**. These data indicate that **1** and **3** were approximately 70% rearranged to **2** and **4**, respectively, without formation of any crossover products containing both phenyl and tolyl moieties.

Table VI. Rearrangement of N-Methyl-N-phenyl-*o*-phenylenediamine (**11**) in Diethyl Ether

Ratio CH_3Li:**11**	Time, hr	Temp, °C	% rearrangement
1.0	52	28	0
1.0	69	110[a]	0
5.0	67	28	55
5.0	163	28	89

[a] A sealed tube experiment.

Rearrangement of N-Methyl-N-phenyl-*o*-phenylenediamine (11). Atmospheric Pressure. **11** (2.5 g, 0.0126 mol) was allowed to react with 40 ml of methyllithium (1.6 *M*, 0.063 mol) in diethyl ether for 163 hr and then hydrolyzed in water (2.27 g, 0.126 mol). The glpc analysis of the ethereal solution indicated 89% rearrangement to N-methyl-N′-phenyl-*o*-phenylenediamine (**12**). The peak assigned to **12** was purified gas chromatographically: nmr (cyclohexane) δ 2.66 (S, 3.0 *Me*N), 4.70 (S, 1.0, *H*NPh), 3.92 (S, 1.0 *H*N-Me), and 6.40–7.21 ppm (M, 10.0, *Ar*).

Anal. Calcd for $C_{13}H_{14}N_2$: C, 78.76; H, 7.12; N, 14.13. Found: C, 78.76; H, 7.18; N, 13.95.

The above reaction was repeated in the presence of N-phenyl-*o*-phenylenediamine, and no product containing two phenyl moieties was detected.

Under similar conditions but using only 1 equiv of methyllithium and a reaction time of 52 hr, no rearrangement of **11** to **12** was detected. Table VI summarizes several experiments done with **11**.