THE JOURNAL OF Organic Chemistry

VOLUME 52, NUMBER 20

OCTOBER 2, 1987

Carbon-Skeletal [1,2] Anionic and Radical Sigmatropic Rearrangements: Group Migratory Aptitudes as a Probe of Charge Type in the 1,2-Shifts of β-Phenyl-β-(2-pyridyl)- and β-Phenyl-β-(4-pyridyl)ethyl Systems[1]

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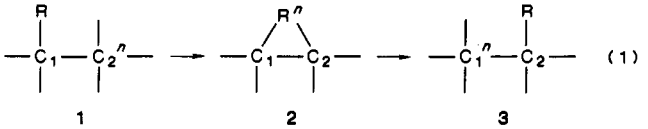
Received December 15, 1986

In order to probe the occurrence and relative ease of carbon-skeletal [1,2] sigmatropic rearrangements of the free-radical, anionic, or radical-anionic type, derivatives of the β,β-diphenyl-β-(2-pyridyl)- and the β,β-diphenyl-β-(4-pyridyl)ethane systems, $PyPh_2CCH_2E$ (A), were treated with reagents expected to generate radical or anionic sites. The ensuing, competitive [1,2]-shifts of the phenyl and/or pyridyl groups were then used as a diagnostic sign of the mechanism of rearrangement. Both the treatment of A (E = *p*-tolyl) with MeLi or KH and the reaction of A (E = Cl) with sodium or lithium in donor solvents caused an exclusive [1,2]-pyridyl shift. Gas chromatographic and mass spectral analyses were able to place the limit of any [1,2]-phenyl shift as under 0.5%. In such alkali metal reactions, persistent aromatic radical-anions were detected by ESR spectroscopy until the completion of the reaction. Such signals and the significant amounts of carbon-carbon bond cleavage products support the formation of pyridyl radical-anions as precursors for such cleavages and [1,2]-pyridyl rearrangements. That such radical-anions could lead to spiro intermediates that promote the [1,2]-pyridyl migrations wins corroboration from the finding that the methiodide of 1-chloro-2-methyl-2-(4-pyridyl)propane can be reduced with lithium in THF to yield the isolable 1,1,6-trimethyl-6-azaspiro[2.5]octa-4,7-diene. The same two chlorides of A responded differently under other rearrangement conditions: (1) in preparing such chlorides from the corresponding alcohols, $PyPh_2CCH_2OH$, with thionyl chloride, the 4-pyridyl isomer underwent a Wagner-Meerwein rearrangement with exclusive [1,2]-phenyl migration; the 2-isomer underwent normal displacement of OH by Cl; (2) toward the free-radical reducing agent, $(n\text{-}Bu)_3SnH$, the 2-chloro isomer underwent both [1,2]-phenyl and -pyridyl shifts, while the 4-chloro isomer underwent neither reduction nor rearrangement; it simply induced the formation of hexa-*n*-butylditin. A similar reducing action was observed with bis(1,5-cyclooctadiene)nickel. These observations are analyzed with the aid of Hückel molecular orbital theory and the rearrangements observed with reducing agents are assessed in terms of three types of mechanisms: (1) authentic [1,2]-anionic shifts; (2) authentic [1,2]-free-radical shifts; and (3) competing electron transfer from the metal to the chloride center or from the metal to the pyridyl ring, which permits anionic rearrangements to compete with rearrangements mediated by radical-anion or dianions, which latter processes form the crucial spiro intermediate by intramolecular nucleophilic displacement on the CH_2Cl group.

Carbon-skeletal [1,2] sigmatropic shifts are one of the most commonly encountered rearrangements in organic chemistry, possibly because they can proceed by a variety of mechanisms (eq 1). In Wagner-Meerwein 1,2-shifts



(1)

cationic carbon appears to foster the shift (**1**, $n = +1$);[4] in Grovenstein-Zimmerman rearrangements anionic carbon is involved (**1**, $n = -1$),[5] and even radical carbon centers can undergo skeletal reorganization (**1**, $n = 0$).[6] Molecular orbital calculations offer some useful insights into the relative ease with which such rearrangements might be expected to take place.[7] Formation of the intermediate or transition state **2** for such [1,2]-shifts (**1** → **3**, eq 1)

(1) Part 23 of the series "Rearrangements of Organometallic Compounds". Previous part: *J. Org. Chem.* **1984**, *49*, 4631.
(2) Present address: Eastman Kodak Company, Rochester, New York 14692.
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(4) (a) Wagner, G. Zh. *Russ. Fiz.-Khim. O-va.* **1899**, *31*, 680. (b) Meerwein, H.; van Emster, K. *Chem. Ber.* **1920**, *53*, 1815.
(5) (a) Grovenstein, E. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 313. (b) Zimmerman, H. A.; Zweig, A. *J. Am. Chem. Soc.* **1961**, *83*, 1196.
(6) Kaplan, L. *J. Am. Chem. Soc.* **1966**, *88*, 4531.
(7) Zimmerman, H. A.; Zweig, A. *J. Am. Chem. Soc.* **1961**, *83*, 1196.

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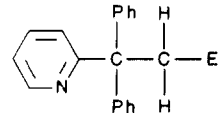
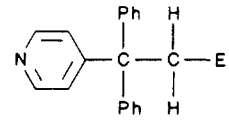
involves putting zero, one, or two electrons into a moderately antibonding orbital, depending upon whether the rearrangement is of the carbenium, free-radical or carbanionic charge type (n = +1, 0, or −1 in eq 1). Consequently, all factors being comparable, the ease of attaining **2** and thus a 1,2-sigmatropic rearrangement should decrease in the order[7] carbenium ion > free radical > carbanion. These theoretical considerations are of especial interest for those situations where rearrangements of different charge type might compete with each other.

In the present study we have sought to test the utility and validity of these HMO predictions for [1,2]-sigmatropic shifts that could involve either free-radical or carbanionic intermediates. In the well-known Grovenstein–Zimmerman rearrangement, β,β,β-triarylethyl halides undergo a skeletal rearrangement to (α,α,β-triarylethyl)-metallics upon treatment with alkali metals in donor solvents.[5] Although such processes have generally been interpreted as proceeding via carbanions, the possible role of free-radical intermediates in certain instances has remained in question.[8] We hoped to make a distinction between these two shifts of different charge type by observing differing migratory aptitudes of the carbon groups (R in eq 1) undergoing rearrangement. As our test substrates we chose the β,β-diphenyl-β-(2-pyridyl)- and β,β-diphenyl-β-(4-pyridyl)ethyl systems **4** and **5**, which were treated under conditions favoring free-radical or anionic reactions. The competition thereupon observed between



4a: E = Cl
4b: E = 4-tolyl
4c: E = I



5a: E = Cl
5b: E = 4-tolyl

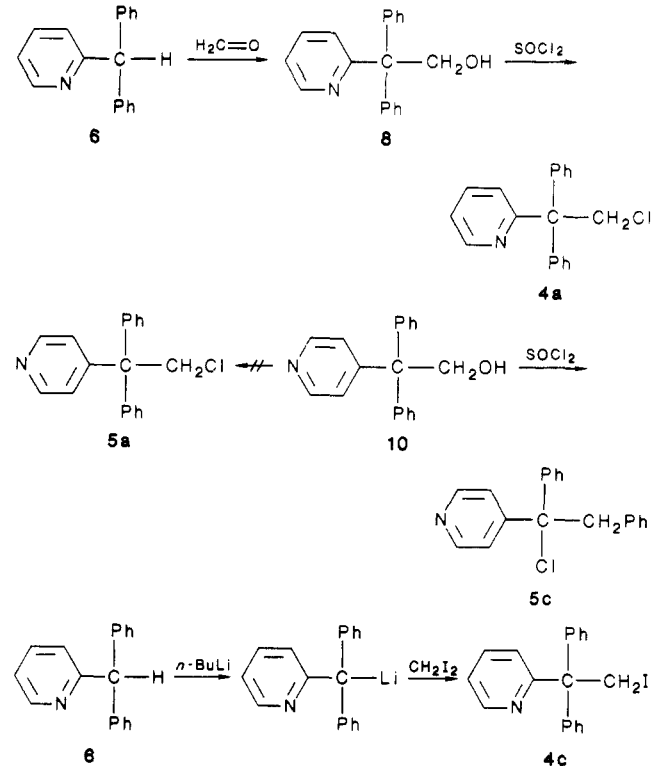
the phenyl and pyridyl groups in the ensuing 1,2-skeletal shift has then served as a probe of the charge type in eq 1. In addition, by the use of model reactions, an attempt was made to decide whether structures of type **2** were intermediates or transition states in such 1,2-shifts and what charge type n might favor the formation of **2**.

Results

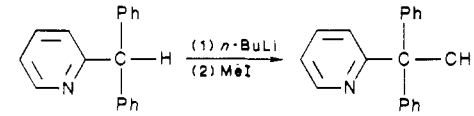
Preparation of the β,β-Diphenyl-β-(2-pyridyl)- and β,β-Diphenyl-β-(4-pyridyl)ethyl Substrates for Rearrangement. It was hoped that both the 2- and 4-(2-chloro-1,1-diphenylethyl)pyridines (**4a** and **5a**) could be prepared in a similar manner, namely, the reaction of the corresponding benzhydrylpyridine with formaldehyde under basic conditions to generate the 2-substituted ethanols **8** and **10** and then the reaction of these alcohols with thionyl chloride to form the desired chlorides (e.g., Scheme I for **4a**). This approach did in fact yield **4a** according to plan, but with alcohol **10**, treatment with thionyl chloride led to a skeletal rearrangement, in a Wagner–Meerwein fashion, and provided instead the product of a [1,2]-phenyl shift, **5c**. However, both chlorides could be obtained from their corresponding benzhydrylpyridines by generating the anions from **6** and **7** and adding methylene chloride (Scheme I). In a similar manner, the requisite iodide, **4c**, could also be obtained without skeletal rearrangement.

(8) Eisch, J.; Kovacs, C. A. *J. Organomet. Chem.* **1970**, *25*, C33. In that publication, what we consider to be 4-(2-chloro-1,1-diphenylethyl)pyridine has now been identified as 4-(1-chloro-1,2-diphenylethyl)pyridine. In this article we show how this isomer was formed in the attempted formation of **5a** from alcohol **10**. Because of this erroneous assumption (i.e., that **5c** was **5a**) we had concluded that free radicals might be involved.

