in fair accord with the result of the behavior of ESR spectra of Cu^{2+} in poly(vinyl alcohol) by Fujiwara.[8]

In general, the following factors are expected to play an important role in holding the unfrozen water. The first factor is that molecules must be necessarily polymer. Exceptions are glycerine and poly(ethylene glycol), which can hold the unfrozen water. The cases of the exceptions could be attributed to the fact that the two molecules possess a unique ability to form strong hydration. The second factor is that sample molecules should hold hydrophilic substituents such as -OH, -COOH, >CO, -CHO, $-CONH_2$, >NH, etc. The amount of unfrozen water remarkably depends upon the amount and the nature of the substituents. The third factor is that sample molecules hold structural specificity. This is not studied yet in the present investigation. This will be seen in the cases of the three-dimensional structures in biological systems such as proteins, for example, "helix-coil", "nature-denatured", and "sol-gel" transformations. The final factor is that sample molecules hold the spatial effect as mentioned in the present paper. This factor is assumed to play often a most significant role in holding the unfrozen water.

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Generation of Spirodihydroaromatic Anions. Chemistry and ^{13}C NMR

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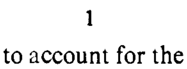
Abstract: A series of salts of 4,4-spiro-1,4-dihydropyridines, **12b,d–h**, has been prepared by cleavage of the corresponding 4,4-spiro-*N*-carboethoxydihydropyridines. NMR investigation shows the salts, except for **12h**, to contain conjugated anions largely unperturbed by counterion and by the nature of the spiro structure about C_4. It is concluded that there is no evidence for interaction between the rings in anions **12b,d–g**. In the case of **12h** the ^{13}C NMR data imply quite a different charge distribution compared to the precursor urethane which was already shown to have any minor interactions between the rings. Urethanes which failed to give stable spiro anions underwent opening (spirocyclopropyl) or cleavage reactions (spirocyclobutyl) as a result of strain in the 4,4 ring. It is concluded that the series of anions studied fails to show evidence for nonclassical structures, and the stability of the anions can be ascribed to the electron-deficient character of pyridine.

While spirodihydroaromatic cations, such as phenonium ions, long postulated as intermediates or transition states in carbonium ion rearrangements,[1] have now been solidly authenticated with spectral techniques,[2,3] the corresponding anions, **1**, have remained comparatively neglected. Such species, first proposed to account for the course of carbanionic rearrangement reactions,[4,5] were later circumstantially implicated from labeling studies[6] and electrophile capture reactions, using CO_2.[7] Thus, for example, the isolation of spiro acid **2** was concluded to imply the short-lived intermediacy of **3**. To unequivocally establish the existence of spirodihydroaromatic anions requires their direct spectroscopic observation. We chose to exploit the electron deficiency of pyridine[8] to stabilize a spiro anion; thus, ^1H NMR was utilized to identify **4** in tetrahydrofuran (THF) solution. Simultaneously, **5** was authenticated in similar fashion.[10]



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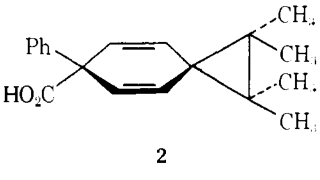

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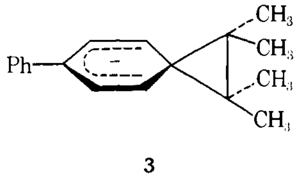

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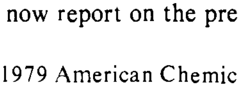

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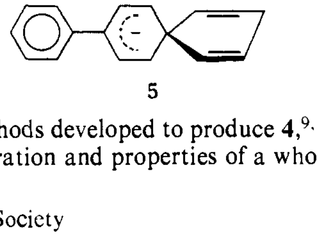

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Using the convenient methods developed to produce **4**,[9,11] we now report on the preparation and properties of a whole

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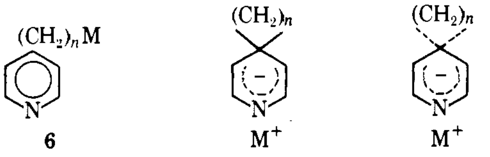
series of 4,4-spirodihydropyridyl metal compounds including one with π bonding in both rings. These species could exist in several forms—**6**, **7**, and **8**—which should be readily distinguishable using the methods of NMR spectroscopy. This is one of the few systems in which a "nonclassical" anion, if it exists, could be easily identified. Possible fast interconversions among **6**, **7**, and **8** could be observed with the NMR line-shape technique.[12] These are the different questions to which this paper is addressed.

