matography on silica gel with an eluent of CH_2Cl_2, mp 74–76 °C. By both ^1H NMR and mass spectral measurements **16** was shown to be free of deuterium.

(b) 2-(2-Chloro-1,1-diphenylethyl)pyridine (4a). A reaction analogous to section a was conducted with **4a**. After 24 h **4a** was recovered unchanged in 93% yield.

A repetition in which 1 molar equiv of 2,2′-bipyridyl was included in the reaction mixture also led to no rearrangement and no reaction.

(c) 2-(2-Iodo-1,1-diphenylethyl)pyridine (4c). A solution of 3.85 g (10 mmol) of **4c**, 2.75 g (10 mmol) of bis(1,5-cyclooctadiene)nickel, and 1.56 g (10 mmol) of 2,2′-bipyridyl in 40 mL of THF was stirred at 25 °C for 24 h. After the usual workup the products were separated on a silica gel column by eluting with methylene chloride to give 39% of 2-(1,2-diphenylethyl)pyridine, 27% of 2-(2,2-diphenylethyl)pyridine, and 10% of 2-(1,1-diphenylethyl)pyridine, as verified by ^1H NMR and IR spectral comparisons with authentic samples.

Tri-*n*-butyltin Hydride Mediated Reductions or Rearrangements. (a) 4-(1-Chloro-1,2-diphenylethyl)pyridine (5c). A solution of 500 mg (1.70 mmol) of tri-*n*-butyltin hydride and 500 mg (1.70 mmol) of **5c** in 5.0 mL of dry, degassed toluene under argon was allowed to react for 24 h at room temperature. Gas chromatographic and mass spectral analysis showed that the only product formed was 4-(1,2-diphenylethyl)pyridine (**16**) in a 34% conversion. Subsequent heating of the reaction mixture for 24 h at 110 °C increased the conversion to 88% (^1H NMR spectral analysis), but still **16** was the only product.

(b) 4-(2-Chloro-1,1-diphenylethyl)pyridine (5a). In a similar reaction of **5a** with the tin hydride, there was no sign of reaction after 24 h at 25 °C. After heating the mixture for 72 h at reflux and hydrolytic workup, only **5a** and hexa-*n*-butylditin were found upon workup. Any reduction of **5a** was under 1%.

(c) 2-(2-Chloro-1,1-diphenylethyl)pyridine (4a). A solution of 990 mg (3.41 mmol) of the tin hydride and 1.00 g (3.41 mmol) of **4a** in 10 mL of dry, degassed toluene under argon was allowed to react for 24 h at room temperature. By gas chromatographic, ^1H NMR, and mass spectral analyses it was shown that 20% of **4a** was converted to a 65:35 ratio of 2-(1,2-diphenylethyl)pyridine and 2-(2,2-diphenylethyl)pyridine. When a separate reaction was conducted for 24 h at 110 °C, the conversion of **4a** to products was 81%; the products consisted of a 57:43 ratio of the same 1,2-diphenyl and 2,2-diphenyl isomers, but now these products were accompanied by 8% of 2-(1,1-diphenylethyl)pyridine.

Preparation of a Spiro Compound Resembling the Structure of the Possible Rearrangement Intermediate in the Pyridyl System. A mixture of 1.0 g (3.2 mmol) of 1-chloro-2-methyl-2-(4-pyridyl)propane methiodide (**23**), 500 mg of finely and freshly cut pieces of lithium, and 3 g of crushed glass was treated with 30 mL of anhydrous THF. When no reaction had started after 30 min, a drop of 1-chloro-2-methyl-2-(4-pyridyl)propane was added to initiate reaction. After a red-brown color developed, the mixture was cooled to 0 °C and stirred for 90 min. The mixture was filtered through glass wool to remove the lithium and the filtrate allowed to fall thereafter into water. The organic phase of the filtrate was taken up into ether and the ether dried over anhydrous $CaSO_4$ and evaporated. The resulting oil **24** was maintained under nitrogen until spectra were measured. All the foregoing isolation steps had to be carried out rapidly because the organic oil was unstable: ^1H NMR ($CDCl_3$) δ 0.19 (s, 2 H, cyclopropyl protons), 0.99 (s, 6 H, *gem*-dimethyl protons), 2.79 (s, 3 H, N-CH_3), 4.05 (d, 2 H, J = 8 Hz, 3-py H), and 5.80 (d, 2 H, J = 8 Hz, 2-py H); MS (70 eV), m/e 149 (M^+). These data are consistent with the structure, 1,1,6-trimethyl-6-azaspiro[2.5]octa-4,7-diene (**24**).

Acknowledgment. We express our gratitude to the Public Health Service for support of this research under Grants CA-10743 and CA-28335. We are indebted to Dr. Andrzej M. Piotrowski for obtaining the data on the nickel(0)-mediated rearrangements.

Registry No. **4a**, 29958-04-1; **4b**, 109975-56-6; **4c**, 109975-57-7; **5a**, 29958-05-2; **5b**, 109975-58-8; **5c**, 95745-22-5; **8**, 109975-59-9; **10**, 109975-60-2; **11**, 24187-15-3; **12**, 5733-74-4; **12a**, 109975-63-5; **13**, 67278-01-7; **14**, 109975-61-3; **15**, 6760-52-7; **16**, 6634-61-3; **16a**, 109975-67-9; **19**, 34995-30-7; **20**, 34995-28-3; **21**, 34995-31-8; **22**, 34995-29-4; **23**, 109975-62-4; **24**, 109975-71-5; **25**, 109975-64-6; **25a**, 109975-65-7; **26**, 109975-68-0; **26a**, 109975-69-1; 2-(diphenylmethyl)pyridine, 3678-70-4; 2-picoline, 109-06-8; bromodiphenylmethane, 776-74-9; 2-benzylpyridine, 101-82-6; benzyl chloride, 100-44-7; 4-benzhydrylpyridine, 3678-72-6; 4-picoline, 108-89-4; diphenylmethyl chloride, 90-99-3; 2-isopropylpyridine, 644-98-4; 4-isopropylpyridine, 696-30-0; 4-methylbenzyl chloride, 104-82-5; 2-*tert*-butylpyridine, 5944-41-2; 4-(1-deuterio-1,2-diphenylethyl)pyridine, 109975-66-8; diphenylmethane, 101-81-5; 2-(2-methylphenyl)-1-(2-methyl-4-pyridyl)-1,1-diphenylethane, 109975-70-4.

Carbon-Skeletal [1,2] Anionic Rearrangements of Tertiary Benzylic Amines: Geometric and Electronic Requirements for Generating the Spiroazacyclopropane Intermediate[1]

John J. Eisch,*† Suresh K. Dua,[2] and Csaba A. Kovacs[3]

Department of Chemistry, State University of New York at Binghamton, Binghamton, New York 13901, and Department of Chemistry, The Catholic University of America, Washington, DC 20017

Received February 19, 1987

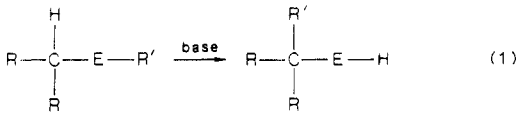
In order to determine the scope and mechanism for the base-promoted rearrangement of tertiary amines, a wide variety of benzylic amines were treated with *n*-BuLi in THF or TMEDA, *n*-BuLi–KO-*t*-Bu mixtures, or KH. The following amines were examined: benzyldimethylamine, benzylmethylphenylamine, benzyldiphenylamine, *N*-benzylcarbazole, *N*-benzyl-1,2,3,4-tetrahydrocarbazole, *N*-benzyl-1,1a,2,3,4,4a-*cis*-hexahydrocarbazole, *N*-(2-phenylethyl)carbazole, *N*-(3-phenylpropyl)carbazole, *N*-(2-chloroethyl)carbazole, *N*-benzyl-9,9-dimethyl-9,10-dihydroacridine, *N*-benzyl-*o*,*o*′-iminodibenzyl, 9-(diphenylamino)fluorene, 9-anilino-9-phenylfluorene, 9-(methylphenylamino)fluorene, and diphenyl(diphenylmethyl)amine. In certain cases, ethylation products were obtained from the interaction of intermediate carbanions with ethylene generated by the decomposition of THF. The results are interpreted in terms of [1,2] intramolecular shifts of aryl groups from nitrogen to benzylic carbon proceeding by way of a bridging aryl transition state or intermediate.