Scheme I

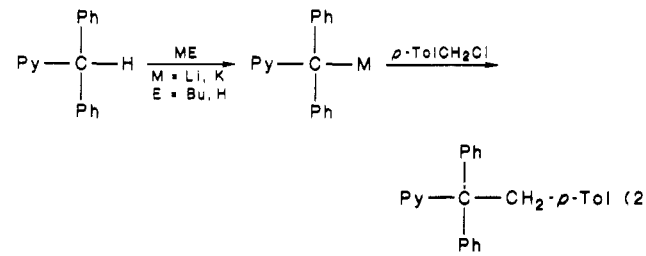


Scheme II



These relationships are illustrated in Scheme I.

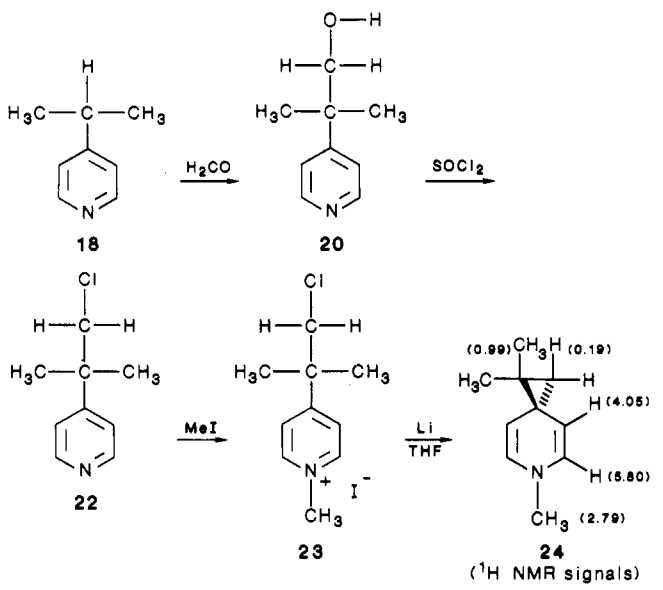
Finally, the preparation of both 2-(4-methylphenyl)-1,1-diphenyl-1-(2-pyridyl)ethane (**4b**) and 2-(4-methyl)-1,1-diphenyl-1-(4-pyridyl)ethane (**5b**) was carried out by simply coupling the metal salts (Li or K) of the (diphenylmethyl)pyridines **6** and **7** with 4-methylbenzyl chloride (eq 2).



Preparation of the Potential Rearrangement Products. The unambiguous syntheses of the possible diphenyl(2-pyridyl)ethanes that could result from these rearrangement reactions, namely 2-(1,1-diphenylethyl)-pyridine (**11**), 2-(2,2-diphenylethyl)pyridine (**12**), and 2-(1,2-diphenylethyl)pyridine (**13**), were achieved by lithiating the appropriate 2-methylpyridine (either 2-(diphenylmethyl)pyridine, 2-methylpyridine itself, or 2-benzylpyridine) with n-butyllithium and then quenching the 2-(lithiomethyl)pyridine derivative with the necessary halide (methyl iodide, diphenylmethyl bromide, or benzyl chloride). The synthesis of the illustrative 2-(1,1-diphenylethyl)pyridine (**11**) is depicted in Scheme II.

In order to gain assurance that the starting 2- and 4-(2-halo-1,1-diphenylethyl)pyridines did not themselves undergo a cationic rearrangement in the reaction medium

Scheme III



of THF, these compounds were individually dissolved in anhydrous THF and allowed to stand for 24 h. In a blank workup, such solutions were then treated with H_2O, and the THF layer was then separated and dried. Removal of the solvent yielded only the unhydrolyzed and unrearranged starting **4a** and **5a**.

In like manner, the syntheses of the possible diphenyl(4-pyridyl)ethanes were conducted in straightforward steps. Again, 4-(1,1-diphenylethyl)pyridine (**14**), 4-(2,2-diphenylethyl)pyridine (**15**), and 4-(1,2-diphenylethyl)pyridine (**16**) proved to be readily discernible from each other by their spectral and chromatographic properties.

Preparation of the β,β-Dimethyl-β-(2-pyridyl)- and β,β-Dimethyl-β-(4-pyridyl)ethyl Chlorides and the Model for a Spiro Intermediate. Both 2-isopropyl- and 4-isopropylpyridines (**17** and **18**) were individually added to formaldehyde and the resulting 2-methyl-2-(2-pyridyl)- and 2-methyl-2-(4-pyridyl)-1-propanols (**19** and **20**) then converted to their chlorides (**21** and **22**) by means of thionyl chloride. The synthesis of the 4-pyridyl isomer is given in Scheme III.

Compound **22** was then quaternized with methyl iodide, and the methiodide **23** was treated in a THF suspension at 0 °C with lithium metal. From this reaction 1,1,6-trimethyl-6-azaspiro[2.5]octa-4,7-diene (**24**) was isolated as an unstable oil. Its proton NMR spectrum, however, was in excellent accord with its cyclopropylic, enaminic structure (Scheme III).

Rearrangements of 2-(2-Chloro-1,1-diphenylethyl)pyridine (4a) and 4-(2-Chloro-1,1-diphenylethyl)pyridine (5a) with Alkali Metals. The individual reactions of **4a** and **5a** in diethyl ether or in tetrahydrofuran, either at low temperatures or 25 °C, led in each case to a single type of [1,2] shift: an exclusive pyridyl shift. By combined gas chromatographic and mass spectral analyses, used in conjunction with authentic samples of the possible rearrangement products, it could be concluded that if any [1,2]-phenyl migration product were formed in these reactions, such a component would have to be present in less than 0.5% (cf. Tables I and II). Workup of such reaction mixtures with D_2O yielded deuteriated rearrangement products (**12a** and **16a**, eq 3 and 4). Small to significant proportions of unrearranged reduction products **11** and **14** were formed in each reaction, but it worthy of note that deuteriolytic workup gave these products in their undeuteriated form. Therefore, they must have acquired their hydrogen during the reaction proper.

Table I. Composition of the Hydrolysis Products from the Reaction of 2-(2-Chloro-1,1-diphenylethyl)pyridine (4a) with Lithium in Tetrahydrofuran at −65 °C as a Function of Time

time, min[a]	$PyPh_2CCH_2Cl$ (**4a**)	% Ph_2CHCH_2Py (**12**)	% $PyPh_2CCH_3$ (**11**)
60	90.5	6.0	3.5[b]
75	89.5	7.2	3.3
90	87.5	7.5	5.0
180	31.0	62.0	7.0
195	29.6	63.0	7.4
210	30.0	61.0	9.0
240[c]	18.0	70.0	12.0

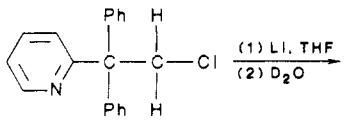
[a] Aliquots were withdrawn with a gas-tight syringe after the stated time and hydrolyzed with D_2O. The organic products were examined by GLPC and ^1H NMR analyses. [b] At no time did the proportion attain a maximum and then decrease (such a buildup would have betokened that **11** was derived from a rapidly formed rearrangement precursor, which then rearranged at a slower rate). [c] The end composition of a reaction conducted at 25 °C for 24 h (500 mg of **4a**, 2.2 equiv of lithium, and 10 mL of THF) was the following: 18% of **4a**, 69.4% of **12**, and 14.2% of **11**; in addition, there was 0.97% of 2-benzhydrylpyridine and 1.4% of 1,1-diphenyl-2-(2-pyridyl)ethene. For a comparable run conducted at 25 °C in diethyl ether for 72 h, the end composition was: 0% of **4a**, 55.5% of **12**, 39.1% of **11**, and 3.83% of 2-benzhydrylpyridine. All gas chromatographic analyses were conducted with a Hewlett-Packard instrument, Model 5880, and fractions identified by a H-P mass spectrometer, Model 5992.

Table II. Compositions of the Hydrolysis Products from the Reaction of 4-(2-Chloro-1,1-diphenylethyl)pyridine (5a) with Sodium Metal and with Lithium Metal in Donor Solvents at 25 °C after Completion of Reaction

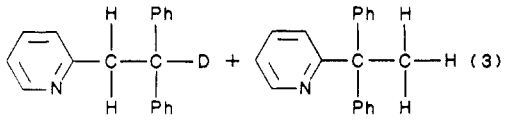
products of metal reacn	Na in THF, 48 h	Na in Et_2O, 72 h	Li in THF, 48 h	Li in Et_2O, 72 h
$4\text{-}PyPh_2C\text{-}CH_2Cl$ (**5a**)	1.4	0.0	0.0	0.0
$4\text{-}Py\text{-}CH_2\text{-}CHPh_2$ (**16**)	80.8	87.4	73.8	73.3
$4\text{-}PyPh_2C\text{-}CH_3$ (**14**)	0.6	0.0	4.5	1.2
$4\text{-}PyPh_2CH$	0.9	2.1	2.7	0.2
Ph_2CH_2	8.3	6.5	15.5	14.5
$4\text{-}PyCH_3$[a-c]	8.0	5.0	3.5	10.8

[a] There were minor components among the reaction products that arose from various solvent–solute–metal interactions; these are neglected in presenting the compositions of these reactions, and the above components are normalized to 100%. [b] The values given for the 4-picoline are usually low, since some of this component was lost upon removal of solvent. [c] All analyses were conducted with a Hewlett-Packard gas chromatograph, Model 5880, and the identity of each sample was verified by collection and measurement of its mass spectrum, ^1H NMR spectrum, and IR spectrum.

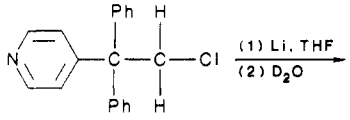
The course of rearrangement in the 2-pyridyl system, **4a**, was followed both by ESR spectroscopy and by the hydrolytic quenching of samples from the reaction mixture over time. A sample of the reaction mixture, withdrawn at −65 °C and free of suspended lithium, showed an intense ESR signal, 25 G in width, that gradually decreased over 2 h at 0 °C. The analysis of the hydrolyzed samples showed a gradual increase in the amount of **11** and **12** (Table I) and no buildup of **11** early in the reaction. From this hydrolysis study one can conclude that the intermediate required for rearrangement was consumed very rapidly as it was formed. However, the ESR data point to a relatively long-lived paramagnetic intermediate, probably of the aromatic radical–anionic type.