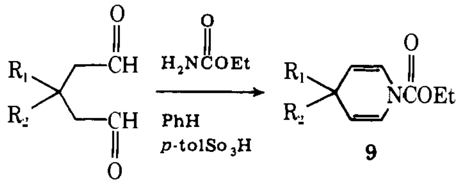


6 **7** **8**

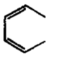
Described below are examples of pyridylalkyl metal species which take the form **6** or **7** as well as one which exhibits interaction between the π structure in *both* rings. While the open form **6** should exhibit pyridine resonance, that for the closed form should be typical of dihydropyridine anions.[9] In principle, one can envisage a series of "nonclassical" species **8**, lying structurally between **6** and **7**, with partial σ bonds connecting the heteroring to the second ring. These would be expected to have (hetero) ring shifts, ^{1}H and ^{13}C, between those for **6** and **7** depending on how much negative charge is located in the heteroring.

Results and Discussion

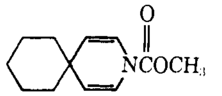
N-Carboxy-4,4-spirodihydropyridines, **9**, were prepared by the condensation of the appropriately substituted glutaraldehyde, **10**, or its acetal with ethyl carbamate and catalytic amounts of *p*-toluenesulfonic acid in benzene.[11,13] Use of a Dean-Stark trap separates water as it is formed and also permits observation of the course of reaction. These compounds are stable for months when stored at 0 °C.



10 **9**

R_1,R_2 = **9a**, $(H)_2$; **b**, $(CH_3)_2$; **c**, $(CH_2)_2$; **d**, $(CH_2)_3$; **e**, $(CH_2)_4$; **f**, $(CH_2)_5$; **g**, $(CH_2)_6$; **h**, 

When **9e** is treated with dimethylmagnesium in ether or *n*-butyllithium in hydrocarbon containing TMEDA, the olefinic proton NMR of the spirourethane at τ 3.35 and 5.2 is replaced by resonances at τ 3.98 and 6.03, respectively. Addition of acid halides returns the olefinic resonances to their original shifts at τ 3.35 and 5.2. Treatment of the cleavage product from **9f** and butyllithium with methyl chloroformate gave the corresponding *N*-carbomethoxy derivative isolated in near-quantitative yield. Thus, we can conclude the initial cleavage product to be a salt of the spirodihydropyridine, **12f**. Spirourethanes **b**,**d**–**h** behaved in a similar fashion with dimethylmagnesium and butyllithium; see below. Except for **12h** these salts of spirodihydropyridines are remarkably stable; they survive reflux in THF for 6 h and have been stored without mishap under refrigeration (0 °C) for 1 year. In contrast, the spirodiene salt turned black after 6 h at room temperature as a result of polymerization of the diene moiety.



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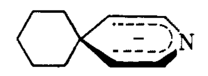
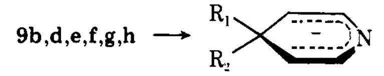


12f



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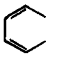
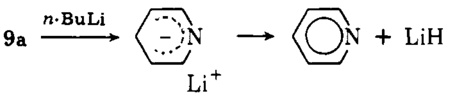
R_1R_2 = **a**, $(H)_2$; **b**, $(CH_3)_2$; **d**, $(CH_2)_3$; **e**, $(CH_2)_4$; **f**, $(CH_2)_5$; **g**, $(CH_2)_6$; **h**, 

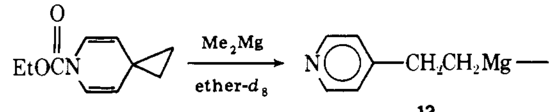
Those urethanes which did not form stable spiro salts exhibited other interesting chemical behavior as described below.

The parent compound of the series *N*-carboethoxy-1,4-dihydropyridine **9a** aromatized immediately on treatment with *n*-butyllithium at −78 °C as evidenced by the development of pyridine NMR absorption in the reaction mixture. No dihydropyridine anion was detected even when the reaction was carried out in the NMR probe, at −50 °C.