Although the base-induced Wittig rearrangement of ethers into alcohols has received considerable attention (eq 1, E = O),[4,5] the nitrogen analogue of this isomerization (eq 1, E = NR′) has been reported only in a few isolated instances.[6–9] Even in these reported instances, the rear-

† Current address: State University of New York at Binghamton.

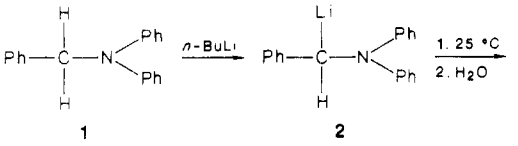
(1) Rearrangement of Organometallic Compounds. 24. Part 23: *J. Org. Chem.*, in press.

0022-3263/87/1952-4437$01.50/0

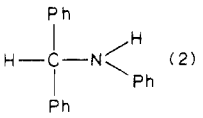


(1)

rangement of a tertiary amine into a secondary amine occurred under such drastic experimental conditions or in such low yields that the scope or pathway of reaction remained obscure. Then in 1971 this research group demonstrated that benzyldiphenylamine (**1**), upon treatment with *n*-butyllithium in THF at 25 °C, underwent rearrangement into benzhydrylaniline (**3**) in high yield.[10] By deuterium labeling of the reaction mixture with D_2O, the intermediacy of lithio derivative **2** was established (eq 2).



1 **2**

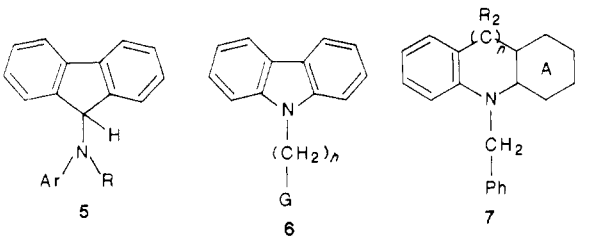


(2)

3

Since this observation showed how smoothly a tertiary amine like **1** could undergo skeletal isomerization, it became important to explore the scope of such a reaction and determine its mechanism. The principal mechanistic questions to be addressed were the following: whether the rearrangement is truly anionic; whether it is intramolecular or intermolecular; and what the steric and electronic requirements are for migration of an organic group from the N to the C center. In particular, it was critical to learn whether an intramolecular [1,2] shift occurred by way of a bridging intermediate (path a) or whether an anionic elimination–readdition process (path b) were operative in this reaction (Scheme I).

To this end, the present investigation examined the tendency of a wide variety of tertiary benzylic amines to undergo rearrangement into secondary amines upon treatment with strong bases. Benzylic amines were chosen, since it was found that *n*-butyllithium could lithiate the benzylic carbon (cf eq 2). The other groups on the benzylic amine were varied, so as to test the steric, electronic, or geometric factors favoring the [1,2] shift from N to C. The types of amines employed for this purpose are typified by structures **4**–**7**. Structure **4** represents an open-chain tertiary benzylic amine bearing H, alkyl, or aryl groups (R, R′, Ar); structure **5** is derived from **4** by the ortho coupling of aryl groups on benzylic carbon. Analogously, **6** has ortho-coupled aryl groups on nitrogen and a variable



5 **6** **7**

number of CH_2 groups between N and function G (Ph or Cl). Finally, **7** has a variable number of CR_2 groups between the ortho-coupled groups on nitrogen, and ring A was aromatic or hydrogenated (4 H or 6 H). By determining which of these amines underwent rearrangement, we have been able to discern the mechanistic features of such processes.

Results

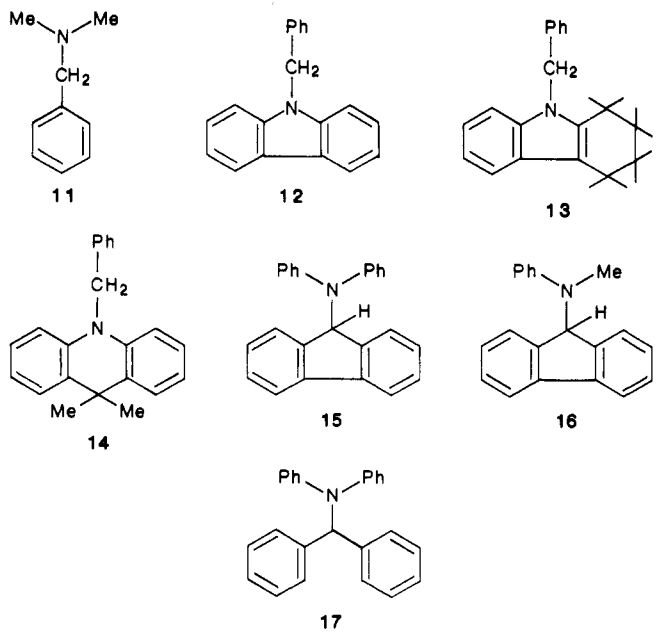
In general, such benzylic amines were metalated on the benzylic carbon (e.g., **2** in eq 2) by either *n*-BuLi in THF solution or a combination of *n*-BuLi and KO-*t*-Bu[11] in hexane suspension. Successful metalation was ascertained by quenching such reactions with D_2O after short contact times (e.g., **4a** in Scheme I). The recovered, unrearranged amine was then analyzed for content and position of the deuteron by mass spectrometry and ^1H NMR spectroscopy. In Table I are listed all the tertiary amines of types **4**–**7** subjected to metalation in this study. With the exception of *N*-(2-chloroethyl)- and *N*-(2-phenylethyl)carbazoles (**8** and **9**), all these amines underwent metalation and subsequent deuteriation to the extent of >90% under the stated reaction conditions. Metalation of the carbazole derivatives **8** and **9** was attempted with lithium metal in THF or with *n*-BuLi and KO-*t*-Bu, respectively. However, if any of the desired benzylic metallic derivative were formed, it immediately underwent β-elimination of the metallocarbazole **10** (Scheme II).

Solutions or suspensions of the other metalated amines were then stirred at the given temperature for the indicated periods of time (Table I). Following a conventional hydrolytic workup, the reaction products were separated by a combination of thin-layer, column, and gas chromatography. In many cases, samples of the expected secondary amine rearrangement products were available, and their presence or absence in the reaction products could be specifically determined. For those cases where little or no rearrangement seemed to occur under these milder conditions, resort was made to prolonged reaction times, higher temperatures, donor solvents (TMEDA, crown ethers), and other bases (KH). When prolonged reaction times were tried, the base was then added in fresh portions periodically.

On the basis of such reaction conditions and analytical procedures, then, it was established that only certain of these tertiary amines underwent rearrangement. It is noteworthy that the following showed *no* tendency to rearrange: benzyldimethylamine (**11**); *N*-benzylcarbazole (**12**); *N*-benzyl-1,2,3,4-tetrahydrocarbazole (**13**); *N*-benzyl-9,9-dimethyl-9,10-dihydroacridine (**14**); 9-(diphenylamino)fluorene (**15**); 9-(methylphenylamino)-fluorene (**16**), and diphenyl(diphenylmethyl)amine (**17**).

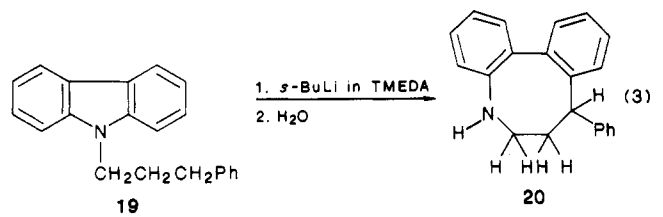
In an attempt to force rearrangement, the potassium derivative of fluorene **15** was heated at 300 °C. This reaction led to C–N bond homolysis, however, for only diphenylamine and fluorene could be found upon workup.