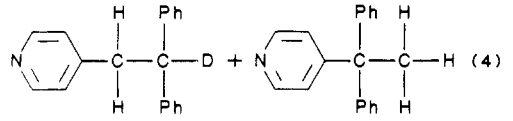
4a



12a 11



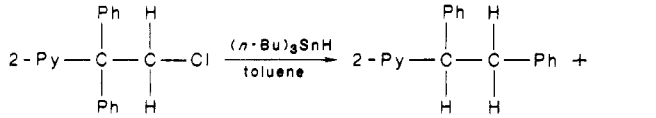
5a



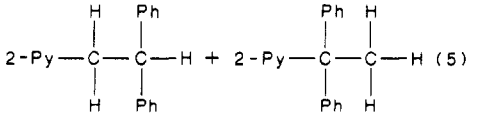
16a 14

In this same connection it is important to note that small but reproducible amounts of the benzhydrylpyridines were formed in these alkali metal reactions, even though starting chlorides **4a** and **5a** were free of them. In addition, reactions of isomer **5a** with these metals produced considerable amounts of diphenylmethane and 4-picoline (Table II). Such products must have resulted from carbon–carbon bond-cleavage reactions proceeding concurrent with the rearrangements.

Rearrangements and Reductions of 2-(2-Halo-1,1-diphenylethyl)pyridines 4a and 4c and of 4-(1-Chloro-1,2-diphenylethyl)pyridine and 4-(2-Chloro-1,1-diphenylethyl)pyridine (5c and 5a) with Tri-*n*-butyltin Hydride and with Nickel(0) Complexes. Isomeric chlorides **4a** and **5a** differed greatly in their ease of reduction or rearrangement with tri-*n*-butyltin hydride in toluene. Compound **4a** underwent reaction slowly at 25 °C to give a 65:35 ratio of **12**/**13** but more rapidly at 110 °C to yield a 58:42 ratio. In both runs, about 8% of the unrearranged reduction product **11** was also formed (eq 5).

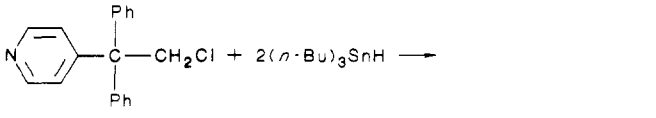


12



13 11

In contrast, isomer **5a** could not be reduced or induced to rearrange even after 72 h of heating it with tri-*n*-butyltin hydride at reflux in toluene. But at the end of this reaction, the hydride had been transformed into hexa-*n*-butylditin (eq 6). However, isomeric chloride **5c** underwent



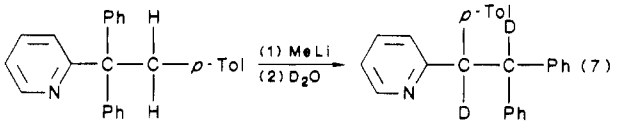
5a

(*n*-Bu)$_3$SnSn(*n*-Bu)$_3$ + H_2 + **5a** (6)

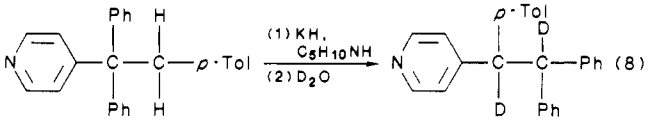
extraordinarily facile reduction to 1,2-diphenyl-1-(4-pyridyl)ethane. Thus, in such a well-documented free-radical reduction process,[9] these three isomeric chlorides underwent reaction in sharply decreasing ease: **5c** > **4a** > **5a**.

It is noteworthy that nickel(0) complexes display a reactivity and pattern parallel to the tin hydride: **5c** undergoes very ready reduction to 1,2-diphenyl-1-(4-pyridyl)ethane with bis(1,5-cyclooctadiene)nickel; although **4a** does not react with (Cod)$_2$Ni or (Cod)(bpy)Ni at 25 °C in THF, its iodo counterpart (**4c**) does react with (Cod)(Bpy)Ni to undergo phenyl vs. pyridyl migration in a 60:40 ratio (**12**/**13**). Only a small amount of reduced, unrearranged **11** was found. When workup with D_2O was conducted, all three products were found to be free of deuterium.

Rearrangements of Anions Formed from 2-(4-Methylphenyl)-1,1-diphenyl-1-(2-pyridyl)ethane (4b) and 2-(4-Methylphenyl)-1,1-diphenyl-1-(4-pyridyl)-ethane (5b). Anions could be produced from the 2-pyridyl isomer **4b** by methyllithium in THF and from the 4-pyridyl isomer **5b** by potassium hydride in THF, with catalytic potassium piperidide. Both anions underwent a prompt 1,2-shift of exclusively the pyridyl groups (eq 7 and 8).



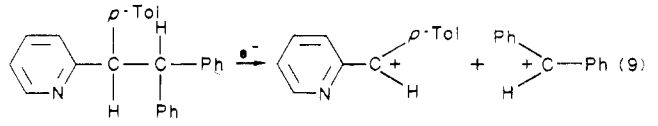
4b 25a



5b 26a

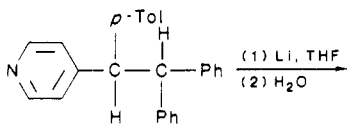
Potassium hydride had to be substituted for methyllithium in abstracting a benzylic proton from **5b**, since the lithium reagent preferentially added, instead, to the azomethine linkage in **5b**. Also, it should be noted that because both benzhydrylic protons in **25** and **26** are quite acidic, the products became dimetalated in the reaction mixture.

The proof of structure for **25** and **26** was established in two ways: (1) clean mass spectral fragmentation at 70 eV into the diphenylmethyl and pyridyl(tolyl)methyl cations (eq 9), and (2) the cleavage of the central ethane C–C bond

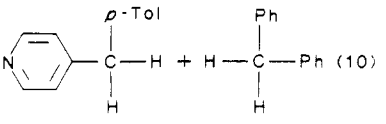


25

by lithium in THF and the identification of the products (eq 10).[10]

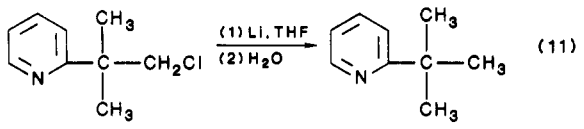


26



(9) Kuivila, H. G. *Acc. Chem. Res.* 1968, *1*, 299.

Attempted Rearrangements of 1-Chloro-2-methyl-2-(2-pyridyl)propane (21) and 1-Chloro-2-methyl-2-(4-pyridyl)propane (22). Both of these chlorides reacted readily with lithium in THF solution at −65 °C. However, in neither case was a product other than the unrearranged *tert*-butylpyridine found (eq 11).



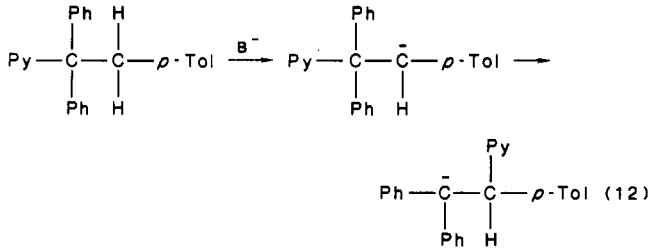
21 (or 22) (or 4-isomer) (11)

Discussion

For a concerted, [1,2]-carbanionic shift, simple Hückel molecular orbital energy comparisons would predict that a 2-pyridyl group or 4-pyridyl group would migrate from a carbon β to a carbanion, in preference to a phenyl group. As depicted in **27** and **28**, the intermediate or transition state is of particularly low energy for two reasons: (1) the bridging α- or γ-carbon of the pyridyl has a relatively low π-electron density in its ground state and hence is more receptive to nucleophilic attack,[11] and (2) the negative charge borne by the bridging pyridyl group in **26** and **27** can be partially localized onto an electronegative atom (N).

27 **28**

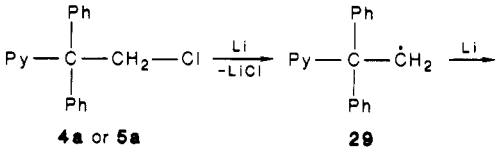
From these considerations it follows that if a carbanion can be generated β to a phenyl and a 2- or 4-pyridyl group, *without allowing a carbon radical to form competitively*, then a [1,2]-pyridyl shift should take place. Indeed, this type of migration is exactly what is observed when **4b** and **5b**, the β,β-diphenyl-β-pyridyl derivatives of *p*-(methylethyl)benzene were treated with methyllithium or potassium hydride, respectively (eq 7 and 8). Therefore, the rearrangement of these two compounds can be judged as authentic carbanionic processes (eq 12). As to whether



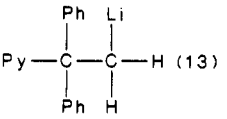
(12)

structures like **27** and **28** are to be viewed as intermediates or transition states, the available evidence favors the former interpretation. Both Fraenkel and Cooper[12] and we have been able to synthesize neutral analogues of such azaspiro-2,5-octadiene structures, as that depicted in **24**.[13] That such neutral systems, which do not have the stabilizing contribution of a negative charge placed on an electronegative atom, are so stable as to permit isolation argues for the transient existence of intermediate anions **27** and **28**.

