Anal. Calcd for $C_{14}H_{14}ClN$: C, 72.55; H, 6.10; N, 6.04. Found: C, 72.71; H, 6.06; N, 5.70.

Photolysis of 7d.—A solution of 3.71 g (0.0146 mol) of **7d** in 650 ml of water was photolyzed according to the procedure for the photolysis of **7a**, using a Vycor sleeve as filter to give 1.05 g (33%) of **8d**: mp 235° dec; pmr (CF_3COOH) δ 8.49 (d, 1 H, α-pyr), 8.11–7.82 (m, 2 H, β- and γ-pyr), 7.56–7.29 (m, 4 H, Ar H), 5.64 (s, 2 H, CH_2), 2.83 ppm (s, 3 H, CH_3); $\lambda_{max}^{H_2O}$ 250 nm (sh, ϵ 1200), 254 (13,304), 317 nm (12,152).

Anal. Calcd for $C_{13}H_{12}ClN$: C, 71.71; H, 5.56; N, 6.43. Found: C, 71.30; H, 5.57; N, 6.15.

Photolysis of 7e.—According to the procedure for the photolysis of **7a**, 3.92 g (0.0146 mol) of **7e** was photolyzed in 650 ml of water for 78 hr. Recrystallization of the residue from ethyl acetate–absolute ethanol gave 0.67 g (20%) of a mixture of **8e** and **8f**, mp 268° dec. The mixture was not separated. However, analysis of the mixture showed ~67% **8f** and 33% **8e** to be present: pmr (CF_3COOH) δ 8.40–7.18 (m, 6 H, Ar H), 5.64 (s, 2 H, CH_2), 2.71 (s, 2 H, $^2/_3CH_3$), 2.51 (m, 3 H, CH_3), 2.37 ppm (s, 1 H, $^1/_3CH_3$); $\lambda_{max}^{H_2O}$ 225 nm (ϵ 14,900), 252 (12,190), 260 (11,700), 311 (10,290).

Anal. Calcd for $C_{14}H_{14}ClN \cdot {}^1/_2H_2O$: C, 70.72; H, 6.22; N, 5.89. Found: C, 70.58; H, 5.99; N, 6.08.

Registry No.—**4a**, 39727-35-0; **4b**, 39727-36-1; **4c**, 39727-37-2; **4d**, 39838-38-5; **4e**, 39727-38-3; **4f**, 39727-39-4; **4g**, 39727-40-7; **4h**, 39727-41-8; **5a**, 39727-42-9; **5b**, 39727-43-0; **6**, 35740-85-3; **7a**, 39727-54-3; **7b**, 39727-55-4; **7c**, 39727-56-5; **7d**, 39727-57-6; **7e**, 39727-58-7; **8a**, 39727-59-8; **8b**, 39727-60-1; **8c**, 39727-61-2; **8d**, 39727-62-3; **8e**, 39727-63-4; **8f**, 39727-64-5; 2-chloro-3-bromomethylquinoline, 35740-82-0; β-picoline, 108-99-6; 2-bromo-3-bromomethylquinoline, 35740-83-1; γ-picoline, 108-89-4; 4-(2-ethyl-1,3-dioxolein-2-yl)pyridine, 39727-67-8; 4-acetylpyridine, 1122-54-9; 2-iodo-3-bromomethylquinoline, 35740-84-2. 3,4-lutidine, 583-58-4; 2-bromopyridine, 109-04-6; *o*-chlorobenzyl chloride, 611-19-8; 3,5-lutidine, 591-22-0; 2,4-lutidine, 108-47-4.

Acknowledgment.—The authors wish to express appreciation to the National Cancer Institute of the NIH for partial support of this project from Grant CA-12149. One author, J. A. B., further expresses appreciation to the Graduate School of the University of New Hampshire for an NDEA and Dissertation Year Fellowship.

Formation of Long-Lived Free Radicals from Acylpyridinium Salts with Alkali

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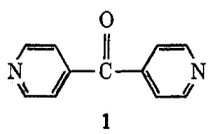
4-Acetylpyridinium methiodide reacted with concentrated aqueous alkali to yield a nonviologenic, stable, long-lived free radical whose esr spectrum indicated molecular symmetry. Several stable nonparamagnetic derivatives of the radical have been prepared and characterized. In contrast to the acetyl and valeryl derivatives, the bulkier alkyl analog 4,4-dimethylvalerylpyridinium salt reacted with hydroxide to yield dimethylviologen radical. On the other hand, di(4-pyridyl)methylcarbinol dimethiodide underwent a several-step transformation when dissolved in concentrated aqueous hydroxide to yield the same symmetrical stable radical as that obtained from 4-acetylpyridinium iodide. The reaction of the latter with sodium ethoxide in alcohol yielded still another radical which is different from that formed in hydroxide. The identity and esr spectra of the radicals and their derivatives and the overall mechanism of reaction are discussed.