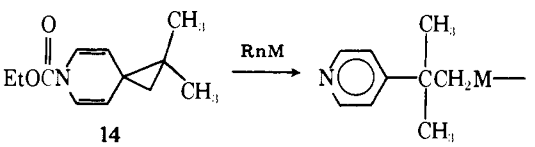
12a

Spirocyclopropylurethane **9c** cleaved with dimethylmagnesium in diethyl ether to give the 2-(4-pyridyl)ethylmagnesium reagent. New proton resonances at τ 1.6 and 2.8, respectively, clearly implicate a 4-substituted pyridine while multiplets at τ 10.58 and 7.42 come from C_1 and C_2 of the 2-pyridylethylmagnesium compound, **13**. Here also no spiro anion could be detected. A similar result was reported previously for the *gem*-dimethyl analogue.[8] Evidently the instability of these spirocyclopropyl anions relative to their open-chain forms must be ascribed to strain in the three-membered ring, since other spiro anions are quite stable. The possibility of a fast 1,2 rearrangement on the NMR time scale was investigated by monitoring the side-chain proton NMR of the cleavage product from 40 to 95 °C. A fast interconversion should average the proton shifts and vicinal couplings on the side chain. In fact, the spectra are identical with those obtained at 30 °C. Furthermore, the NMR spectrum of this cleavage

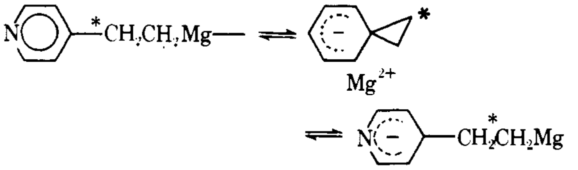


9c **13**

$Me_3COMgOEt$

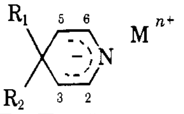


14 **15**



(1)

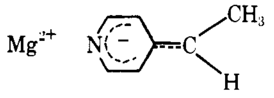
Table I. Dihydropyridine Anions ^1H NMR Data



cleavage reagent	solvent	R_1, R_2	shifts, τ		$J_{2,3}$, Hz
			2, 6	3, 5	
n-BuLi	hexane	CH_3, CH_3	3.75	5.70	6.5
n-BuLi/TMEDA	hexane	CH_3, CH_3	4.04	6.10	7.2
n-BuMgBr	THF	CH_3, CH_3	4.00	*a*	7.4
$(CH_3)_2Mg$	DME	$(CH_2)_3$	3.88	*a*	8.0
$(CH_3)_2Mg$	THF	$(CH_2)_3$	4.10	5.80	6.5
n-BuLi/TMEDA	hexane	$(CH_2)_4$	3.79	6.02	7.6
$(n\text{-}Bu)_2Mg$	THF	$(CH_2)_4$	3.70	5.72	7.6
n-BuLi/TMEDA	hexane	$(CH_2)_5$	4.00	5.99	8.0
$(CH_3)_2Mg$	DME	$(CH_2)_5$	3.98	*a*	8.0
CH_3MgBr	THF	$(CH_2)_5$	4.01	*a*	8.0
n-BuLi/TMEDA	hexane	$(CH_2)_6$	4.01	6.00	8.0
$(CH_3)_2Mg$	DME	$(CH_2)_6$	4.04	*a*	7.00
CH_3Li	diethyl ether	$(CH)_4$	4.70	*a*	7.00
$(CH_3)_2Mg$	THF	$(CH)_4$	4.79	*a*	6.00

[a] Resonance obscured by solvent.

product did not change after storage of the sample for 6 months or even heating to 90 °C in the sealed tube. Thus, there is also no evidence for a proton shift to **16.**



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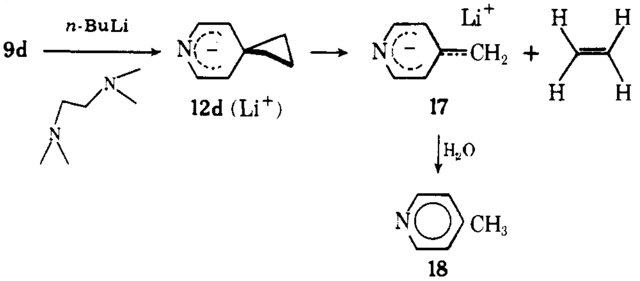
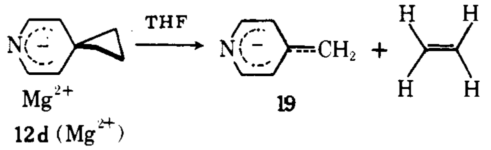
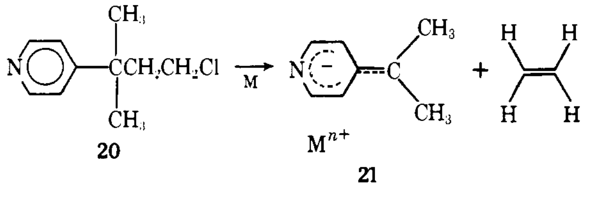
While the spirocyclobutylurethane **9d** cleaved with dimethylmagnesium to the stable spiromagnesium salt the corresponding reaction with butyllithium gave fragmentation products directly, as observed in the ^1H NMR spectrum. This