In contrast with the rearrangements of **4b** and **5b**, the rearrangements of β,β-diphenyl-β-(2-pyridyl)- and β,β-diphenyl-β-(4-pyridyl)ethyl chlorides with lithium metal do run the risk of the competitive formation of carbon radicals and carbanions, because the formation of the carbanion is undoubtedly stepwise (eq 13).[14] If the



4a or **5a** **29**



30

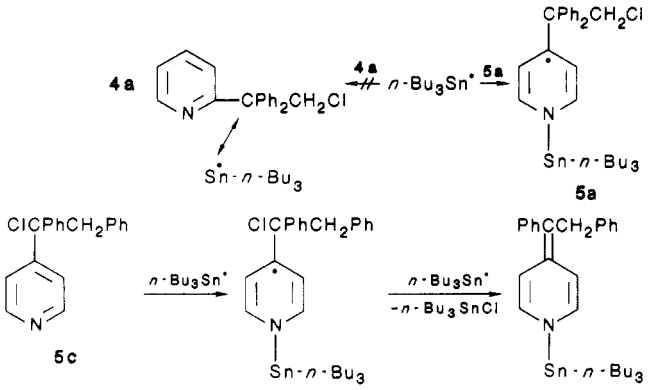
transient lifetime of **29** is sufficiently long, then [1,2] radical shifts may take place in competition with [1,2] anionic shifts of **30**. It should be recalled that in fact HMO theory suggests that radical shifts ought to be *faster* than anionic shifts.[7] Such radical shifts may signal their occurrence by the kind of migratory aptitude shown by the β-phenyl and β-pyridyl groups. Indeed, data on the attack of alkyl radicals on aromatic and azaaromatic rings indicate that phenyl groups can compete with pyridyl groups for alkyl radicals.[15]

For example, methyl radicals generated from the thermal decomposition of acetyl peroxide attack pyridine only three times as readily as they do benzene.[16] Taking into account the sites in the pyridine ring suffering attack, methyl radicals attack an α-position in pyridine 4.70 times more readily than one position in a benzene ring.[15] Likewise, a γ-position is only 1.13 times more reactive than a single benzene position. These relative reactivities toward radicals were obtained for a pyridine uncomplexed with any proton or metal ion. Such complexation would confer a positive charge on the pyridine ring and thereby would be expected to reduce the reactivity of the pyridine nucleus even further toward radical attack.[17]

From the exclusive migration of the pyridyl group in the alkali-metal reactions of both 2-(chloro-1,1-diphenylethyl)pyridine (**4a**) and 4-(chloro-1,1-diphenylethyl)pyridine (**5a**), one can rule out the intervention of either any carbocationic or any free-radical process. The exclusive [1,2]-phenyl migration observed for the reaction of thionyl chloride with β-(4-pyridyl)-β,β-diphenyl-1-ethanol (**10**) gives assurance of how a cationic process would tend to rearrange. Analogously, the response of 2-(chloro-1,1-diphenylethyl)pyridine (**4a**) to tri-*n*-butyltin hydride (eq 5) shows that were a free-radical process to be involved, then both phenyl and pyridyl migrations should be observed in comparable amounts. Neither of these outcomes

(10) Eisch, J. J. *J. Org. Chem.* **1963**, *28*, 707.
(11) Eisch, J. J.; Gilman, H. *Chem. Rev.* **1957**, *57*, 525.
(12) Fraenkel, G.; Cooper, J. W. *J. Am. Chem. Soc.* **1971**, *93*, 7228.
(13) Kovacs, C. A. Doctoral Dissertation, Catholic University of America, Washington, DC, 1972, p 206.
(14) Garst, J. F.; Deutch, J. E.; Whitesides, G. M. *J. Am. Chem. Soc.* **1986**, *108*, 2490.
(15) Levy, M.; Swarc, M. *J. Am. Chem. Soc.* **1955**, *77*, 1949.
(16) Kharasch, M. S.; Rowe, J. L. *J. Org. Chem.* **1951**, *16*, 905.
(17) (a) Gritter, R. J.; Godfrey, A. W. *J. Am. Chem. Soc.* **1964**, *86*, 4724. (b) The proximity of strongly electron-attracting groups (CO_2H, Cl, $COClCCl_3$, and CF_3) is known to suppress the rate of radical chlorinations of adjacent C–H bonds. (Ash, A. B.; Brown, H. C. *J. Am. Chem. Soc.* **1955**, *77*, 4019). A similar electron-withdrawing complexation of M^+ on the pyridyl nitrogen should retard attack of R• on the pyridine nucleus, unless specific complexation of the radical center directs radical attack (compare structure **34** and the work of Abramovitch: Ambramovich, R. A. In *Advances in Heterocyclic Chemistry*; Katritzky, A. R., Boulton, A. J., Eds.; Academic: New York, 1966; Vol. 6, p 322, footnote i.

Scheme IV



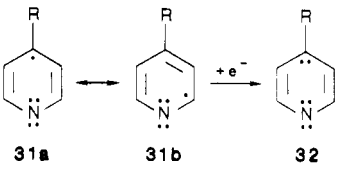
has been observed experimentally with alkali metals. Noteworthy is that phenyl migration with lithium or sodium metal reactions can be put at less than 0.5% of the products.

From these results it can be deduced that the reaction of **4a** with either tri-*n*-butyltin hydride or a nickel(0) complex proceeds stepwise through abstraction of the chlorine atom of **4a** either by the *n*-$Bu_3Sn^•$ radical or a single-electron transfer by nickel(0) to **4a** and subsequent loss of chlorine anion.[9,18] It is known that the 2,2,2-triphenylethyl radical rearranges extremely rapidly ($k = 3.6 \times 10^5$ s^{-1} at 25 °C); were any such radical an important intermediate, then some phenyl migration would have been detected. The failure to do so with either the 2-pyridyl or 4-pyridyl isomers, **4a** or **5a**, argues persuasively against the role of radicals in these alkali-metal reductions.

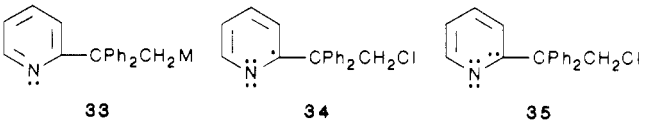
The differing behavior of tri-*n*-butyltin hydride toward **4a** (which undergoes rearrangement–reduction) and toward **5a** (which does not reduce nor rearrange) is pertinent, we believe, to the mechanism of the alkali-metal reactions of **4a** and **5a**. The chain-carrying radical in the reducing action of tri-*n*-butyltin hydride is thought to be the *n*-Bu_3Sn radical.[9] This radical can attack the chlorine of **4a** without serious steric hindrance or electronic competition from the pyridine ring. The presence of the CPh_2CH_2Cl substituent at the 2-pyridyl position would sterically retard the *n*-Bu_3Sn radical from attachment to the ring nitrogen; hence, normal attack at the chlorine can ensue. With **5a**, however, such a *n*-Bu_3Sn radical is not hindered from attaching itself to the nuclear nitrogen (as for example occurs in the reduction of C=N linkages by tin hydrides[19]) and thus interfering with abstraction of the chlorine atom necessary for reduction or rearrangement. In this viewpoint it is noteworthy that isomeric **5c**, by contrast, does undergo very facile reduction with tri-*n*-butyltin hydride, in fact, more readily than either **5a** or **4a**. With this isomer (Scheme IV), such complexation with the nitrogen would be expected to aid in the abstraction of the benzylic chlorine. Eventually, in the case of the complexation of **5a** with the tri-*n*-butyltin radical, the tri-*n*-butyltin radical would dimerize to the observed hexa-*n*-butylditin.

This tendency of the pyridine nucleus to coordinate with transient radicals, either from such fragments as $R_3Sn^•$,[19] $R_3Si^•$,[20] or alkali metals ($M^•$)[21] has much precedent in the chemistry of pyridine derivatives.[22] In summary, it can be stated that pyridine systems are readily reduced by radicals or sources of electrons. Indeed, there is ample evidence to support the conclusion that the pyridine nucleus is both thermodynamically and kinetically a better electron acceptor than many other reducible functional groups attached to it, such as chlorine. This general statement is borne out by particular observations when either **4a** or **5a** was reduced by sodium or lithium metal in donor solvents. Monitoring of these reaction mixtures by ESR spectroscopy revealed the presence of strong, broad signals, whose width (25 G) is consistent with the presence of aromatic radical–anions like **31**.[23] It is interesting to note that such signals persist until consumption of the chlorides **4a** and **5a** and then decay. There is clear evidence that the electron affinity of a pyridine nucleus surpasses that of a benzene ring in such donor solvents.[24] Therefore, even though the broad signal cannot be analyzed and assigned by means of its hyperfine structure, there is little doubt the ESR signal arises from a pyridine-substituted radical–anion. From Hückel molecular orbital calculations, the electron spin would be expected to be concentrated at the α- and γ-positions, with the greater spin at the γ-positions. Such theoretical considerations accord well with the course of the bimolecular reduction of pyridine, in which coupling of intermediate radical–anions occurs principally through the γ-positions[25] (Scheme V). Placement of a substituent (R) at the γ-position would prevent the expected dimerization from taking place. In addition, there may be both radical–anions (**31**) and dianions (**32**) present in such systems,[26] but of course the latter would exhibit no ESR signal.

Scheme V



Thus, under the conditions of the alkali-metal rearrangement of **4a** and **5a**, there exists the possibility of two types of intermediates: the organometallic reagents formed by the replacement of the chlorine by an alkali metal, **33**, and the radical–anion or dianion formed from the addition of one or more alkali metal atoms to the pyridinoid nucleus, ion pairs **34** and **35**. Either type of intermediate



would be expected to lead to exclusively a [1,2]-pyridyl

(18) (a) Tsou, T. T.; Kochi, J. K. *J. Chem. Soc.* **1979**, *101*, 6319. (b) Alkyl halides have been shown to undergo insertion of Ni(0) into their carbon–halogen bonds. Thereafter, depending upon the ligands on the nickel, the adduct $RNiL_nX$ may be isolated (Jolly, P. W.; Wilke, G. *The Organic Chemistry of Nickel*; Academic: New York, 1974; Vol. 1, pp 169–174) or the adduct may decompose into radicals, which can couple in the characteristic manner: Takahashi, S.; Suzuki, Y.; Sonogashira, K.; Hagihara, N. *J. Chem. Soc., Chem. Commun.* **1976**, 839.

(19) Neumann, W. P.; Heymann, E. *Justus Liebigs Ann. Chem.* **1965**, *683*, 24.

(20) Ponomarev, S. V.; Becker, H. P.; Neumann, W. P.; Schroeder, B. *Justus Liebigs Ann. Chem.* **1975**, 1895.

(21) Eisch, J. J.; Thompson, R. M. *J. Org. Chem.* **1962**, *27*, 4682.

(22) Kaim, W. *Acc. Chem. Res.* **1985**, *18*, 160.

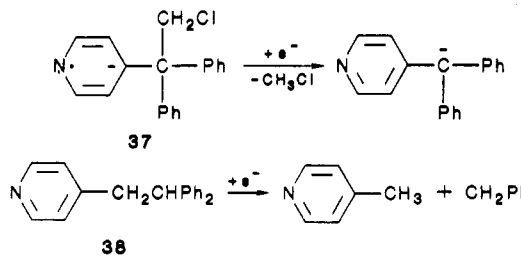
(23) Although the ESR signals observed in the lithium reactions of **4a** and **5a** displayed no discernible hyperfine structure that would permit exact identification, the 25-G width of the persistent signals is of the magnitude displayed by radical–anions of monocyclic aromatics: Eisch, J. J.; Smith, L. E. *J. Organomet. Chem.* **1984**, *271*, 83.