We have recently reported[4–6] on the formation of several different long-lived free radicals from methiodide derivatives of di(4-pyridyl) ketone (**1**). The dimethiodide of **1**, in an unusual reaction, yielded rapidly the stable viologen cation radical **2** on simple mixing



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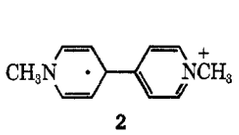

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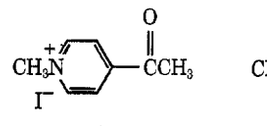
with concentrated aqueous hydroxide.[5] Since the long-lived pyridinyl radicals remain of high research interest because of their relevancy to basic chemical and biological reactions,[7–14] we have extended the study of N-heteroaromatic methiodides with bases to other acylpyridinium salts. In this paper, we report the formation of a nonviologen, stable, symmetrical radical from 4-acetylpyridinium methiodide **3** in aqueous alkali. Whereas the nonbranched homolog of **3**, 4-valerylpyridine methiodide (**4**), behaved analogous to **3**, its bulkier 4,4-dimethyl derivative **5** yielded dimethylviologen (**2**) with aqueous hydroxide in a manner resembling that of the dimethiodide of **1**. On the other hand, the same stable radical obtained



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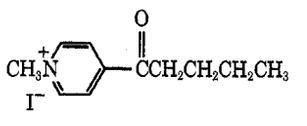

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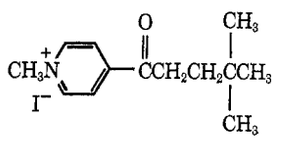

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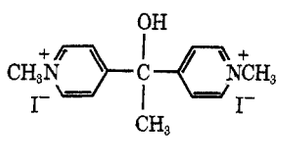

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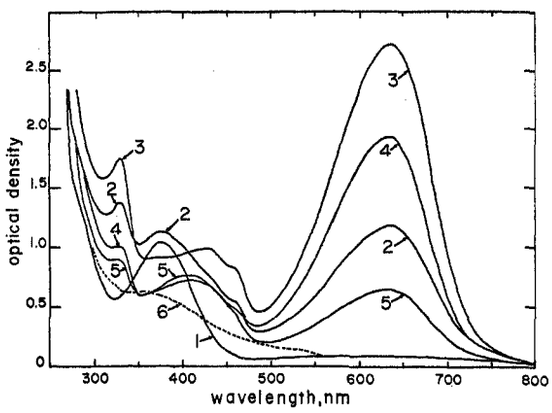
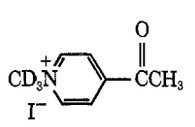


Figure 1.—Changes in the uv–visible absorption spectrum of a degassed 1.5×10^{-3} M solution of 4-acetylpyridine methiodide in ~1 N NaOH: (1) after mixing, (2) 3 hr, (3) 24 hr, (4) 212 hr, (5) 598 hr, (6) open to air.

from **3** was generated from an apparently unrelated compound, di(4-pyridyl)methylcarbinol dimethiodide (**6**), in the same reaction with aqueous hydroxide. Structurally different stable radicals were obtained from **3** with ethoxide in ethanol or with secondary amines in aprotic solvents.