(2) Current address: 104, Sant Nagar, New Delhi 110065, India.
(3) Current Address: Eastman Kodak Co., Rochester, NY 14692.
(4) Wittig, G. *Angew. Chem.* **1954**, *66*, 10.
(5) Schöllkopf, U. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 763.
(6) *N,N*-Dibenzylaniline, dibenzylmethylamine and some related amines were found to react with $NaNH_2$ under extreme conditions to give hydrocarbon products, which were thought to have arisen through anionic rearrangement: Johnstone, R. A. W.; Stevens, T. S. *J. Chem. Soc.* **1960**, 3346.
(7) Tertiary amine derivatives of 9-aminofluorene were observed to rearrange by action of $LiAlH_4$ in THF: Dahn, H.; Solms, U. *Helv. Chim. Acta* **1951**, *34*, 907.
(8) Cockburn, W. F.; Johnstone, R. O. W.; Stevens, T. S. *J. Chem. Soc.* **1960**, 3340.
(9) 4,4-Dimethyl-2-phenylpyrroline was formed in 19% yield by the action of *n*-butyllithium on 1-benzyl-3,3-dimethylazetidine: Anderson, A. G., Jr.; Wills, M. T. *J. Org. Chem.* **1967**, *32*, 3241.
(10) Eisch, J. J.; Kovacs, C. A. *J. Organomet. Chem.* **1971**, *30*, C97.
(11) Schlosser, M.; Hartmann, J. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 508.



To gain assurance that rearrangement had not occurred before decomposition, the expected rearrangement product, 9-anilino-9-phenylfluorene (18) was heated as its lithium salt at 180 °C. But only aniline and 9-phenylfluorene were detectable upon workup. Therefore, 9-(diphenylamino)fluorene is not converted into 9-anilino-9-phenylfluorene, nor is the latter convertible into the former (Scheme III).

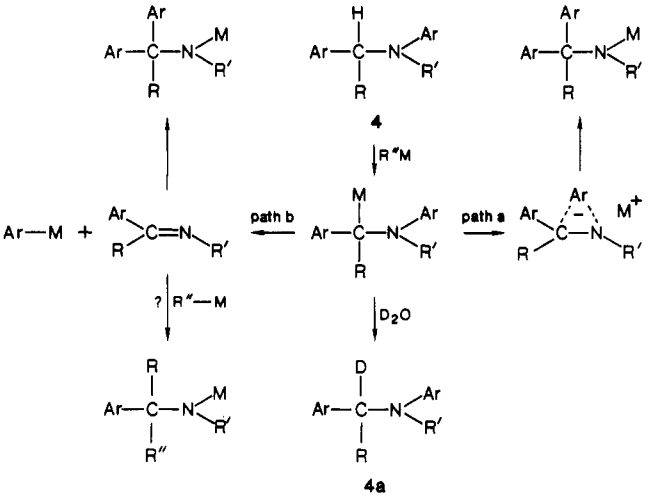
The remaining tertiary amines in Table I underwent rearrangement to secondary amines with varying ease. The structure of the secondary amine product was readily verified, in most cases, by spectral and chromatographic comparisons with authentic samples. The rearrangement product of *N*-(3-phenylpropyl)carbazole (19) was clearly established as 5-phenyl-5,6,7,8-tetrahydrodibenzo[*e*,*g*]-azocine (20) by spectral means (eq 3).



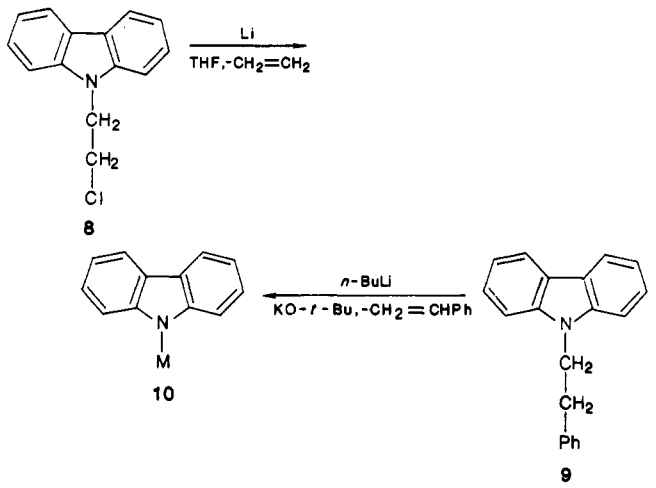
In order to corroborate that the rearrangement product from *N*-benzyl-1,1a,2,3,4,4a-*cis*-hexahydrocarbazole (21) was 6-phenyl-1,1a,2,3,4,4a,5,6-*cis*-octahydrophenanthridine (22), an unambiguous synthesis of 22 was carried out, as outlined in Scheme IV.

In those cases where the tertiary amine underwent rearrangement, the reaction proceeded very cleanly. Specifically, there was *no* indication of any significant amount of *n*-butyl group incorporation into the reaction products. Detectable amounts of *n*-butyl-derived products would be expected, were an elimination–readdition mechanism operative in these rearrangements (cf. path b, Scheme I). However, for prolonged reactions with *n*-butyllithium in THF solution, considerable proportions of ethyl group incorporation were observed. In fact, with benzylmethylphenylamine an 89% yield of such an ethylated product (24) was formed. Since 25 was not formed in reactions of *n*-BuLi and KO-*t*-Bu in hexane, 25 is undoubtedly formed by the interaction of the intermediate benzylic lithium 26 with the ethylene generated by the decomposition of THF through *n*-BuLi[12,13] (Scheme V).

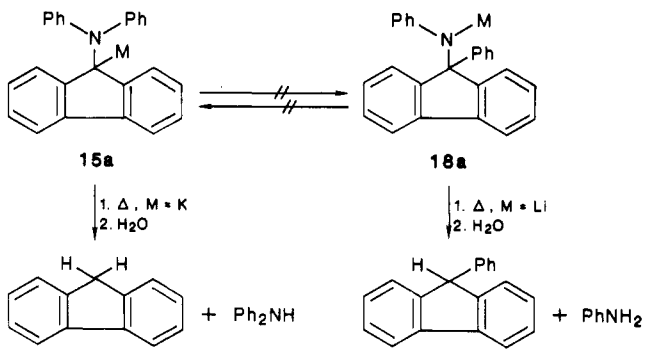
Scheme I



Scheme II



Scheme III



Discussion

An analysis of the scope and experimental conditions of these amine rearrangements permits an insight into the operative reaction mechanism. Three aspects deserve attention: (1) the polar or free-radical character of the actual intermediates involved; (2) the intermolecular or intramolecular course of rearrangement; (3) for an intramolecular course, the involvement of a bridging intermediate in the [1,*n*] shift or of fragments generated in a solvent cage. Experimental evidence sheds light on each of these possibilities.

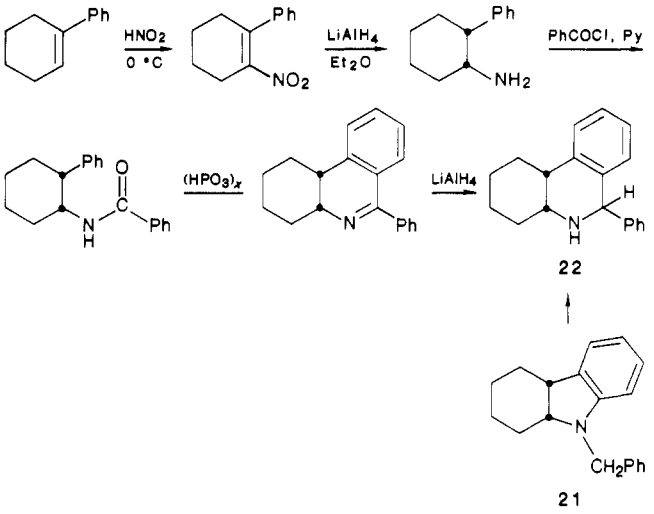
(12) Bates, R. B.; Kroposki, L. M.; Potter, D. E. *J. Org. Chem.* **1973**, *38*, 322.
(13) Eisch, J. J.; Tsai, M. R. *J. Organomet. Chem.* **1982**, *225*, 5.