(24) Eisch, J. J.; Gilman, H. *Chem. Rev.* **1957**, *57*, 525.

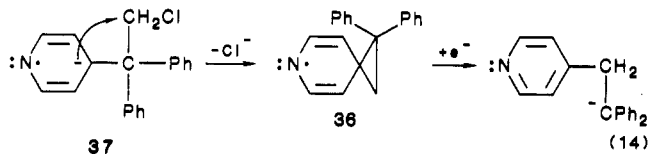
(25) Thus, the action of sodium on pyridine gives principally 4,4′-bipyridine and the combined action of zinc and acetic anhydride on pyridine yields *N,N′*-diacetyl-1,1′,4,4′-tetrahydro-4,4′-bipyridine (cf. ref 24).

(26) Dianions of pyridine derivatives are likely involved in the reduction of 4-methylpyridine under Birch conditions to give the 1,4-dihydro compound: Birch, A. J.; Karakhanov, E. A. *J. Chem. Soc., Chem. Commun.* **1975**, 480.

Scheme VI



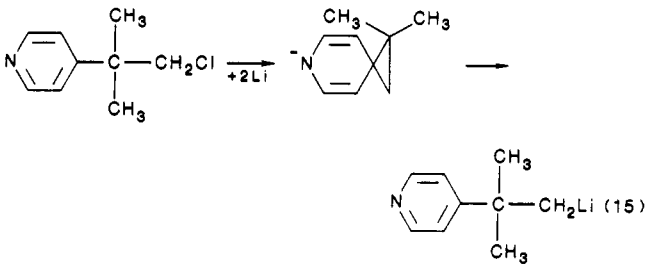
migration: **33** by the well-known carbanionic rearrangement, as exemplified by the behavior of the carbanions of **4b** and **5b**; **34** or **35** by an intramolecular nucleophilic attack of the 4-carbanionic center on the carbon of the CH_2Cl group (eq 14).



Because of the greater ease with which the pyridine nucleus accepts electrons and because of the persistent ESR signal during the rearrangement (and its decay thereafter), we judge that radical–anionic and dianionic intermediates **34** and **35** are the more significant intermediates in these pyridyl migration reactions. The spiro intermediate **36** certainly gains in credibility through our finding that we can actually isolate such a spiro structure by the very conditions used in these rearrangements, namely, treating methiodide **23** with lithium metal in THF (Scheme III). Moreover, the presence of radical–anions and dianions in these systems helps to explain the origin of carbon–carbon bond-cleavage products in these reactions: the formation, for example, of 4-benzhydrylpyridine, diphenylmethane, and 4-picoline in the alkali-metal reactions of **5a** is nicely explicable by the minor decomposition of intermediates **37** and **38** by cleavage of weaker benzylic C–C bonds (Scheme VI).

Although the formation of rearranged product more likely proceeds via radical–anions (eq 14), clearly the reduced, unrearranged products (**11** and **14**, eq 3 and 4) must come from direct interaction of the carbon–chlorine bonds in **4a** and **5a** with the alkali metal. It should be noted that such simple reduction amounts to 1% or less with sodium in THF at 25 °C over 48 h and only 4.5% with lithium in THF under the same conditions with the 4-pyridyl isomer **5a**. With the 2-pyridyl isomer **4a** the proportion of simple reduction to **11** rises to 14% with lithium in THF at 25 °C for 24 h and goes up to 39% with lithium in diethyl ether at 25 °C for 72 h. Now what is known about organosodium and organolithium intermediates like **33** is that sodium or lithium compounds are destroyed by THF much more rapidly than by ether and that sodium compounds attack solvent much more readily than lithium compounds. Accordingly, if organometallic intermediates like **33** were important in these rearrangements, then sodium reactions in THF should have given the larger proportions of simple reduction to **11** and **14**, respectively. That such an outcome was *not* observed argues that intermediates like **33** are insignificant or minor participants in these rearrangements of pyridyldiphenylethyl derivatives. The most rapid rearrangements of **5a**, namely, those conducted with sodium metal in THF, take place because sodium metal in such a Lewis basic solvent is the most rapid source of electrons for the formation of the crucial radical–anionic intermediate, **37**. The more efficient rearrangement of **5a**, compared with **4a**, can be ascribed to the higher π-electron density at the γ-position in **37**, thus making it a better nucleophile than **34** in forming the crucial spiro intermediate.

Finally, the conversion of both β,β-dimethyl-β-(2-pyridyl)ethyl chloride (**21**) and β,β-dimethyl-β-(4-pyridyl)ethyl chloride (**22**) into their corresponding lithium reagents, without skeletal rearrangement, is consistent with the view that radical–anions are also involved with these systems. In these compounds, the spiro intermediate formed would also open to form the more stable carbanion. Because of the geminal dimethyl groups, the spiro intermediate would cleave to form the unrearranged skeleton (eq 15).



Experimental Section

General Procedures. All melting points were determined with a Thomas-Hoover capillary melting point apparatus and are uncorrected. Infrared spectra (IR) were recorded on a Perkin-Elmer spectrometer Model 137 or Model 337, equipped with sodium chloride optics. Proton magnetic resonance spectra (^1H NMR) were obtained with a Varian spectrometer, Model A-60, on neat samples or on 10% solutions in pure solvents. The values are reported on the δ scale in parts per million with reference to internal or external tetramethylsilane, followed by the relative proton intensities and the coupling constants (J) in hertz. A Varian V4502 ESR spectrometer was used for the detection of paramagnetic intermediates in these pyridine systems. 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. Mass spectra of solids and liquids were obtained on a Varian MAT spectrometer, Model CH5, and those of gases on a Consolidated Electrodynamics instrument, Model CEC-21-620A. Elemental analyses were performed by the Spang Microanalytical Laboratory, Ann Arbor, MI.

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 procedures.[27] Solvents of reagent grade were used in all reactions. The anhydrous ethyl ether (Fisher) was used directly; the hexane and 1,2-dimethoxyethane were dried just before use by distilling from the sodium ketyl of benzophenone under a dry nitrogen atmosphere; the tetrahydrofuran (Baker) was stored overnight over sodium hydroxide pellets, then heated at reflux for 24 h over freshly cut pieces of sodium metal, distilled under a nitrogen atmosphere from the sodium, and finally redistilled from lithium aluminum hydride just prior to use; the dimethyl sulfoxide was stirred with calcium hydride and then subjected to distillation under reduced pressure. Both pyridine and *N,N,N',N'*-tetramethylethylenediamine were dried by heating them at reflux for 12 h over calcium hydride.

Hydrolyses were generally conducted by the slow addition of a 5% aqueous HCl solution, subsequently making the system basic, and then extracting the organic product into ethyl ether. The solvent was removed after drying over anhydrous magnesium sulfate. The organolithium reagents were analyzed by established titrimetric procedures.[28]

(27) Eisch, J. J. *Organometallic Syntheses*; Academic: New York, 1981; Vol. 2.
(28) Gilman, H.; Cartledge, F. K. *J. Organomet. Chem.* 1964, 2, 447.

Starting Materials and Reference Compounds. 2,2-Diphenyl-2-(2-pyridyl)ethanol (8). A stirred solution of 4.90 g (20 mmol) of 2-(diphenylmethyl)pyridine (Aldrich Chemical) in 70 mL of anhydrous ethyl ether was treated dropwise at 0 °C with 13.7 mL of 1.6 N *n*-butyllithium in hexane. After the red solution had been stirred for 1 h at 25 °C, it was cooled below −40 °C, and a current of formaldehyde gas (made from the thermal cracking of 12.0 g (0.4 mol) of paraformaldehyde) was passed into the solution. After the red color had disappeared, the reaction mixture was brought to 25 °C and maintained there for 2 h. The colorless suspension was treated with 200 mL of 3 N aqueous NaOH. Separation, drying ($MgSO_4$), and evaporation of the organic layer provided 4.50 g (82%) of crude **8**, mp 105–110 °C. From 95% ethanol, colorless **8** was obtained, mp 121–123 °C: ^{1}H NMR (CCl_4) δ 4.60 (s, 2 H, CH_2O), 5.20 (s, 1 H, OH), 7.0–7.8 (m, 13 H), and 8.80 (d, 1 H, J = 6 Hz, 2-py H); IR (CS_2) 3450 cm^{-1}. Anal. Calcd for $C_{19}H_{17}NO$: C, 82.88; H, 6.22; N, 4.09. Found: C, 82.76; H, 6.22; N, 4.08.

2-(2-Chloro-1,1-diphenylethyl)pyridine (4a). A mixture of 10.0 g (36.4 mmol) of **8** and 8.60 g (73.0 mmol) of thionyl chloride in 100 mL of benzene was heated at reflux for 30 min, in order to dispel the SO_2 formed. The reaction mixture was evaporated and the residual oil dissolved in a 1:1 (v/v) mixture of chloroform and benzene. The solution was washed until neutral with aqueous $NaHCO_3$, dried ($CaSO_4$), and evaporated. The resulting oil was crystallized from ether–petroleum ether (bp 30–60 °C) to give 7.58 g (51%) of colorless **4a**, mp 81–82 °C: ^{1}H NMR ($CDCl_3$) δ 4.82 (s, 2 H, CH_2Cl), 7.0–7.56 (m, 3 H), 7.28 (s, 10), and 8.61 (d, 1 H, J = 5 Hz, 2-py H); IR (CS_2) no absorption between 3100 and 3600 cm^{-1}. Anal. Calcd for $C_{19}H_{16}ClN$: C, 77.68; H, 5.49; N, 4.77. Found: C, 77.88; H, 5.39; N, 4.74.

Alternatively, this compound could be prepared on a 20-mmol scale from 2-benzhydrylpyridine by the same procedure given for the synthesis of 4-(2-chloro-1,1-diphenylethyl)pyridine; the yield was 75% of a product melting at 86–87 °C but having the same IR, ^{1}H NMR, and mass spectral characteristics.