Results

When crystalline methiodide **3** was mixed with 1 N sodium hydroxide in the absence of oxygen, a deep blue color developed progressively.[15] The colored solutions were intensely paramagnetic. Changes in the uv–visible absorption spectrum of a degassed 1.5×10^{-3} M solution of **3** in 1 N aqueous hydroxide are shown in Figure 1. It is apparent that the blue color is caused by the progressive formation of a visible absorbing species with a prominent band centered at 635 nm and several overlapping and less intense bands in the 300–500 nm regions. One can also see that after reaching a maximum, the concentration of the visible-absorbing species diminishes slowly in about 1 week following mixing. Although numerous curves have been recorded throughout this transformation, only a few are shown in Figure 1 for clarity. Sufficient spectra were recorded to determine accurately the kinetics of the radical disappearance and its half-life in the absence of oxygen. The esr spectrum of a blue solution prepared by dissolving crystalline **3** in aqueous hydroxide is shown at the top of Figure 2. The intensity of the esr signal paralleled the absorbance at 635 nm, suggesting that the blue color is associated with the paramagnetic species. On admission of air both the 635-nm absorption (curves 2–5, Figure 1) and esr signal disappeared. As expected, the N-methyl-d_3 analog of **3**, compound **7**, reacted with concentrated hydroxide to give uv–visible absorption spectra indistinguishable from those of **3** shown in Figure 1. On the other hand, the esr spectrum, shown at the top of Figure 3, was distinctly different from that obtained with **3**.



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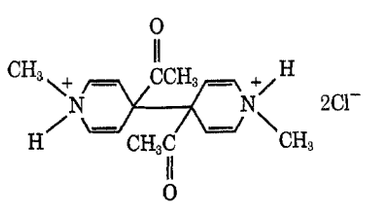
In order to uncover chemical evidence regarding the identity of the detected free radical, several large-scale (gram-size) reactions of **3** with 1 N sodium hydroxide have been carried out. When the concentrated blue solution prepared with 2 N sodium hydroxide was allowed to stand overnight, green crystals with metallic luster and weak paramagnetic properties precipitated. Although these crystals can be filtered in an inert atmosphere, their inherent instability in the presence of air prevented accurate elemental analysis and other direct analytical tests. A 10^{-4}–10^{-5} M solution of green crystals in degassed DMSO gave the visible absorption shown in Figure 4, curve 1 which changed progressively as indicated with decrease in the intensity of the band at 625 nm and concomitant increase in concentration of a component absorbing at λ_{max} 445 nm. The presence of an isosbestic point at 505 nm suggests a clean 1:1 transformation.

When redissolved, the emerald green solid melting at 236–238° reexhibited all the spectroscopic and chemical properties of its precursor blue free radical. In spite of its lability the green, crystalline compound could be preserved for several days under refrigeration in an inert atmosphere. It reacted vigorously with concentrated H_2SO_4, forming a stable red solution which gave the uv–visible absorption spectrum shown in Figure 5. The uv–visible spectrum remained unchanged for weeks and the solution was diamagnetic. The analogous red, crystalline hydrochloride prepared from the green solid and 0.5 M HCl was quite stable and therefore lended itself to thorough characterization. Elemental analysis, nmr (in D_2O), ir, and uv–visible spectra were all consistent with dihydrochloride structure **8**. In addition the nmr spectrum of the green solid in 100% D_2SO_4 agreed with trication structure **9**. Thus, comparison of the nmr spectra of **8** in D_2SO_4



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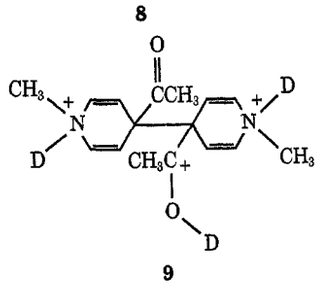

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and D_2O with that of **3** in DMSO-d_6 and D_2SO_4 allowed good assignments of individual nmr signals shown in Figure 6.

It is interesting that 4-acetylpyridinium iodide **3** yielded structurally different stable radicals when

(15) The requirement for absence of oxygen is not stringent for the formation of the radical. If the aqueous hydroxide was not degassed prior to mixing, the blue color of the radical develops after some initial delay. On the other hand, initial deoxygenation by numerous freeze–thaw cycles under high vacuum causes the immediate appearance of the blue color on mixing. Such samples were used for the recordings in Figure 1.