Table I. Base-Promoted Rearrangements of Tertiary Amines

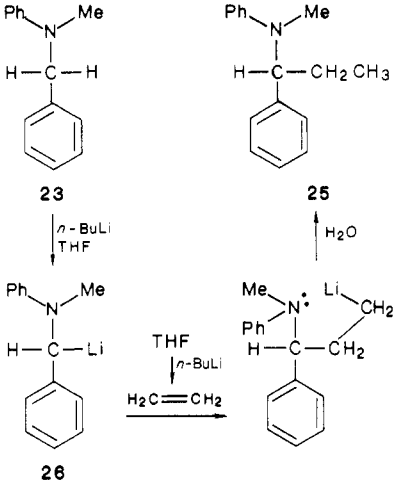
amine	base	solvent[a]	time, h	temp, °C	product[b] (% yield)
benzyldimethylamine (**11**)	*n*-BuLi (KO-*t*-Bu)	C_6H_{14}	0.5	25	unrearr; metalat
benzylmethylphenylamine (**23**)	*n*-BuLi	THF	72	30	unrearr; ethylat **25**
	n-BuLi (KO-*t*-Bu)	C_6H_{14}	48	65	rearr, **33** (66)
benzyldiphenylamine (**1**)	*n*-BuLi	THF	48	25	rearr, **34** (80)
N-benzylcarbazole (**12**)	*n*-BuLi	THF	72	25	unrearr; metalat
	n-BuLi (KO-*t*-Bu)	C_6H_{14}	72	65	unrearr; metalat
N-benzyl-1,2,3,4-tetrahydrocarbazole (**13**)	*n*-BuLi (KO-*t*-Bu)	C_8H_{18}	72	110	unrearr; metalat
	n-BuLi (KO-*t*-Bu)	C_6H_{14}	100	65	unrearr; metalat
N-benzyl-1,1a,2,3,4,4a-*cis*-hexahydrocarbazole (**21**)	*n*-BuLi (KO-*t*-Bu)	C_6H_{14}	96	65	rearr, **22** (52)
N-(2-phenylethyl)carbazole (**9**)	*n*-BuLi (KO-*t*-Bu)	C_6H_{14}	72	65	carbazole (95), styrene
N-(3-phenylpropyl)carbazole (**19**)	*n*-BuLi (TMEDA)	C_6H_{14}	240	65	rearr, **20** (7)
N-(2-chloroethyl)carbazole (**8**)	Li	THF	13	25	carbazole (94)
N-benzyl-9,9-dimethyl-9,10-dihydroacridine (**14**)	*n*-BuLi (KO-*t*-Bu)	C_6H_{14}	72	65	unrearr; metalat
N-benzyl-*o,o'*-iminodibenzyl (**27**)	*n*-BuLi	THF	72	25	rearr; ethylat (36)
	n-BuLi (KO-*t*-Bu)	C_6H_{14}	72	65	rearr, **28** (80)
9-(diphenylamino)fluorene (**15**)	*n*-BuLi (KO-*t*-Bu)	C_6H_{14}	96	65	unrearr; metalat
	KH		3	300	diphenylamine (69) fluorene (78)
9-anilino-9-phenylfluorene (**18**)	*n*-BuLi	mesitylene	72	170	9-phenylfluorene (78), aniline
9-(methylphenylamino)fluorene (**16**)	*n*-BuLi (KO-*t*-Bu)	mesitylene	72	170	unrearr; metalat
diphenyl(diphenylmethyl)amine (**17**)	*n*-BuLi (KO-*t*-Bu)	C_6H_{14}	72	65	unrearr; metalat
N-(triphenylmethyl)amine (**32**)	*n*-BuLi (KO-*t*-Bu)	C_6H_{14}	72	65	unrearr; metalat

[a] With the reagents *n*-butyllithium and potassium *tert*-butoxide the reaction mixture formed a solid suspension in the alkane. [b] The abbreviations "unrearr" and "metalat" indicate *unrearranged*, but *metalated* starting material; "rearr" betokens that the tertiary amine had rearranged to the designated secondary amine in the indicated isolated yield. In some cases, the starting amine or product were ethylated ("ethylat") by the ethylene from the THF.

Scheme IV



Scheme V



First, there is no doubt that in both successful and unsuccessful rearrangements a benzylic metal derivative is formed relatively rapidly (cf. **4a** in Scheme I). Thus, the subsequent rearrangement could occur anionically via such a derivative. However, just because an anionic intermediate is involved at the start of a reaction does *not* compel the subsequent reaction to be anionic.[14] Through SET processes such anions could generate radicals, which might be the real intermediates (eq 4).[15] In the present study,

$$\text{R–M} + \text{acceptor} \rightleftharpoons \text{R}^{\bullet} + \text{M}^{+}\,(\text{acceptor})^{-} \qquad (4)$$

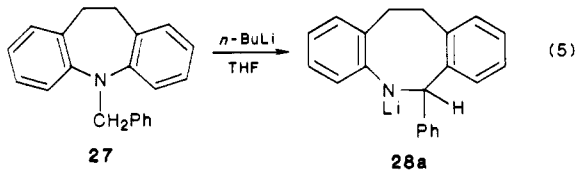
however, various tests for the occurrence of free radicals were uniformly negative. Reaction solutions were found not to display any ESR signal, nor were any telltale side products of radical processes, such as R–R, detected. Furthermore, in the ^{1}H NMR monitoring of these rearrangements, no negative or enhanced signals diagnostic of CIDNP phenomena were observed. Moreover, as exemplified by the rearrangement of benzyldiphenylamine (**1**, eq 2), the reaction could be monitored to completion without the appearance of any broadening of the proton resonances: e.g., the CH_2 signal at 4.99 ppm remained narrow as it diminished, while the new signal of the CHLi group grew in at 4.23 ppm; the sharp 4.23 signal gradually gave way to the equally narrow signal at 5.36 ppm (Ph_2CH). Thus, there is no evidence for any radical participation in this reaction.

Second, as to the intramolecular or intermolecular nature of the rearrangement, the observed scope of the reaction favors the former. Were an intermolecular reaction involving an elimination–readdition sequence involved (path b, Scheme I), it is incomprehensible, for example, why benzyldiphenylamine (**1**) should rearrange and *N*-benzylcarbazole (**12**) should not. Similarly, there should be no reason why amines **11**–**17** could not rearrange via path b. A further argument against an intermolecular mechanism is the failure to observe, in any such rearrangement, products formed from the interception of the supposed intermediate ArRC=NR by the metalating agent R″M. Thus, in the reaction of benzyldiphenylamine (**1**) with *n*-butyllithium, no $CH_3CH_2CH_2CH_2CHPhNHPh$ was found in the reaction products.

(14) Peterson, D. J.; Ward, J. F. *J. Organomet. Chem.* **1974**, *66*, 209.
(15) Eisch, J. J. *Pure Appl. Chem.* **1984**, 56, 35.

Third, a variant of the intermolecular path b would be where the elimination fragments ArRC=NR′ and ArM (Scheme I) were formed in a solvent cage and thus reacted with each other more rapidly than an external R″M. Such an outcome would give the semblance of an intramolecular reaction. But against this possibility it can be argued that it would still not be obvious why such amines as **11–17** fail to rearrange. Thus, any modification of an elimination–readdition pathway can be ruled out.

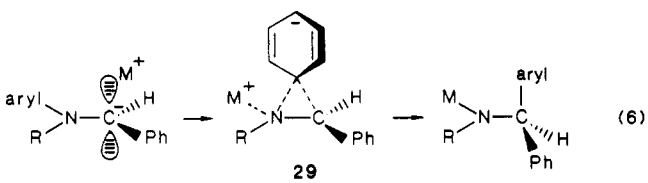
In considering the scope of these amine rearrangements, several points are noteworthy: (a) aryl groups migrate exclusive of any alkyl or cycloalkyl migration; (b) in the series of dibenzoazacycloalkadienes generalized by structure **7** (A = benzo, n = 0–2), only when n = 2 was rearrangement observed (eq 5); (c) with the *N*-benzylcarbazoles



(5)

27 **28a**

and -hydrocarbazoles, only the cis hexahydro member rearranged (Scheme IV); and (d) among the *N*-(phenylalkyl)carbazoles, only the 3-phenylpropyl derivative rearranged (eq 3). These reaction limitations combined with an anionic, intramolecular view of the reaction lead to a mechanism involving a nucleophilic attach of the benzylic carbanion upon the π-cloud of the adjacent N-bonded aryl group. Such a view suggests a transition-state or bridging intermediate (**29**) in which the migrating aryl group is partially bonded to both the N and C centers (eq 6). In

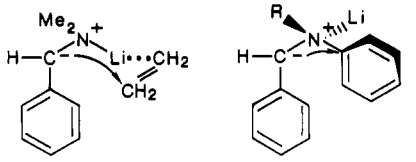


(6)

29

order to attain **29**, it is clear that the migrating aryl group must present its π-face to the carbanionic center so that its antibonding π-orbitals can accept electron density. If the aryl group is geometrically constrained in a plane, so as to prevent such overlap with the benzylic carbanion, clearly **29** would not be energetically accessible. This view nicely explains the failure of *N*-benzylcarbazoles and amines **11–17** to rearrange. One might raise the possibility that the failure of *N*-benzylcarbazole to rearrange may be due rather to the stabilizing aromaticity of the pyrrole aromatic sextet. But this objection can be dismissed by noting the occurrence of a [1,3] shift, albeit slow, with *N*-(3-phenylpropyl)carbazole (**19**). Thus, a necessary condition for such rearrangements is that the migrating aryl must be able to rotate so that its π-face can overlap with the carbanionic center. However, although this is a necessary condition, it is not sufficient; witness the failures of fluorenylamines **15** and **16** and of diphenylmethylamine **17** to rearrange. In these cases, the highly delocalized character of the carbanions likely makes them inferior nucleophiles for the process depicted in eq 6. As is seen from the attempts to force a carbanionic rearrangement, ultimately a free-radical decomposition occurs in preference to the sought-for polar process (Scheme III).