2-(2-Iodo-1,1-diphenylethyl)pyridine (4c). Treatment of a stirred solution of 4.9 g (20.0 mmol) of 2-(benzhydryl)pyridine in 50 mL of ethyl ether with 13.7 mL of 1.6 N *n*-butyllithium at 0 °C gave a dark red solution. After 30 min a solution of 21.4 g (80.0 mmol) of diiodomethane in 50 mL of ether was added dropwise over 60 min. The resulting mixture was stirred for 12 h and worked up in the usual way to give an oil, which was chromatographed on neutral alumina with benzene as the eluent. The colorless solid obtained was recrystallized from ether to provide 5.5 g (72%) of **4c**, mp 72–74 °C: ^{1}H NMR (CCl_4) δ 4.46 (s, 2 H, CH_2I), 6.9–7.66 (m, 3 H), 7.23 (s, 10 H), and 8.40 (d, 1 H, J = 5 Hz, 2-py H); IR (CCl_4) no absorption between 3100 and 3600 cm^{-1}. Anal. Calcd for $C_{19}H_{16}IN$: C, 59.23; H, 4.19; N, 3.64. Found: C, 59.24; H, 4.18; N, 3.85.

2-(1,1-Diphenylethyl)pyridine (11). In the usual way (vide supra), 200 mmol of the (diphenyl-2-pyridylmethyl)lithium reagent (**7a**) was generated and treated with a solution of 34.0 g (240 mmol) of methyl iodide in 100 mL of ethyl ether. After the solution was stirred for 3 h, the usual workup gave 19.2 g (91%) of crude **11**, which was recrystallized from ether–petroleum ether (bp 30–60 °C) to provide colorless crystals, mp 54–56 °C (lit.[29] mp 50–51 °C): ^{1}H NMR (CCl_4) δ 2.22 (s, 3 H, CH_3), 6.90–7.67 (m, 13 H), and 8.66 (d, 1 H, J = 5 Hz, 2-py *H*); IR (neat) 925 cm^{-1} (s), but none at 1150 cm^{-1}.

2-(2,2-Diphenylethyl)pyridine (12). A solution of 66 mL of 1.6 N *n*-butyllithium in hexane was added dropwise to a stirred solution of 9.3 g (100 mmol) of anhydrous 2-picoline in 200 mL of ethyl ether. After the brown solution was stirred for 2 h, it was treated with a solution of 25.0 g (105 mmol) of bromodiphenylmethane in 150 mL of ether. After the mixture was stirred 16 h, 20 mL of EtOH was added and the organic layer extracted with four 200-mL portions of aqueous 4 N HCl. From the remaining organic layer 5.9 g of 1,1,2,2-tetraphenylethane, mp 203–205 °C, was isolated.

The aqueous extract was made basic with aqueous NaOH, and the liberated amines were extracted into ether. Drying and evaporating the ether gave an oily residue, whose distillation gave crude **12**, bp 195–200 °C (0.8 mm), 5.2 g (20%). Recrystallization from ethanol yielded colorless **12**, mp 75–76 °C (lit.[30] mp 75.5 °C): ^{1}H NMR (CCl_4) δ 3.49 (d, 2 H, J = 7.5 Hz, CH_2), 4.62 (t, 1 H, J = 7.5 Hz, C*H*), 6.72–7.58 (m, 3 H), 7.25 (s, 10 H), and 8.52 (d, 1 H, J = 5 Hz, 2-py *H*); IR (neat) no band at 925 cm^{-1}, but one at 1150 cm^{-1}.

2-(1,2-Diphenylethyl)pyridine (13). A stirred and cooled solution of 8.5 g (50.0 mmol) of 2-benzylpyridine (Aldrich Chemical) in 150 mL of ethyl ether was treated dropwise with 31 mL of 1.6 N *n*-butyllithium in hexane. The reddish brown solution was stirred for 30 min and treated with a solution of 6.3 g (50.0 mmol) of benzyl chloride in 30 mL of ether. The usual workup yielded an oil, which was distilled at 188–193 °C, 6.1 g (46%) of **13**: ^{1}H NMR ($CDCl_3$) 3.08–4.36 (m, 5 H, $CHCH_2$), 6.2–7.4 (m, 13 H), and 8.24 (d, 1 H, J = 5 Hz, 2-py H). Anal. Calcd for $C_{19}H_{17}N$: C, 87.99; H, 6.61; N, 5.40. Found: C, 87.80; H, 6.61; N, 5.44.

2,2-Diphenyl-2-(4-pyridyl)ethanol (10). A mixture of 44.0 g (0.18 mol) of 4-benzhydrylpyridine (Aldrich Chemical) and 700 mL of a 35–40% aqueous solution of formaldehyde was heated at reflux for 5 days. After cooling, the aqueous solution was extracted with ether, and the ethereal extracts were washed with three 100-mL portions of 4 N aqueous NaOH. The ether layer was then dried over anhydrous $CaSO_4$ and evaporated. Crystallization of the resulting residue from ether gave 21.0 g (43%) of colorless **10**, mp 126–128 °C: ^{1}H NMR ($CDCl_3$) δ 2.75 (s, H, OH), 4.63 (s, 2 H, CH_2O), 6.90–7.50 (m, 12 H), and 8.45 (m, 2 H, J = 5 Hz, 2-py H); IR (CS_2) 3600 (s) and 3300 (br) cm^{-1}. Anal. Calcd for $C_{19}H_{17}NO$: C, 82.88; H, 6.22; N, 5.09. Found: C, 82.69; H, 6.35; N, 4.88.

An attempt was made to prepare **10** by removing a proton from the $CHPh_2$ group of 4-benzhydrylpyridine with *n*-butyllithium and then treating the resulting lithio derivative with gaseous CH_2O. This attempt failed because the *n*-butyllithium added instead to the azomethine likage.

4-(1-Chloro-1,2-diphenylethyl)pyridine (5c). In the attempt to convert **10** into 4-(2-chloro-1,1-diphenylethyl)pyridine (**5a**) with thionyl chloride, a Wagner–Meerwein rearrangement involving an exclusive [1,2]-phenyl shift occurred. Thus, a mixture of 15.0 g (54.0 mmol) of **10** and 19.8 g (167 mmol) of thionyl chloride in 50 mL of benzene was heated at reflux for 20 min. The reaction mixture was concentrated by evaporation, the residual oil taken up in chloroform, and the solution washed with saturated aqueous $NaHCO_3$ and with water. The chloroform solution was dried over $MgSO_4$ and then evaporated to leave an oil, which was recrystallized from ethanol to provide 7.6 g (47%) of colorless **5c**, mp 127–129 °C: ^{1}H NMR ($CDCl_3$) δ 3.81 (s, 2 H, CH_2Ph), 6.70–7.39 (m, 12 H), and 8.47 (d, 2 H, J = 5 Hz, 2-py H); IR (CS_2) no absorption, 3100–3600 cm^{-1}. Anal. Calcd for $C_{19}H_{16}ClN$: C, 77.68; H, 5.49; N, 4.77. Found: C, 77.66; H, 5.55; N, 4.76.

That a rearrangement had occurred in the course of allowing **10** to react with thionyl chloride was shown by the following properties of the product (**5c**): (a) the CH_2 of **10** shifted upfield in the ^{1}H NMR spectrum from 4.6 to 3.8 ppm; (b) the melting point of **5c** changed from 126–127 to 210–215 °C by allowing a sample to melt and resolidify (formation of the hydrochloride of 4-(1,2-diphenylethenyl)pyridine); and (c) the mass spectrum of **5c** displayed a parent peak at 293 (56) but had an intense peak at 202 (87), which signifies the loss of a $PhCH_2$ group. In contrast, authentic **5a** has its base peak (100) at 244, which accords with a loss of CH_2Cl.

4-(2-Chloro-1,1-diphenylethyl)pyridine (5a). An authentic sample of **5a** was prepared in the following manner: Under argon a stirred solution of 5.0 g (20.4 mmol) of 4-benzhydrylpyridine in 20 mL of dry hexane was treated with 820 mg (20.4 mmol) of potassium hydride. After 5 h the red solution was slowly introduced into 100 mL of freshly dried and distilled methylene chloride. The red color was immediately discharged, but the mixture was stirred for 1 h. Workup with water, separation of the organic layer and drying over $MgSO_4$, evaporation of the solvent, and column chromatography of the residue on silica gel gave the crude product. Recrystallization from CH_2Cl_2 yielded

(29) Heer, J.; Surry, E.; Hofmann, K. *Helv. Chim. Acta* **1955**, *38*, 134.

(30) Hnevsova, V.; Ernest, I. *Collect. Czech. Chem. Commun.* **1960**, *25*, 1468.

71% of **5a**, mp 111–112 °C: ^{1}H NMR ($CDCl_3$) δ 4.55 (s, 2 H), 7.1–7.3 (m, 13 H), and 8.4–8.6 (m, 2 H); MS (70 eV), weak peak at 293, 244 (100). Anal. Calcd $C_{19}H_{16}ClN$: C, 77.68; H, 5.49; N, 4.77. Found: C, 77.48; H, 5.35; N, 4.90.

4-(1,2-Diphenylethyl)pyridine (16). A stirred solution of 8.5 g (50 mmol) of 4-benzylpyridine (Aldrich Chemical) in 50 mL of ethyl ether was treated dropwise at 0 °C with 50 mL of a 1.6 N solution of *n*-butyllithium in hexane. The dark brown solution was stirred at 25 °C for 45 min and then recooled to 0 °C while being treated dropwise with a solution of 6.3 g (50 mmol) of benzyl chloride in 50 mL of ether. After 3 h a solution of 2 N aqueous NaOH was added, and the mixture was worked up in the usual manner. The residual organic oil was distilled to give a fraction, **16**, bp 145–150 °C (0.2 mm), that was recrystallized from ether–petroleum ether (bp 30–60 °C), mp 74–76 °C: ^{1}H NMR (CCl_4) δ 3.29 (d, 2 H, J = 8 Hz, CH_2), 4.15 (t, 1 H, J = 8 Hz, CHPhPy), 6.88–7.25 (m, 12 H), and 8.35 (d, 2 H, J = 5 Hz, 2-py *H*); IR (CS_2) 825 (s), 995 (s) cm^{-1}; MS (70 eV), *m/e* (relative intensity) 259 (46), 168 (100), and 91 (32). Anal. Calcd for $C_{19}H_{17}N$: C, 87.99; H, 6.61; N, 5.40. Found: C, 87.75; H, 6.67; N, 5.36.