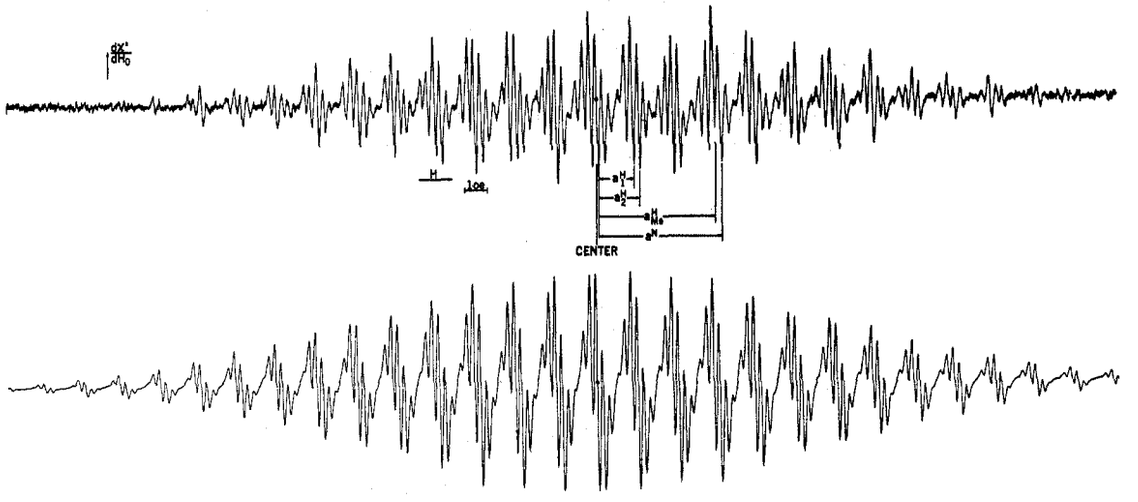


Figure 2.—Top: esr spectrum of 4-acetylpyridine methiodide in 1 *N* aqueous NaOH. Bottom: computer-simulated spectrum with hyperfine splitting constants $a^N = 5.39$, $a_1^H = 1.54$, $a_{CH_3}^H = 5.10$, and $a_2^H = 1.80$.

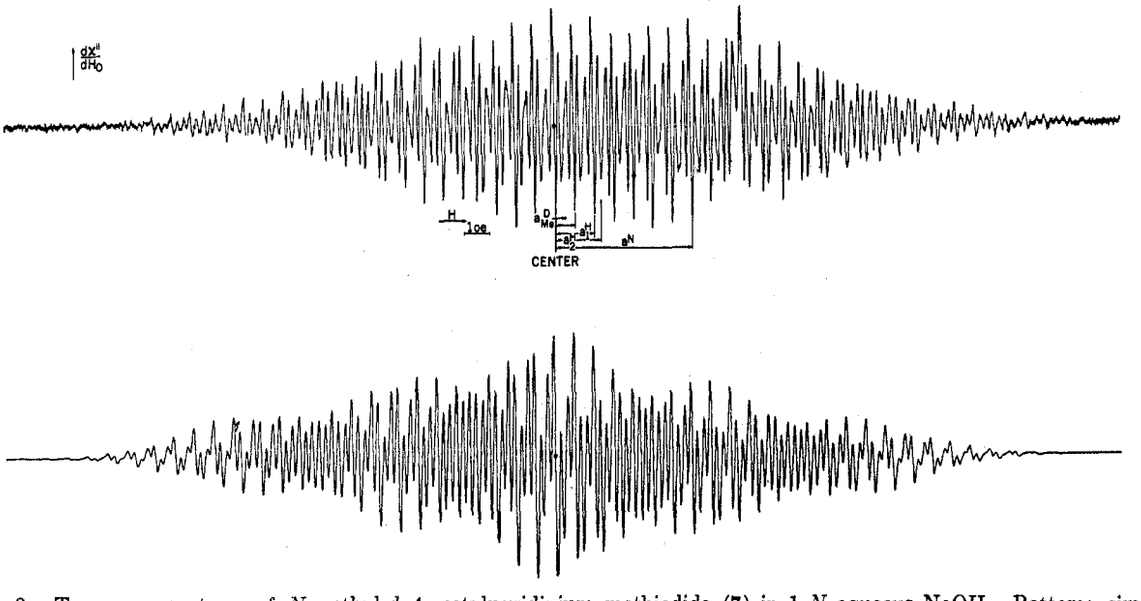


Figure 3.—Top: esr spectrum of *N*-methyl-d_3-4-acetylpyridinium methiodide (**7**) in 1 *N* aqueous NaOH. Bottom: simulated spectrum with hyperfine splitting constants $a^N = 5.39$, $a_1^H = 1.54$, $a_{CD_3}^D = 0.79$, and $a_2^H = 1.80$.

treated with ethoxide in alcoholic solution or with secondary amines in nonprotic solvents.