Such nucleophilic attack on aromatic carbon–carbon unsaturation, as involved in forming **29**, may seem difficult. However, there is reason to think that the adjacent nitrogen and metal gegenions play an activating role. Thus, although benzylic lithium reagents are reported not to react with ethylene,[16] the benzylic lithium reagent derived from **23** does so readily (Scheme V). From this, the indication is that possibly coordination of the lithium ion on nitrogen favors the zwitterion **30** and thus nucleophilic attack on ethylene. It is noteworthy that an analogous zwitterion can be envisioned for the intramolecular carbanionic rearrangements reported here (**31**).



30 **31**

Experimental Section

Instrumentation. All melting points were determined with a Thomas-Hoover capillary melting point apparatus and are uncorrected. Infrared spectra (IR) were recorded either on a Perkin-Elmer 457 or 238B grating spectrophotometer, and the samples were prepared in solution as KBr pellets or as mineral oil mulls. The proton nuclear magnetic resonance spectra (^{1}H NMR) were measured with a Varian spectrometer, Model EM 360. The values are reported on the δ scale with reference to internal tetramethylsilane, followed by the relative proton intensities and the coupling constants (J) in hertz. Mass spectra were determined with either an MS/902 CIS 2 instrument, a V6 Datasystem 2040 computerized recorder, or a Varian MAT spectrometer, Model CH5. Vapor-phase chromatographic analysis (VPC) and isolations were carried out on an F&M chromatograph, Model 720, equipped with a 6 ft × 0.25 in. column of 10% SE-30 silicone gum rubber on Chromosorb P. Elemental analyses were performed by Atlantic Microlab, Atlanta, GA.

Inert Reaction Media. All preparations and reactions involving air- and moisture-sensitive organometallic intermediates were conducted under an atmosphere of dry, oxygen-free nitrogen, with adherence to published precedures.[17] Solvents of reagent grade were used in all reactions. Peroxides were removed from diethyl ether and tetrahydrofuran (THF) by passing such solvents through a column of neutral alumina under nitrogen. The eluted solvents were then allowed to reflux over $LiAlH_4$ for 5 h and then distilled. Alkane solvents were likewise allowed to reflux over and then to be distilled from $LiAlH_4$. Aromatic hydrocarbons (benzene, toluene, and mesitylene) were washed consecutively with concentrated H_2SO_4, water, aqueous NaOH, and aqueous NaCl before being dried over anhydrous $MgSO_4$. Finally, they were allowed to reflux over CaH_2 for 6 h before being distilled.

Alcohols, such as ethanol and methanol, were refluxed over CaO for 4 h and then distilled. *N,N,N′,N′*-Tetramethylethylenediamine (TMEDA) was stored over NaOH pellets overnight, refluxed over fresh slices of sodium metal, and then distilled. The final TMEDA was stored over activated Linde molecular sieves 4A under nitrogen. Pyridine was stored over KOH pellets (20 g/kg) for 2 weeks; then it was distilled from a mixture of KOH pellets and Linde molecular sieves ₺A.

Reaction Procedures. The organolithium reagents were either purchased or prepared by known procedures.[18] All such reagents were analyzed just before every use by established titrimetric methods.[18] All reactions conducted in the range 50–120 °C were carried out in a constant-temperature bath of paraffin oil. A Wood's metal bath with an insulating mantle was used for higher temperatures. Temperatures below 0 °C were maintained with dry ice slurries in various solvents or liquid nitrogen–solvent slushes.[19]

Hydrolytic workup of reactions generally involved the slow addition of 5% aqueous HCl solution, subsequently making the

(16) Bartlett, P. D.; Tauber, S. J.; Weber, W. P. *J. Am. Chem. Soc.* **1969**, *91*, 6362.
(17) Eisch, J. J. *Organometallic Syntheses*; Academic: New York, 1981; Vol. 2, pp 3–37.
(18) Eisch, J. J. *Organometallic Syntheses*; Academic: New York, 1981; Vol. 2, pp 89–100.
(19) Weast, R. B., Ed. *Handbook of Chemistry and Physics*, 58th ed.; The Chemical Rubber Co.: Cleveland, OH, 1977; p D-215.

mixture basic with aqueous KOH solution, and then extracting the organic product into diethyl ether. The solvent was removed by evaporation after drying the solution over anhydrous $MgSO_4$. The residue was examined by thin-layer (TLC), column (CC), or gas (VPC) chromatography. In deuterium-labeling experiments, the reaction product(s) was isolated and its ^1H NMR spectrum was recorded; diminution or disappearance of a given proton signal identified the site of deuteriation.

Starting Materials. Benzyldimethylamine (**11**), *N*-methylaniline, diphenylamine, carbazole, *N*-phenylanthranilic acid, *o,o'*-iminodibenzyl, 9-bromofluorene, and benzhydryl bromide were purchased and, where necessary, purified before use.[20]

The following amines were synthesized by published procedures: 1,1a,2,3,4,4a-*cis*-hexahydrocarbazole,[21] 1,2,3,4-tetrahydrocarbazole,[22] 9,10-dimethyl-9,10-dihydroacridine,[23] 9-anilino-9-phenylfluorene (**18**),[24] and *N*-(triphenylmethyl)aniline (**32**).[25]

Secondary amines were converted into tertiary, usually *N*-benzylamines by modifications of the following typical procedure for preparing benzyldiphenylamine (**1**). Thus, to a stirred solution of 8.5 g (50 mmol) of diphenylamine in 100 mL of anhydrous THF was added dropwise 35 mL of 1.6 M *n*-butyllithium in hexane. After the resultant mixture was stirred for 1.5 h, a solution of 6.3 g (50 mmol) of benzyl chloride in 20 mL of THF was added over a 90-min period. The reaction mixture was stirred for 16 h at room temperature, and then 50 mL of water was introduced. The organic layer was augmented with diethyl ether, separated, dried over anhydrous $CaSO_4$, and evaporated to leave 12.3 g (93%) of crude **1**. The pure product was crystallized from ethanol: mp 88–89 °C (lit.[26] mp 88.5 °C); 82% yield.

In a similar manner, the following compounds were prepared from their secondary amine precursors (spectral and elemental analytical data given if such data have not been published): (a) benzylmethylphenylamine (**23**);[23] (b) *N*-benzylcarbazole (**12**);[27,28] (c) *N*-benzyl-1,2,3,4-tetrahydrocarbazole (**13**);[29] (d) *N*-benzyl-1,1a,2,3,4,4a-*cis*-hexahydrocarbazole (**21**);[30] (e) *N*-(2-phenylethyl)carbazole (**9**);[31] (f) *N*-(3-phenylpropyl)carbazole (**19**);[31] (g) *N*-(2-chloroethyl)carbazole (**8**);[31] (h) *N*-benzyl-*o*-iminodibenzyl (**27**).[32] (i) *N*-benzyl-9,9-dimethyl-9,10-dihydroacridine (**14**): pale yellow crystals from ethanol; mp 168–169 °C; ^1H NMR ($CDCl_3$) δ 1.55 (s, 6 H), 5.1 (s, 2 H), 6.6–7.4 (m, 13 H). Anal. Calcd for $C_{22}H_{21}N$: C, 88.29; H, 7.02. Found: C, 88.27; H, 7.09.