4-(2,2-Diphenylethyl)pyridine (15). Although very inefficient due to competitive addition of *n*-butyllithium to the azomethine linkage, this method did provide a sample of known **15**. Thus, a solution of 66 mL of 1.6 N *n*-butyllithium in hexane was added dropwise to a stirred solution of 9.3 g (0.10 mol) of 4-picoline in 200 mL of ethyl ether. After 90 min a solution of 20.0 g (0.10 mol) of diphenylmethyl chloride in 150 mL of ether was added dropwise over 16 h. The reaction mixture was quenched with 50 mL of ethanol and then water. The organic layer was extracted with 4 N aqueous HCl. The aqueous layers were made basic with 4 N aqueous NaOH and the liberated amine taken up in ether. The ethereal extract was dried over $CaSO_4$ and evaporated to leave a brown oil, which was recrystallized from ether–petroleum ether (bp 30–60 °C). Colorless **15** resulted, which melted at 70–72 °C (lit.[31] mp 70–74 °C), 3.2 g (13%): ^{1}H NMR (CCl_4) δ 3.35 (d, 2 H, J = 8 Hz, CH_2), 4.26 (t, 1 H, J = 8 Hz, $CHPh_2$), 6.92 (d, 2 H, J = 6 Hz, 3-H py), 7.22 (s, 10 H), and 8.36 (d, J = 6 Hz, 2-H py); IR (CS_2) 805 (s), 985 (s) cm^{-1}.

2-Methyl-2-(2-pyridyl)-1-propanol (19). In a procedure similar to that used to prepare **8**, 24.2 g (0.2 mol) of 2-isopropylpyridine in 1 L of ethyl ether were treated with 137 mL of 1.6 N *n*-butyllithium. Then the resultant lithium salt of the pyridine was cooled to 0 °C and treated with gaseous formaldehyde.

Usual workup and distillation provided 6.7 g (22%) of **19**, bp 76–79 °C (0.7 mm) (lit.[12] bp 95 °C (10 mm)): ^{1}H NMR ($CDCl_3$) δ 1.32 (s, 6 H), 3.75 (s, 2 H, CH_2O), 5.12 (s, 1 H, O*H*), 6.97–7.82 (m, 3 H), and 8.40 (d, 1 H, J = 5 Hz, 2-py *H*); IR (neat) 3400 cm^{-1}.

1-Chloro-2-methyl-2-(2-pyridyl)propane (21). The usual treatment of **19** with thionyl chloride on a 35-mmol scale, as in preparing **4a**, gave a 50% yield of **21**, bp 47–49 °C (0.4 mm) (lit.[12] bp 80 °C (8 mm)): ^{1}H NMR ($CDCl_3$) δ 1.40 (s, 6 H), 3.86 (s, 2 H), 6.99–7.77 (m, 3 H), and 8.59 (d, 1 H, J = 5 Hz, 2-py *H*).

This compound did not undergo quaternization even after heating 600 mg of it with 15 mL of methyl iodide in a sealed tube for 28 h at 70 °C.

2-Methyl-2-(4-pyridyl)-1-propanol (20). In a procedure analogous to the preparation of **19**, 0.80 mol of 4-isopropylpyridine was heated with an excess of aqueous formaldehyde. Usual workup, followed by distillation, provided 84% of **20** as a colorless oil, which solidified upon standing, bp 110–112 °C (0.5 mm) (lit.[12] bp 105 °C (1.0 mm)), mp 33–34 °C: ^{1}H NMR (CCl_4) δ 1.30 (s, 6 H), 3.60 (s, 2 H, CH_2O), 6.02 (s, 1 H, O*H*), 7.32 (d, 2 H, J = 6 Hz, 3-py *H*), and 8.32 (d, 2 H, J = 6 Hz, 2-py *H*); IR (neat) 3310 (OH), 1615, and 815 cm^{-1}.

1-Chloro-2-methyl-2-(4-pyridyl)propane (22). In the usual manner described for **4a**, 35 mmol of **20** was converted to **22** in 55% yield, bp 69–71 °C (0.3 mm); ^{1}H NMR (CCl_4) δ 1.30 (s, 6 H), 3.66 (s, 2 H, CH_2Cl), 7.30 (d, 2 H, J = 6 Hz), and 8.67 (d, 2 H, J = 6 Hz, 2-py *H*); IR (neat) 1600 and 820 cm^{-1}.

1-Chloro-2-methyl-2-(4-pyridyl)propane Methiodide (23). A mixture of 10.0 g (59 mmol) of **22** and 40 mL of methyl iodide was allowed to stand for 4 days at 25 °C. The resulting yellow precipitate was collected and recrystallized from ethanol, 15.8 g (82%), mp 150–152 °C: ^{1}H NMR ($CDCl_3$) δ 1.57 (s, 6 H), 3.92 (s, 2 H, CH_2Cl), 4.72 (s, 3 H, NMe), 8.25 (d, 2 H, J = 7 Hz, 2-py *H*), and 9.30 (d, 2 H, J = 7 Hz, 2-py *H*). Anal. Calcd for $C_{10}H_{15}ClIN$: C, 38.55; H, 4.85; N, 4.49. Found: C, 38.55; H, 4.48; N, 4.60.

2-(4-Methylphenyl)-1,1-diphenyl-1-(2-pyridyl)ethane (4b). A stirred solution of 12.3 g (50 mmol) of 2-(diphenylmethyl)-pyridine (Aldrich Chemical) in 50 mL of ethyl ether was treated at 0 °C with 44 mL of 1.7 N *n*-butyllithium in hexane. After 90 min of further stirring the blood-red solution was treated dropwise with 8.4 g (60 mmol) of 4-methylbenzyl chloride in 30 mL of ether. The resulting pale yellow solution was stirred for 60 min and then worked up in the usual way. The crude **4b** was recrystallized from petroleum ether (bp 30–60 °C) to yield 12.7 g (73%) of colorless **4b**, mp 118–119 °C: ^{1}H NMR ($CDCl_3$) δ 2.25 (s, 3 H), 4.1 (s, 2 H), 6.4–7.65 (m, 17 H), and 8.45–8.75 (m, 1 H); MS (70 eV), *m/e* (relative intensity) 349 (M^+, 11), 244 (100), and 167 (31). Anal. Calcd for $C_{26}H_{23}N$: C, 89.39; H, 6.59. Found: C, 89.31; H, 6.65.

2-(4-Methylphenyl)-1,1-diphenyl-1-(4-pyridyl)ethane (5b). A suspension of 9.0 g (225 mmol) of potassium hydride was washed thrice with dry, deoxygenated hexane, the hexane wash being removed by syringe after the hydride had settled out. Then a solution of 12.3 g (50 mmol) of 4-(diphenylmethyl)pyridine (Aldrich Chemical) in 50 mL of anhydrous tetrahydrofuran was added to the hydride and the mixture heated to reflux for 3.5 h. After gas evolution had ceased a solution of 8.4 g (60 mmol) of 4-methylbenzyl chloride in 30 mL of ether was added, and the deep orange color of the anion faded. The solution was heated at reflux for 2 h and then worked up in the usual way. The crude product was recrystallized from ethyl ether to provide 12.4 g (71%) of **5b**, mp 122–124 °C: ^{1}H NMR ($CDCl_3$) δ 2.2 (s, 3 H), 3.9 (s, 2 H), 6.3–7.25 (m, 16 H), and 8.37 (d, 2 H, 2-py *H*); MS (70 eV), *m/e* (relative intensity) 349 (M^+, 9), 244 (100), 165 (23), and 105 (81). Anal. Calcd for $C_{26}H_{23}N$: C, 89.39; H, 6.59. Found: C, 89.33; H, 6.73.

Rearrangements of 2-(2-Pyridyl)ethyl Systems with Alkali Metal Reagents. (a) Products from 2-(2-Chloro-1,1-diphenylethyl)pyridine (4a). A solution of 4.0 g (13.6 mmol) of **4a** in 20 mL of THF was treated with 300 mg (43 mmol) of freshly cut lithium pieces and stirred for 1 h at −30 °C and 3 h at 25 °C. The reaction was quenched with 10 mL of ethanol, the lithium pieces were separated, and the filtrate was treated with aqueous 4 N NaOH. The organic components were extracted into ethyl ether and the ether layer dried over $CaSO_4$ and evaporated to leave 3.4 g of an oil (97% of dehalogenated product). Its ^{1}H NMR spectrum in $CDCl_3$ showed the product to be a 9:1 ratio of 2-(2,2-diphenylethyl)pyridine (**12**) and 2-(1,1-diphenylethyl)-pyridine (**11**). No other significant product could be detected. Furthermore, the oil was distilled at 175–180 °C (1.5 mm) and the distillate recrystallized from ethanol to give colorless **12**, mp 76–77.7 °C. By mixture mp, IR, and ^{1}H NMR comparisons it was identical with authentic **12**.

(b) Deuterium Labeling of Products from 4a. In a reaction analogous to that in section a, 2.7 g of **4a** was allowed to react with 300 mg of lithium, but the reaction mixture was quenched with 2.0 mL of D_2O (99.8%). The reaction products were separated by distillation and by TLC on silica gel with a developer of a pentane–ether pair. The rearranged product **12** melted at 75–77 °C: ^{1}H NMR (CCl_4) δ 3.46 (s, 2 H) [no signal at δ 4.62], 6.69–7.60 (m, 3 H), 7.28 (s, 10 H), and 8.55 (d, 1 H, J = 5 Hz); MS (70 eV), *m/e* (relative intensity) 260 (60), 168 (100).

The separated reduced product, 2-(1,1-diphenylethyl)pyridine (**11**) was found to be undeuteriated, as shown by ^{1}H NMR and mass spectral examination.

(c) Time Study of Reaction Products upon Hydrolysis. Since studies showed that the reaction of **4a** with lithium occurred gradually at −65 °C, a mixture of 2.0 g (6.8 mmol) of **4a** and 500 mg of fresh lithium pieces in 30 mL of THF was stirred vigorously at −65 °C. Through a rubber septum on the flask samples were withdrawn periodically with a nitrogen-flushed gas-tight syringe and hydrolyzed with D_2O. The organic products were monitored by convenient signals in the ^{1}H NMR spectrum. The relative amounts of starting chloride **4a**, rearranged product **12**, and reduced product **11** are tabulated vs. time in Table I.

(31) F. Hoffmann La-Roche Co. Patent Neth. Appl. 6 511 532, 1966; *Chem. Abstr.* **1966**, *65*, 3847a.

Similar conversions were monitored for reactions in THF and in diethyl ether, conducted respectively for 24 and for 72 h at 25 °C.