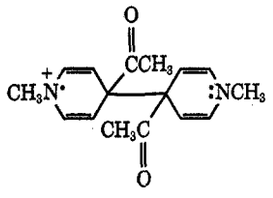
Both 4-acetylpyridine methiodide (**3**) and its CD_3 derivative **7** reacted with sodium ethoxide in ethanol to give the same brown-green free radical whose uv–visible absorption spectrum showed prominent bands at 326 and 435 nm and a weaker broad band around 735 nm. Its esr spectrum in approximately 1 *N* sodium ethoxide is displayed in Figure 7. Despite the fact that the line width is remarkably narrow, about 100 mOe, the complexity of the spectrum, showing approximately 250 distinct lines, did not allow accurate determination of the splitting constants.

The fact that both compounds **3** and **7** gave the same paramagnetic species in EtOH–NaOEt may be explained in two ways: either the CH_3 or CD_3 groups no longer exist in the free radical, or fast exchange of methyl deuterons takes place in the presence of the powerful alkoxide base. The behavior of **7** in ethoxide is mentioned here mainly to exhibit the contrast with its reaction in aqueous hydroxide.

The reaction of 4-acetylpyridinium iodide with pyrrolidine in deoxygenated dimethoxyethylene (DME) resembled more that with aqueous hydroxide, since **3** and **7** yielded two different stable radicals whose esr spectra are shown in Figure 8. Neither the radicals formed in alcoholic ethoxide nor those in DME–pyrrolidine were identical with those prepared in aqueous hydroxide.

Discussion

The reaction of 4-acetylpyridinium iodide with concentrated aqueous hydroxide yielded a long-lived new free radical for which we tentatively propose structure **10**. This structure was derived from a



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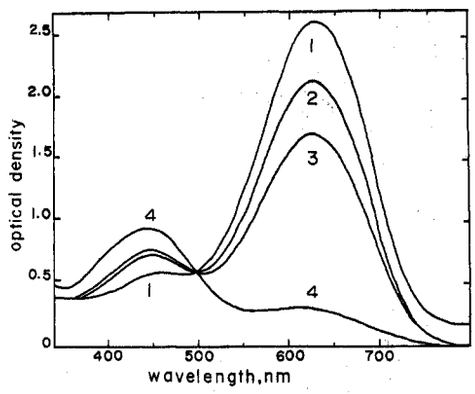


Figure 4.—Visible absorption of 12 in degassed dimethyl sulfoxide at different times: (1) after solubilization, (2) 135, (3) 195, and (4) 540 min later.

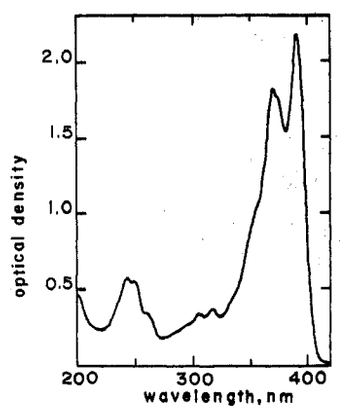


Figure 5.—Uv absorption spectrum of 12 in deoxygenated H_2SO_4.

variety of spectroscopic and other analytical tests on radical **10** itself and on some of its more stable derivatives such as dihydrochloride **8** and trication **9**.

It is conceivable that by reacting with the hydroxide counterion, the *N*-methylacetyl pyridinium cation undergoes reduction to a Kosower-type radical **11**, which in turn reacts with the pyridinium ion of **3** to give radical ion **10** (see Scheme I). Radical **10** can be further reduced to diamagnetic species **12**. The uv–visible absorption spectrum of **12** in DMSO (Figure 4) is very similar to that of radical **10** (Figure 1). This is compatible with their structural similarity. The fact that aqueous solutions of **12** were paramagnetic is readily understood in view of the reformation of radical **10** by either one of the two paths shown in Scheme I. The absence of both hydroxide and iodide ions in **12** was shown by the negative test with silver nitrate. Compound **12** reacted quickly with hydrochloric and perdeuterated sulfuric acids to form **8** and **9**, respectively.