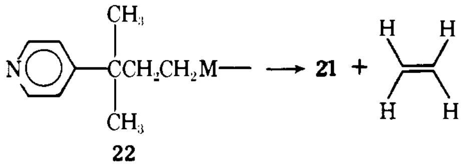
result was also observed on refluxing the magnesium salt in THF for 24 h. We previously reported a similar reaction when



3-(4-pyridyl)-3-methyl-1-chlorobutane was reacted with lithium or magnesium.[8] This latter fragmentation could have



taken place during the reaction of the halide with metal. However, it is more reasonable that *all* these results are due to 1,2 elimination of *stable species* from an open-chain organometallic intermediate. The faster fragmentation of the lithium derivative, compared to the magnesium compound,



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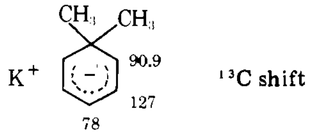
accords with Grovenstein's finding that more ionic organometallic compounds fragment faster.[14]

NMR data, both ^{13}C and ^1H, for the spiro anions are collected in Tables I and II; carbon shifts for the urethanes are in Table III. Shifts were assigned by analogy to the urethanes[11-13] and the known effects of charge on chemical shift.[15,16] In general, converting a urethane to a dihydropyridine salt causes proton shielding of 0.65 ppm at $H_{2(6)}$ and 0.8 ppm at $H_{3(5)}$ in the salts **12b,d-h**. In the carbon-13 resonance the corresponding increments are ca. 17 ppm deshielding at $C_{2(6)}$ and 15 ppm shielding at $C_{3(5)}$. These shift changes are so similar among the salts, where the loop about the C_4 is saturated, that one may conclude that interaction between the rings is too weak to detect. A similar conclusion applies to the precursor urethanes.[11]

Also of interest is the relative insensitivity of the ring shifts in the spiro salts to counterions.[9] This imples the cation-anion distance in the ion pairs to be large enough so that the electric field due to the cation has only a minor effect on the ring shifts of the anion. Therefore, these salts, most likely, exist as separated ion pairs.

The carbon-13 ring shifts of the anions exhibit the alternating variations typical of odd conjugated anions.[18] In fact, the ring shifts of **12b** (4,4-dimethyl) are very similar to those of the 1,1-dimethylcyclohexadienyl anion as obtained for the lithium salt in the presence of TMEDA[19] *and* the potassium salt in liquid ammonia-d_3;[20] see **23**. The calculations of Olah,



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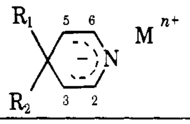
Asensio, Mayr, and Schleyer predict this anion to have no discernible 1,5-π interaction.[23] This conclusion, backed now by our NMR data, applies with equal force to all the salts described in this paper.

The methyl ^{13}C and proton resonances of **12b** are magnet-

Table II. ^{13}C Chemical Shifts



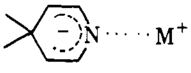
cleavage reagent	solvent	R_1, R_2	shifts[a] $C_{2,6}$	$C_{3,5}$	C_4	α	β	γ
n-BuLi/TMEDA	hexane	CH_3, CH_3	127.9	91.7	30.8	33.0		
$(CH_3)_2Mg$	THF	$(CH_2)_3$	134.9	103.2	23.6	33.6	13.2	
n-BuLi/TMEDA	hexane	$(CH_2)_4$	137.1	103.0	30.1	46.3	22.1	
n-BuLi/TMEDA	hexane	$(CH_2)_5$	138.3	101.8	30.1	46.2	33.4	19.9
n-BuLi/TMEDA	hexane	$(CH_2)_6$	137.1	103.3	29.1	46.6	30.7	21.5
CH_3Li	diethyl ether	$(CH)_4$	140.2	91.8	57.0	153.6	123.5	
$(CH_3)_2Mg$	THF	$(CH)_4$	137.9	91.1	56.9	154.2	123.3	

[a] Shifts in parts per million with respect to tetramethylsilane.

ically equivalent at room temperature, an effect which persists to −80 °C, below which temperature high viscosity of the solution and lower solubility of this salt make it impossible to obtain a high-resolution spectrum. The simplest explanation is that the 1,4-dihydropyridine anion is planar. The NMR data of Olah et al. for cyclohexadienyl anion[20] as well as the results of MINDO-3 calculations for the 1,4-dihydropyridine[21] anion support this latter conclusion.