(d) Electron Spin Resonance Spectra of the Reaction of 4a with Lithium. A reaction using the same quantities of reagents and the same conditions as employed in section c was initiated at −65 °C. After 90 min samples were withdrawn and transferred to nitrogen-filled ESR tubes equipped with rubber septa. Such tubes were maintained and examined at −60 °C by ESR spectroscopy. Such samples gave an intense, broad (25 G) signal. When the samples were brought to 0 °C, the signal gradually decreased and then disappeared over 2 h.

(e) Products from 2-(4-Methylphenyl)-1,1-diphenyl-1-(2-pyridyl)ethane (4b). A stirred solution of 3.49 g (10 mmol) of **4b** in 30 mL of THF was treated dropwise at 0 °C with 10 mL of 1.25 M methyllithium in ethyl ether. The resulting deep red solution was stirred at 25 °C for 18 h and then quenched with 100 mL of water. The organic part was taken up in ether and the ether layer dried and then concentrated. The ^{1}H NMR spectrum of the crude product showed 55% of **4b** and 45% of 1-(4-methylphenyl)-2,2-diphenyl-1-(2-pyridyl)ethane (**25**).

When the reaction was rerun with 2.2 equiv of methyllithium, an 80% conversion to **25** was attained. By recrystallization from ligroin (bp 60–90 °C), pure **25** was isolated, mp 193–194 °C: ^{1}H NMR ($CDCl_3$) δ 2.05 (s, 3 H), 4.6–5.1 (q, 2 H), 6.3–7.3 (m, 17 H), and 8.4 (d, 1 H, J = 5 Hz, 2-py *H*); MS (70 eV), m/e (relative intensity) 349 (M^+, 29), 182 (96), 167 (100), and 152 (17). Anal. Calcd for $C_{26}H_{23}N$: C, 89.39; H, 6.58. Found: C, 89.36; H, 6.60.

(f) Deuterium Labeling of Products from 4b. A reaction between 340 mg (1.0 mmol) of **4b** in 5 mL of THF with 2.5 mmol of MeLi, followed by quenching with D_2O, led to the isolation of **25a**. In the ^{1}H NMR spectrum of **25a**, the signals at 4.6–5.1 ppm, corresponding to two protons, were missing. In addition, the mass spectrum had its parent peak at 351 (39) and peaks at 183 (88) and 168 (100).

(g) Attempted Rearrangement of 1-Chloro-2-methyl-2-(2-pyridyl)propane (21). To a stirred mixture of 500 mg of freshly cut lithium pieces and 2 g of crushed glass in 15 mL of THF was added dropwise a solution of 1.0 g (5.9 mmol) of **21** in 10 mL of THF. When the mixture developed color, the temperature was lowered to −65 °C and kept there for 1 h. The mixture was then brought to 25 °C and stirred there for 2 h. The red solution was hydrolyzed and worked up in the usual manner. The crude product (750 mg) displayed an ^{1}H NMR spectrum in agreement with that of 2-*tert*-butylpyridine and did not contain signals expected for 2-isobutylpyridine, a commercial sample of which was available for comparison: ^{1}H NMR ($CDCl_3$) δ 1.36 (s, 9 H), 6.72–7.60 (m, 3 H), and 8.52 (d, 1 H, J = 5 Hz, 2-py H).

Rearrangements of 2-(4-Pyridyl)ethyl Systems with Alkali-Metal Reagents. (a) 4-(1-Chloro-1,2-diphenylethyl)pyridine (5c). A stirred mixture of finely and freshly cut lithium pieces and 2 g of crushed glass in 20 mL of THF was treated dropwise at 25 °C with a solution of 2.92 g (10 mmol) of **5c** in 30 mL of THF. When the mixture developed color, it was cooled below −65 °C. After 1 h at this temperature and 3 h at 25 °C the reaction mixture was quenched with 10 mL of ethanol. Thereupon water and ether were added, and the separated ethereal layer was dried over $CaSO_4$. Evaporation of the ether fraction gave 2.25 g (88%) of pyridine products. The TLC analysis of the oil on silica gel with development by a 25:10 mixture of pentane and ether (v/v, with a few drops of 1-butanol) showed the clear presence of **16** and the absence of **15**. By distillation at 160–162 °C (0.4 mm), 4-(1,2-diphenylethyl)pyridine (**16**) was isolated. Its identity was confirmed by mixture mp, IR, NMR, and TLC characteristics.

(b) Deuterium Labeling. When the foregoing was worked up with D_2O, the final isolated product was shown to be 4-(1-deuterio-1,2-diphenylethyl)pyridine (**16a**) by its mass spectrum (m/e (relative intensity) 260 (48), 169 (100), and 91 (34)) and its ^{1}H NMR spectrum (absence of the one-proton triplet at 4.15 ppm).

(c) 4-(2-Chloro-1,1-diphenylethyl)pyridine (5a). This compound was treated with sodium in THF solution, sodium in diethyl ether solution, lithium in THF solution, and lithium in diethyl ether solution. In each case, 500 mg (1.6 mmol) of **5a** was treated with 4.0 mol of the metal in 10 mL of solvent. The results are given in Table II. In all cases, only pyridyl migration was observed (**16**); no phenyl migration product (**15**), even in traces, could be discerned. Moderate to significant amounts of simple reduction (to 1,1-diphenyl-1-(4-pyridyl)ethane or 4-(1,1-diphenylethyl)pyridine (**14**)) and further cleavage products (4-benzhydrylpyridine, diphenylmethane, and 4-picoline) could be ascertained.

(d) Products from 2-(4-Methylphenyl)-1,1-diphenyl-2-(4-pyridyl)ethane (5b). A 150-mg sample of potassium hydride in mineral oil was washed thrice with dry, deoxygenated hexane and then admixed with 77 mg (2 mmol) of **5b**, 5 mL of THF, and two drops of piperidine. The mixture turned bright orange upon being heated at reflux and was further heated for 48 h. Usual workup gave an organic product that by ^{1}H NMR analysis proved to be about a 1:1 mixture of **5b** and 1-(4-methylphenyl)-2,2-diphenyl-1-(4-pyridyl)ethane (**26**). Column chromatography on neutral alumina yielded 37% of **26**, mp 170–171.5 °C: ^{1}H NMR ($CDCl_3$) δ 2.12 (s, 3 H), 4.65 (s, 2 H), 6.7–7.15 (m, 16 H), and 7.72 (m, 2 H); MS (70 eV), m/e (relative intensity) 349 (M^+, 32) and 167 (100). Anal. Calcd for $C_{26}H_{23}N$: C, 89.36; H, 6.59. Found: C, 89.02; H, 6.91.

(e) Deuterium Labeling of Products from 5b. A mixture of 350 mg (1.0 mmol) of **5b**, 40 mg (1.0 mmol) of KH, and one drop of piperidine in 5 mL of THF was heated at reflux for 20 h and then quenched with 1.0 mL of D_2O. Usual workup gave an organic oil whose ^{1}H NMR spectrum displayed a very small amount of absorption in the 4.85-ppm region, indicative of extensive deuteriation at this site. Separation by preparative TLC on alumina gave deuteriated **26a**, 1-(4-methylphenyl)-2,2-diphenyl-1-(4-pyridyl)ethane. Spectral data: ^{1}H NMR ($CDCl_3$) δ 2.3 (s, 3 H), 6.7–7.1 (m, 16 H), and 8.15 (m, 2 H); MS (70 eV), m/e (relative intensity) 351 (M^+, 26), 183 (25), 168 (100), and 167 (100).

(e) Confirmation of the Structure of the Reaction Product from 5b and Potassium Hydride. A solution of 350 mg (1.0 mmol) of **26** in 10 mL of THF was treated with 350 mg (50 mmol) of lithium pieces and the mixture heated at reflux for 3 h. Usual workup and ^{1}H NMR spectral analysis of the organic product showed the presence of about 50% of diphenylmethane which was isolated by gas chromatography.

(f) Attempted Rearrangement of 2-(4-Methylphenyl)-1,1-diphenyl-2-(4-pyridyl)ethane (5b) with Methyllithium. A solution of 1.75 g (5.0 mmol) of **5b** in 5.0 mL of THF was treated dropwise at 0 °C with 4.0 mL of 1.25 N methyllithium in ether. The deep-red reaction mixture was stirred overnight at 25 °C and then worked up in the usual manner. The gummy organic product, 1.53 g, displayed only one main component on TLC analysis. Passage of the product through a column of neutral alumina with a benzene eluent gave a product whose spectral data are consistent with the structure being 2-(2-methylphenyl)-1-(2-methyl-4-pyridyl)-1,1-diphenylethane: ^{1}H NMR ($CDCl_3$) δ 2.48 (s, 3 H, CH_3), 2.7 (s, 3 H, CH_3), 4.0 (s, 2 H, CH_2), 6.33–7.2 (m, 17 H); MS (70 eV), m/e (relative intensity) 363 (M^+, 4.2), 258 (100), 165 (47) and 105 (72).

(g) Attempted Rearrangement of 1-Chloro-2-methyl-2-(4-pyridyl)propane (22). A solution of 5.0 g (30 mmol) of **22** in 60 mL of THF was allowed to react with 1.0 g of finely and freshly cut lithium at 25 °C until color developed. The mixture was then cooled to 0 °C and stirred for 90 min. After 4 h of additional stirring at 25 °C the mixture was hydrolyzed and worked up in the usual way. A 91% recovery of the pyridine products (3.5 g) was realized. This product displayed an ^{1}H NMR spectrum identical with that of 4-*tert*-butylpyridine; specifically, no peaks attributable to 4-isobutylpyridine were in evidence: ^{1}H NMR (neat) δ 1.23 (s, 9 H), 7.28 (d, 2 H, J = 5 Hz, 3-py *H*), and 8.55 (d, 2 H, J = 5 Hz, 2-py *H*).

Nickel-Mediated Reductions or Rearrangements. (a) 4-(1-Chloro-1,2-diphenylethyl)pyridine (5c). A solution of 2.92 g (10 mmol) of **5c** and 5.50 g (20 mmol) of bis(1,5-cyclooctadiene)nickel[32] in 40 mL of THF was stirred at 25 °C for 24 h and then treated with D_2O. After exposure to air the mixture was treated with aqueous 6 N HCl and ether. The ethereal layer was dried and evaporated to yield crude 4-(1,2-diphenylethyl)-pyridine (**16**), which was isolated in pure form by column chro-

(32) Im, K. R. Doctoral Dissertation, State University of New York at Binghamton, 1979, p 100.

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]

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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-

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

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