Diphenyl(diphenylmethyl)amine (**17**) and 9-(diphenylamino)fluorene (**15**) were prepared from the reaction of diphenylamine with benzhydryl bromide and with 9-bromofluorene, respectively.[33]

Attempted and Successful Rearrangements of Amines.

a. Benzyldimethylamine (11). A solution of 1.0 g (7.2 mmol) of **11** in 50 mL of dry hexane at 0 °C was first treated with 910 mg (8.2 mmol) of unsolvated potassium *tert*-butoxide and then with 5.6 mL of 1.45 M *n*-butyllithium in hexane. The resulting red suspension was stirred for 30 min at 0 °C and for 30 min at 25 °C. Quenching the reaction mixture with D_2O and working up in the usual manner led to the recovery of only unrearranged **11**, whose ^1H NMR and MS analyses showed it to be >95% monodeuteriated and in the benzylic methylene (PhCHD) position.

b. Benzylmethylphenylamine (23). (1) In THF with *n*-Butyllithium. A solution of 50 mL of 2.1 M *n*-butyllithium in hexane was added dropwise to a stirred solution of 9.8 g (50 mmol) of **23** in 150 mL of THF at 0 °C. (A sample was withdrawn and quenched with D_2O. Examination of the recovered **23** by ^1H NMR spectroscopy showed it to be monodeuteriated at the benzylic carbon). After 72 h at 25–30 °C, the reaction mixture was worked up in the usual hydrolytic manner. The residual organic oil was distilled at 0.8 mm pressure to give a main fraction, bp 145–147 °C, which by ^1H NMR analysis was shown to be a 1:3.5 mixture of **23** and methylphenyl(1-phenyl-1-propyl)amine (**25**). The latter product was separated in pure form from the starting material by preparative gas chromatography on a 6-ft column of 10% UC-W98 on Chromosorb P: ^1H NMR (CCl_4) δ 0.94 (t, 3 H, J = 7 Hz), 1.92 (quintet, 2 H, J = 7 Hz), 2.68 (s, 3 H), 2.85 (t, 1 H), 6.56–7.7 (m, 10 H); IR (neat) no absorption >3100 cm^{-1}; MS (m/e, 70 eV) 225 (10), 196 (100). Anal. Calcd for $C_{16}H_{19}N$: C, 85.29; H, 8.50; N, 6.22. Found: C, 85.59; H, 8.17; N, 6.27.

An experiment similar to that described for THF, except that a cis,trans mixture of 2,5-dimethyltetrahydrofuran was substituted for THF, led to *no* deuteriation of the recovered **23**.

(2) In Hexane with *n*-Butyllithium. To a solution of 2.0 g (10.2 mmol) of **23** in 50 mL of anhydrous hexane containing 1.7 mL of TMEDA was added 24 mL of 1.25 M of *n*-butyllithium in hexane. Stirring the reaction mixture for 1 h at 25–30 °C and then quenching with D_2O led to *no* deuterium incorporation into the recovered **23**.

Similarly, lithiation of **23** in hexane with *tert*-butyllithium met with no success.

(3) In Hexane with *n*-Butyllithium and Potassium *tert*-Butoxide. A solution of 2.0 g (10.2 mmol) of **23** in 50 mL of hexane was treated successively with 1.2 g (11 mmol) of potassium *tert*-butoxide and with 24 mL of 1.25 M *n*-butyllithium in hexane. The resulting red suspension was stirred for 60 min at 25–30 °C, after which a portion was quenched with D_2O. A ^1H NMR spectral analysis of recovered **23** showed that the benzylic carbon had been monodeuteriated. The balance of the reaction mixture was heated at reflux for 48 h and then worked up hydrolytically. The ^1H NMR spectrum of the organic products showed a mixture of **23** and (diphenylmethyl)methylamine (**33**). Column chromatography on silica gel and elution with a 3:1 (v/v) mixture of ethyl acetate and hexane provided a 66% yield of **33**: mp 38–40 °C (lit.[34] mp 40–41 °C); ^1H NMR ($CDCl_3$) δ 2.55 (s, 3 H), 4.7 (s, 1 H), 7.2–7.5 (m, 10 H); IR (mineral oil) 3400 cm^{-1}.

c. Benzyldiphenylamine (1). To a stirred solution of 3.9 g (15 mmol) of **1** in 40 mL of THF was added 30 mL of 1.6 M *n*-butyllithium in hexane. The reaction mixture, which had promptly turned deep red, was stirred for 48 h and then hydrolyzed. The recovered organic product (3.9 g) was shown by ^1H NMR spectral analysis to contain a 4:1 ratio of rearranged product to **1**. By fractional recrystallizations from ethanol a pure sample of *N*-benzylhydrylaniline (**34**), mp 56–58 °C, was isolated. Its identity was verified by mixture melting point and IR comparisons with an authentic sample.

A similar lithiation of **1** was continued for only 60 min and then quenched with D_2O. The recovered starting material, mp 87–89 °C from ethanol, was shown by ^1H NMR and MS analyses to be fully monodeuteriated as $Ph_2NCHDPh$.

In another experiment, the use of catalytic amounts (5%, molar basis) of *n*-butyllithium with **1** did not lead to any discernible rearrangement after 48 h.

d. *N*-Benzylcarbazole (12). A stirred solution of 1.24 g (5 mmol) of **12** in 30 mL of THF was treated with 10 mL of 1.6 M *n*-butyllithium in hexane. The reaction mixture, which first turned green and then deep red, was allowed to stir for 72 h at 25–30 °C and then hydrolyzed. The crude organic residue was shown by IR, ^1H NMR, and thin-layer chromatographic analyses to contain only starting material. Specifically, no 6-phenyl-5,6-dihydrophenanthridine (**35**), the possible rearrangement product of **12**, could be detected in the reaction mixture.

An authentic sample of **35**, for use in the aforementioned analysis by spectral and TLC means, was synthesized by treating 1.8 g (10 mmol) of phenanthridine in 20 mL of THF with 25 mL of 0.47 M phenyllithium in ether.[28] After 2 h of reaction at 25–30 °C, a hydrolytic workup, *while maintaining a nitrogen atmo-*

(20) Recrystallization, column chromatography, and distillation under reduced pressure were employed to obtain samples that were homogeneous by TLC, ^1H NMR, and GC criteria.

(21) Gribble, G. W.; Hoffman, J. H. *Synthesis* **1977**, 859.
(22) Nakazaki, M. *Bull. Chem. Soc. Jpn.* **1961**, *34*, 334.
(23) Tweedsie, V. L.; Allabashi, J. C. *J. Org. Chem.* **1961**, *26*, 3676.
(24) Cheeseman, G. W. H. *J. Chem. Soc.* **1959**, 452.
(25) Gilman, H.; Eisch, J. J. *J. Am. Chem. Soc.* **1957**, *79*, 4423.
(26) Desai, J. *J. Indian Inst. Sci.* **1924**, 235.
(27) Brown, B. B.; Smith, P. A. S. *J. Am. Chem. Soc.* **1951**, *73*, 2435.
(28) Gilman, H.; Nelson, R. D. *J. Am. Chem. Soc.* **1948**, *70*, 3316.
(29) Nakazaki, M. *Bull. Chem. Soc. Jpn.* **1961**, *34*, 335.
(30) Gribble, G. W.; Hoffman, J. H. *Synthesis* **1977**, 860.
(31) Pielichowski, J.; Kyzio, J. *J. Polym. Sci., Polym. Lett. Ed.* **1975**, *12*, 257.
(32) Looker, J. . *J. Org. Chem.* **1971**, *36*, 2681.
(33) Schonberg, A.; Singer, E. *Chem. Ber.* **1965**, *98*, 812.
(34) Ingold, C. K.; Wilson, C. L. *J. Chem. Soc.* **1933**, 1493.

sphere, gave a colorless oil, which was crystallized from ethanol to yield 6-phenyl-5,6-dihydrophenanthridine (**35**): mp 110–112 °C (under nitrogen); 75% yield; ^{1}H NMR ($CDCl_3$) δ 3.73 (s, 1 H, NH (verified by exchange with D_2O)), 5.26 (s, 1 H, CH), 6.1–7.5 (m, 13 H).

Another lithiation of **12** was conducted as described above, except that the reaction was terminated after 60 min by quenching with D_2O. The recovered *N*-benzylcarbazole was recrystallized from ethanol as needles, mp 117–118 °C. Its ^{1}H NMR spectrum showed a broad, one-proton singlet at 5.26 ppm, corresponding to the grouping, PhCHD, and its mass spectrum had its parent ion at 258.