While the main influence responsible for the shifts in the dihydropyridine anions is charge,[16] other effects contribute also. For instance, the significant deshielding at $C_{2(6)}$ of 17 ppm in the anions compared to the urethanes must be due in part to the unshared electron pair on nitrogen, **24.** Mixing of ground and n→π* excited states causes a paramagnetic contribution to the $C_{2(6)}$ shift. Such an effect has already been shown to be responsible for the ortho carbon shifts in pyridine and the diazines;[22] a variation of it applies in similar fashion to shifts in aryllithiums.[23] Also, variations in the covalency of possible metal ion complexes at nitrogen would change the n→π* excitation energies and in turn the $^{13}C_{2(6)}$ shift. That this shift varies so little among the salts studied supports the proposal that they exist as separated ion pairs.

24



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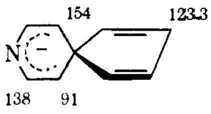
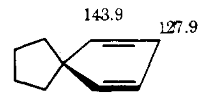
Using the salts with saturated loops about C_4 as models for minimum interaction between the rings one can discuss the effect of introducing unsaturation into the 4,4 loop. Salt **12h** is the first example of a spiro anion with π bonding in both rings. Thus, the introduction of two double bonds in **12h** causes (carbon-13) shielding of 9 ppm at $C_{3,5}$ but leaves the shift of $C_{2,6}$ unchanged, compare to **12e–g.** The resonances at α and β are deshielded and shielded, respectively, compared to model compounds **26** and **27**. Thus, the dienylic unsaturation about C_4 in **12h** appears to act as an electron donor to the heteroring. Interestingly, calculations of π-electron densities in a model spiro anion, **28,** lead to a similar trend. The π MOs of **28** were calculated to second order starting with the two π loops and using a spiro exchange interaction between their termini of 0.1β.[24]



12h



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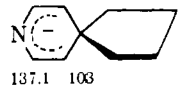

12e

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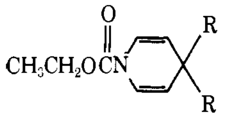
Table III. ^{13}C NMR Shifts[a] for Spirourethanes[b]



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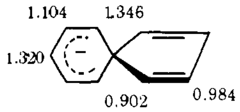
	R, R	$C_{2,6}$	$C_{3,5}$	C_4
a	H, H	123.7	105.9	22.5
b	CH_3, CH_3	120.3	115.9	30.8
c	$(CH_2)_2$	123.2	113.9	18.7
d	$(CH_2)_3$	120.3	114.8	37.8
e	$(CH_2)_4$	120.1	114.8	41.3
f	$(CH_2)_5$	120.6	114.3	33.9
g	$(CH_2)_6$	119.5	115.8	36.4
h	$(CH)_4$	124.0	106.2	54.1

[a] Shifts from tetramethylsilane. [b] Solvent $CDCl_3$.



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Altogether what we have learned here is that 4,4-spirodihydropyridine metal compounds exist in solution in *one* of two forms, either as pyridylalkyl metal compounds, **6**, or as salts containing 4,4-spiro-1,4-dihydropyridine anions. That spiro anions in this series are stable at all must be ascribed to the electron-deficient character of pyridine. Phenylalkyl metal compounds have, to this date, never been reported to exist in the spiro form. However, *p*-biphenylyl does stabilize a spiro anion as described by Grovenstein.[10]

No evidence has been uncovered here for nonclassical spiro species, **8**, intermediate between the open, **6**, and fully closed, **7**, forms. The one open-chain species, **13**, does not undergo fast 1,2 rearrangement.

In contrast to these results, the one species with π structure in both rings does show some interaction between the rings. This result is currently under investigation via molecular orbital calculations.