In further attempts to effect rearrangement, a solution of 2.0 g (8.8 mmol) of *N*-benzylcarbazole in 80 mL of hexane was treated with 960 mg (8.5 mmol) of potassium *tert*-butoxide and 18.7 mL (23.5 mmol) of 1.25 M *n*-butyllithium in hexane. The mixture was stirred for 60 min at 25–30 °C, and then a small portion was withdrawn and quenched with D_2O. The **12** recovered from this sample was shown to be fully monodeuteriated at the benzylic carbon. The rest of the lithiation mixture was heated under reflux for 72 h, and thereupon the whole mixture was hydrolyzed. Only the starting carbazole **12** was isolated (93%) and no 6-phenyl-5,6-dihydrophenanthridine was detected.

In an experiment that was identical with the foregoing, except that octane (bp 126–127 °C) was substituted for hexane, a reaction period of 72 h at reflux also failed to produce any rearrangement to **35**.

e. *N*-Benzyl-1,2,3,4-tetrahydrocarbazole (13). A solution of 2.0 g (7.6 mmol) of **13** in 100 mL of hexane was treated with 970 mg (8.7 mmol) of potassium *tert*-butoxide and 17.2 mL of 1.33 M *n*-butyllithium in hexane. After the red suspension was stirred for 60 min at 25–30 °C, a small portion was withdrawn and treated with D_2O. The ^{1}H NMR spectrum of the recovered **13** showed only one proton on the benzylic carbon. Heating the rest of the lithiation mixture at reflux for 100 h and hydrolytic workup gave a 90% recovery of **13** and no detectable rearrangement product.

f. *N*-Benzyl-1,1a,2,3,4,4a-*cis*-hexahydrocarbazole (21). A solution of 2.0 g (7.6 mmol) of **21** in 70 mL of hexane was treated with 17.2 mL (23 mmol) of 1.34 M *n*-butyllithium in hexane and 950 mg (8.5 mmol) of potassium *tert*-butoxide. The mixture was stirred for 60 min at 25–30 °C, and then a sample was treated with D_2O. (The **21** recovered from this sample was shown to be monodeuteriated at the benzylic carbon.) The balance of the reaction mixture was stirred under reflux for 96 h and then hydrolyzed. The recovered organic product was analyzed by ^{1}H NMR spectroscopy and was shown to contain **21** and a new component. Separation of the components was effected by dissolving the oil in anhydrous MeOH, passing dry HCl gas into the methanolic solution until reaching pH 3.0, evaporating the methanol, and extracting the residue with ether. Upon evaporation of the ether extract the residual oil was subjected to column chromatography on silica gel by eluting with a 99:1 (v/v) hexane–ether gradient. In this manner, 800 mg (52%) of pure 6-phenyl-1,1a,2,3,4,4a,5,6-*cis*-octahydrophenanthridine (**22**) was isolated as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 1.2–2.8 (m, 9 H), 3.3–3.8 (m, 2 H), 5.15 (d, 2 H), 6.8–7.7 (m, 9 H); IR (mineral oil) 3360 cm^{-1}; MS (*m/e*) 263 (M^+). Anal. Calcd for $C_{19}H_{21}N$: C, 86.64; H, 8.04; N, 5.32. Found: C, 86.58; H, 8.13; N, 5.58.

g. *N*-(2-Phenylethyl)carbazole (9). A solution of 2.0 g (7.4 mmol) of **9** in 80 mL of hexane was admixed with 900 mg (8 mmol) of potassium *tert*-butoxide and 14 mL (22.2 mmol) of 1.6 M *n*-butyllithium in hexane. The reaction mixture, which turned brick red immediately, was stirred at 25–30 °C for 60 min and a sample withdrawn to test for metalation in the usual way. The recovered **9** showed no deuterium incorporation.

The metalation mixture was then set at reflux for 72 h and then hydrolyzed. The organic layer was found to contain only styrene and carbazole, mp 245–246 °C (95%).

h. *N*-(3-Phenylpropyl)carbazole (19). A solution of 3.0 g (10.5 mmol) of **19** in 100 mL of hexane was admixed with 1.6 mL of TMEDA (11 mmol) and 10.5 mL (11.5 mmol) of 1.1 M *sec*-butyllithium in hexane. The mixture was stirred for 60 min at 25–30 °C and then tested by a D_2O quench for lithiation. The test was negative. The reaction mixture was then stirred at reflux for 240 h, during which time a 10.5-mL portion (11.5 mmol) of *sec*-butyllithium was added every 48 h. Hydrolytic workup and column chromatographic separation of the rearrangement product on silica gel with a 9:1 (v/v) chloroform–hexane eluent provided 150 mg (6.6%) of pure 5-phenyl-5,6,7,8-tetrahydrodibenzo[*e*,*g*]-azocine (**20**) as an oil: ^{1}H NMR ($CDCl_3$) δ 1.1–2.3 (m, 4 H), 3.3–3.6 (m, 1 H, NH), 4.4–4.8 (m, 1 H), 6.3–7.3 (m, 13 H); IR (neat) 342 cm^{-1}. Anal. Calcd for $C_{21}H_{19}N$: C, 88.42; H, 6.66. Found: C, 88.37; H, 6.61.

A reaction of **19** with potassium *tert*-butoxide and *n*-butyllithium in hexane led to neither metalation nor rearrangement, even after 72 h at reflux. The starting material was recovered in 92% yield.

i. *N*-(2-Chloroethyl)carbazole (8). A solution of 2.0 g (8.7 mmol) of **8** in 60 mL of THF was cooled to −70 °C and then treated with 134 mg (19.7 mg atom) of small, freshly cut pieces of lithium metal. The mixture was stirred for 60 min at −70 °C and then 12 h at 20–25 °C. Hydrolytic workup gave 1.36 g (94%) of carbazole, mp 245–246 °C.

j. *N*-Benzyl-9,9-dimethyl-9,10-dihydroacridine (14). A solution of 1.0 g (3.4 mmol) of **14** in 40 mL of hexane was treated with 300 mg (3.5 mmol) of potassium *tert*-butoxide and 4.6 mL (10.5 mmol) of 2.3 M *n*-butyllithium in hexane. The resulting brick red suspension was stirred for 60 min at room temperature and a sample then quenched with D_2O. By ^{1}H NMR and MS analyses the recovered **14** was shown to be fully monodeuteriated at the benzylic carbon. The balance of the metalation mixture was stirred under reflux for 72 h. Hydrolytic workup led to the recovery of **14** in 87% yield but gave no sign of any other products.

k. *N*-Benzyl-*o*,*o*′-iminodibenzyl (27). (1) In THF with *n*-Butyllithium. A solution of 2.0 g (7 mmol) of **27** in 50 mL of anhydrous THF was treated with 16.5 mL of 1.27 M *n*-butyllithium in hexane. The color changed from yellow to red within 15 min. After 60 min at 20–25 °C the D_2O quench test showed that recovered **27** was fully monodeuteriated at the benzylic carbon. The balance of the reaction mixture was stirred at 25–30 °C for 72 h. Hydrolytic workup yielded a yellow oil, which was recrystallized from an ethyl acetate–hexane pair to give 1.6 g (88%) of 6-ethyl-6-phenyl-5,6,11,12-tetrahydrodibenzo[*b*,*f*]azocine (**36**): mp 124–125 °C; ^{1}H NMR ($CDCl_3$) δ 2.2–4.3 (m, 10 H), 6.3–7.5 (m, 13 H); IR (mineral oil) 3450 cm^{-1}; MS (*m/e*) 313 (M^+). Anal. Calcd for $C_{23}H_{23}N$: C, 88.17; H, 7.34. Found: C, 88.21; H, 7.39.

(2) In Hexane with *n*-Butyllithium and Potassium *tert*-Butoxide. Heating 2.0 g (7 mmol) of **27** with 800 mg (7 mmol) of potassium *tert*-butoxide and 21 mmol of *n*-butyllithium in 80 mL of hexane for 72 h led to the isolation upon hydrolysis of 1.6 g (80%) of 6-phenyl-5,6,11,12-tetrahydrodibenzo[*b*,*f*]azocine (**28**); mp 105–106 °C from EtOAc–hexane (lit.[35] mp 105–106 °C).