Experimental Section

All the dihydropyridines studied were synthesized via the condensation of 3,3-disubstituted glutaraldehydes with ethyl or methyl carbamate in the presence of *p*-toluenesulfonic acid. The details of the synthesis are described elsewhere.[11,13] Dimethylmagnesium was obtained by stirring dimethylmercury with triply sublimed magnesium in THF at room temperature. Dimethylmagnesium was transferred to other ethers by first removing as much THF as possible by bulb-to-bulb distillation. Residual solid was dissolved in the desired solvent. Removal of solvent from this latter preparation followed by addition of the new solvent completed the transfer procedure.

All ethers were distilled just before use from Grignard solutions, butylmagnesium bromide. Hydrocarbons and *N,N,N′,N′*-tetramethylethylenediamine were distilled from lithium aluminum hydride or calcium hydride.

General Method for the Preparation of Dihydropyridine Salts. The reactions were carried out in NMR tubes protected with rubber serum caps. These tubes and syringes were previously flamed and flushed with argon and the reactions carried out under a positive pressure of argon. The organometallic reagent was added to the spirourethane at 0 °C using a syringe. Dry, oxygen-free tetramethylsilane was then added to the reaction mixture as an internal standard for NMR studies. The tube was then sealed and NMR spectra were obtained.

Cleavage by *n*-Butyllithium. *n*-Butyllithium (1.5 mL, 1.5 M in hexane, 2.25 mmol) was added dropwise to the dihydropyridine (0.75 mmol) at 0 °C. After 30 min at 0 °C, the mixture was allowed to come to room temperature and stored at this temperature for 2 h. The spectrum of this solution was recorded.

Cleavage by *n*-Butyllithium/TMEDA. A mixture of dihydropyridine (0.74 mmol) in *N,N,N′,N′*-tetramethylethylenediamine (0.26 g, 2.25 mmol) was cooled to −25 °C. *n*-Butyllithium (1.5 mL, 1.5 M in hexane, 2.25 mmol) was added to the mixture dropwise and the mixture allowed to come to room temperature during a period of 1 h. The spectrum of this solution was recorded.

Cleavage by Grignard Reagents. Methylmagnesium bromide (2.25 mL, 2.25 mmol, 1 M in ether) was syringed into the *N*-carboethoxy-1,4-dihydropyridine (0.75 mmol) under argon at 0 °C. The mixture was stirred at 0 °C for 30 min and then at room temperature for 24 h before determination of the NMR spectra.

Cleavage Using Dimethylmagnesium. Dimethylmagnesium 2 M in the ether of choice (0.5 mL, 1 mmol) was added to the *N*-carboethoxy-1,4-dihydropyridine (0.34 mmol) under argon at 0 °C. The reaction mixture was stirred for 24 h before NMR spectra were obtained.

Cleavage of 9d with Butyllithium/TMEDA. Following the general procedure just described, **9d** was reacted with butyllithium in the presence of TMEDA. The ^{1}H NMR spectrum contained resonances for 4-picolyllithium and ethylene. Hydrolysis and the usual workup of this reaction mixture gave 0.18 g of 4-picoline, 89% based on **9d**, using gas chromatography.

Cleavage of 9d with Dimethylmagnesium. Cleavage of **9d** with dimethylmagnesium in THF following the general procedure above gave on heating ethylene and 4-picolylmagnesium, the latter observed with ^{1}H NMR and later isolated, on workup, as 4-picoline, 0.25 g, 79% yield based on **9d**.

NMR Spectra. ^{1}H and ^{13}C NMR spectra were obtained using the Bruker HX-90 NMR spectrometer operating in the Fourier transform mode and for proton spectra alone a Varian A-60A instrument was sometimes used.

Samples used for ^{13}C NMR were degassed with three freeze–thaw cycles and sealed into 8-mm o.d. NMR tubes. The 8-mm tube was wrapped with Teflon tape and centered snugly inside a 10-mm o.d. NMR tube. The annulus contained $CDCl_3$ for field frequency lock. Typical experimental parameters follow: sweep width 5000 Hz, sampling interval 100 μs, delay time 200 μs, pulse width 4 μs (25° flip), data table 16 384 points. Typically, 1024 scans were collected. Proton decoupling was obtained with a center band frequency of 89.999 800 MHz modulated into a band-pass of greater than 1000 Hz with 10 W of power. Exponential multiplication, $e^{i\mathrm{TC}N}$ (with TC $= -1.6$, $N = 16384$, i is point index), of the free induction decay was used to increase the signal-to-noise ratio. This procedure gave a computer resolution of 0.610 Hz/data point.

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