(1) 9-(Diphenylamino)fluorene (15). A solution of 1.0 g (3 mmol) of **15** in 150 mL of hexane was treated with 350 g (3.1 mmol) of potassium *tert*-butoxide and 5.6 mL of 1.6 M *n*-butyllithium in hexane. After being stirred for 60 min, a sample was quenched with D_2O and the recovered **15** shown to be deuteriated at the 9-fluorenyl carbon. Allowing the reaction mixture to stir under reflux for 96 h led, upon workup, only to the recovery of starting **15** (89%).

Other attempted rearrangements to 9-anilino-9-phenylfluorene (**18**) were uniformly unsuccessful: (1) *n*-butyllithium in toluene at reflux for 96 h; (2) *n*-butyllithium in mesitylene at reflux; (3) potassium hydride in refluxing mesitylene; (4) potassium *tert*-butoxide and *n*-butyllithium at 200 °C.

However, heating **15** with an equimolar amount of KH (4 mmol) at 300 °C for 3 h gave, upon hydrolytic workup and column chromatographic separation on silica gel with a $CHCl_3$–hexane gradient, 69% of diphenylamine, mp 51–53 °C, and 78% of fluorene, mp 112–114 °C.

m. 9-Anilino-9-phenylfluorene (18). Attempts to induce rearrangement of **18** either by heating in hexane with potassium *tert*-butoxide and *n*-butyllithium or by heating in THF with *n*-butyllithium were unsuccessful. Only **18** was recovered (91–93%).

However, upon dissolving 1.0 g (3 mmol) of **18** in 30 mL of mesitylene and adding 7.3 mL of 1.6 M *n*-butyllithium, a suspension was formed. This mixture was stirred under reflux for

(35) Van Binst, G. *Org. Magn. Reson.* **1976**, *8*, 618.

72 h and then hydrolyzed. Column chromatography of the organic product on silica gel (1:1 (v/v) of $CHCl_3$–hexane) provided aniline and 9-phenylfluorene: 560 mg (78%; mp 146–147 °C.

n. 9-(Methylphenylamino)fluorene (16). Heating **16** in hexane with potassium *tert*-butoxide and *n*-butyllithium caused metalation at the 9-fluorenyl carbon but led to no rearrangement, even when the reagents were heated in refluxing mesitylene.

o. Diphenyl(diphenylmethyl)amine (17). Although this compound was metalated at the benzhydrylic carbon by *n*-butyllithium with either THF or potassium *tert*-butoxide, no rearrangement ensued.

Likewise, when the expected rearrangement product of **17**, namely *N*-(triphenylmethyl)amine (**32**), was heated with *n*-butyllithium, no rearrangement to **17** was observed.

Synthesis of Authentic 6-Phenyl-1,1a,2,3,4,4a,5,6-*cis*-octahydrophenanthridine (22). A solution of 5 g (32 mmol) of 1-phenylcyclohexene in 125 mL of ether was admixed with 125 mL of a saturated aqueous solution of $NaNO_2$. The mixture was rapidly stirred at 0 °C, while dilute aqueous H_2SO_4 was added dropwise. A deep blue color developed; addition of the acid was continued until the color changed to yellow. The ether layer was separated, dried over anhydrous $MgSO_4$, and then treated with a 50 mL solution of sodium methoxide in MeOH (prepared from 1.2 g of sodium metal and 50 mL of MeOH) for 15 min. The reaction mixture was then poured into water, and then ether was added. The separated dried ether layer was evaporated and the organic residue distilled at 3 mm pressure to give 75% of 1-nitro-2-phenylcyclohexene, bp 145–150 °C.[35]

A suspension of 5.0 g of $LiAlH_4$ in 100 mL of ether was stirred at 0 °C, while a solution of 8.0 g (41.5 mmole) of 1-nitro-2-phenylcyclohexene in 50 mL of ether was introduced dropwise. The mixture was then stirred for 24 h at 25–30 °C and hydrolyzed. Acid extraction of the ether layer and basifying the extract gave 2.0 g of *cis*-1-amino-2-phenylcyclohexane. Since its ^1H NMR spectrum was indicative of high purity, it was used directly.

The foregoing amine (2.0 g) was dissolved in 20 mL of anhydrous pyridine and 2.0 mL of benzoyl chloride added dropwise. After the mixture was heated on the steam bath for 60 min, it was poured into cold water. The water suspension was extracted with ether, and the ether extract was dried and evaporated. Crystallization of the residue from petroleum ether afforded 2.2 g of *cis*-1-benzamido-2-phenylcyclohexane, mp 153–155 °C.

This benzamido derivative (1.0 g) was dissolved in 3.0 g of polyphosphoric acid, heated to 155 °C, and then admixed with 3.0 g of $POCl_3$. After the mixture was heated for 4 h at 155–160 °C, it was cooled and then quenched with an aqueous Na_2CO_3 solution. Usual acid-extraction separation yielded 500 mg of 6-phenyl-1,1a,2,3,4,4a-*cis*-hexahydrophenanthridine, mp 160–161 °C (from ethanol).

Reduction of this phenanthridine with $LiAlH_4$ in ether solution was conducted in the manner described for *cis*-1-nitro-2-phenylcyclohexene. The resulting 6-phenyl-1,1a,2,,4,4a,5,6-*cis*-octahydrophenanthridine was isolated as a colorless oil (65%) and had spectral properties identical with those exhibited by **22**, the rearrangement product from *N*-benzyl-1,1a,2,3,4,4a-*cis*-hexahydrocarbazole (**21**, section f).[35]

Acknowledgment. We appreciate the support of this research provided by Grants CA-10743 and CA-28335 from the National Cancer Institute of the Public Health Service. Valuable experimental help was provided by Drs. Tonson Abraham, Mohammad Behrooz, and Andrzej Piotrowski.

Registry No. **1**, 606-87-1; **8**, 1140-35-8; **9**, 95249-59-5; **11**, 103-83-3; **12**, 19402-87-0; **13**, 17017-63-9; **14**, 110045-74-4; **15**, 110045-75-5; **16**, 1989-30-6; **17**, 14158-21-5; **18**, 110045-76-6; **19**, 110045-73-3; **20**, 110045-77-7; **21**, 65673-87-2; **22**, 110115-18-9; **23**, 614-30-2; **25**, 74484-47-2; **27**, 13080-72-3; **28**, 30319-16-5; **32**, 5824-40-8; **33**, 3963-62-0; **34**, 1865-12-9; **35**, 56243-27-7; **36**, 110045-78-8.

Group 14† Organometallic Reagents. 4.[1] Stereodynamics of Substituted Dioxastannolanes. Carbon-13 and Tin-119 NMR Studies

Claudio Luchinat

Laboratorio di Chimica Inorganica e Bioinorganica, Dipartimento di Chimica, Universita' di Firenze, 50121 Florence, Italy

Stefano Roelens*

C.N.R.—Centro di Studio sulla Chimica e la Struttura dei Composti Eterociclici e loro Applicazioni, 50121 Florence, Italy

Received August 26, 1986

The stereodynamics of some ring-substituted dioxastannolanes have been investigated by ^{13}C and ^{119}Sn dynamic NMR spectroscopy in concentrated chloroform solution and compared with those of the unsubstituted dioxastannolane. Results show that dioxastannolanes are dynamic species, subject to complex equilibria. Substitution on the ring carbons allowed discrimination between intermolecular aggregation equilibria, which form mostly dimers along with higher oligomers, and an intramolecular process within the dimer. A mechanism is proposed for the latter process that accounts for the inversion of configuration at tin and implies an exchange of tin atoms between diol moieties. The high-energy barrier for the intramolecular process suggests that dioxastannolanes in solution have a dimeric structure with two apical and one equatorial Sn–O bonds at room temperature but become fluxional at higher temperatures. The stereochemical and reactional implications of these findings are discussed.

Introduction

Organostannoxanes are useful intermediates in organic synthesis because of their reactivity and selectivity toward electrophilic reagents.[2] These features have been ascribed to the tendency of stannoxanes, in particular dioxastannolanes, to associate to dimers and higher aggregates that can act as templates in a reaction. This effect has been proposed to account for the organotin-mediated acylation, alkylation, and oxidation of polyhydroxy compounds such

† In this paper the periodic group notation is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

(1) Part 3: Ricci, A.; Roelens, S.; Vannucchi, A. *J. Chem. Soc., Chem. Comm.* **1985**, 1457.

(2) For a recent review, see: David, S.; Hanessian, S. *Tetrahedron* **1985**, *41*, 643.

0022-3263/87/1952-4444$01.50/0