Free radical **10** exhibited visible absorption with λ_{max} in the 600–700-nm range, which is characteristic of viologen-like radicals. Its ir spectrum retained the carbonyl stretching band at 1640 cm^{-1}. The nmr spectrum of diamagnetic trication **9** in D_2SO_4 was indistinguishable from that of the dihydrochloride **8** in D_2SO_4. Qualitatively, dihydrochloride **8** also showed evidence for preservation of the acetyl groups of **3** by forming 2,4-dinitrophenylhydrazone (mp 184°) and a positive iodoform test. Probably the most convincing evidence for structure **10** is the esr spectrum

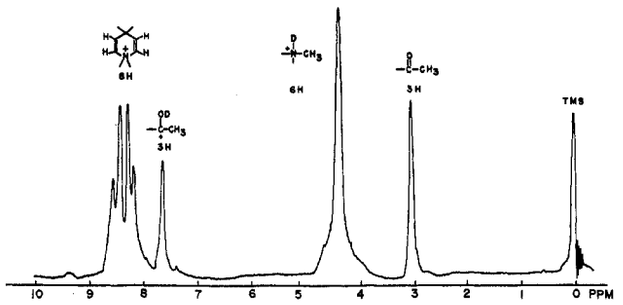
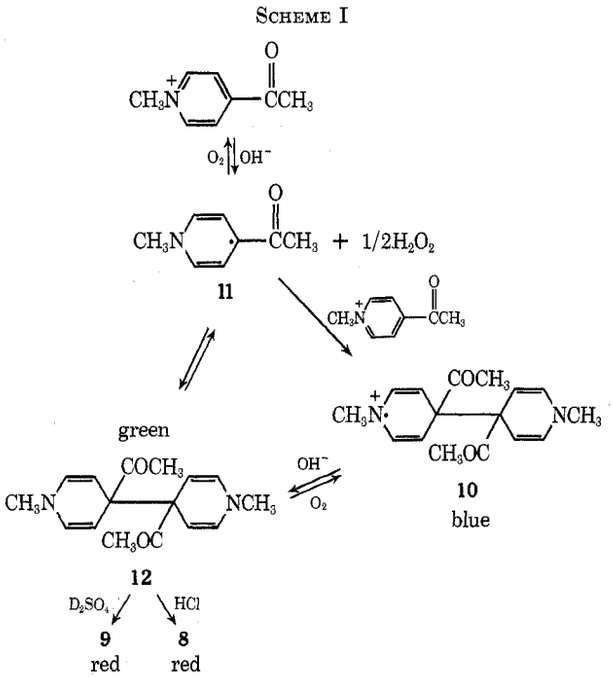
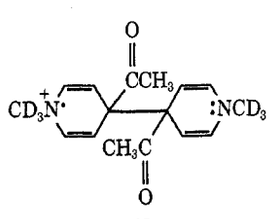


Figure 6.—Nmr spectrum of **12** in D_2SO_4. Identical spectrum obtained for **8** in D_2SO_4.

SCHEME I



of the blue aqueous solution shown in Figure 2. The hyperfine splitting constants indicated on the diagram were determined very accurately by computer analysis, since the fit between simulated and experimental curves is extremely sensitive to even very slight changes in the values of the hyperfine splitting constants. Very useful information was obtained from the comparison of esr spectra of **10** (NCH_3) with that of the free radical derived from the NCD_3 analog of **3**, structure **13**.



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The spectrum of the radical cation **13** containing NCD_3 groups should differ from that containing NCH_3 groups only in the splitting constants of the deuterons. Indeed, the hyperfine splitting constants a^N = 5.39 Oe, a_1^H (α to N) = 1.54 Oe, and a_2^H (β to N) = 1.80 Oe are identical for the two free radicals derived from **3** and **7**, whereas $a^H_{CH_3}$ (from NCH_3) = 5.10 Oe in **10** and $a^D_{CD_3}$ = 0.79 Oe in **13**. Since $a^H_{CH_3}/a^D_{CD_3}$ should be equal to the gyromagnetic ratio of H to D,

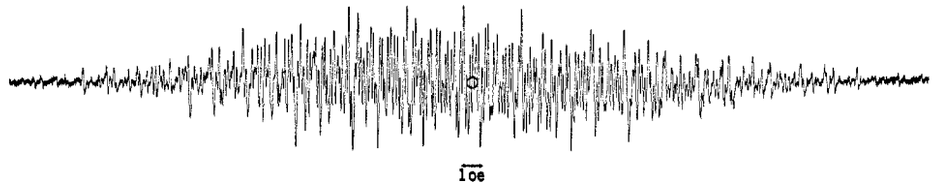


Figure 7.—Esr spectrum of 4-acetylpyridine methiodide in sodium ethoxide–ethanol solution.

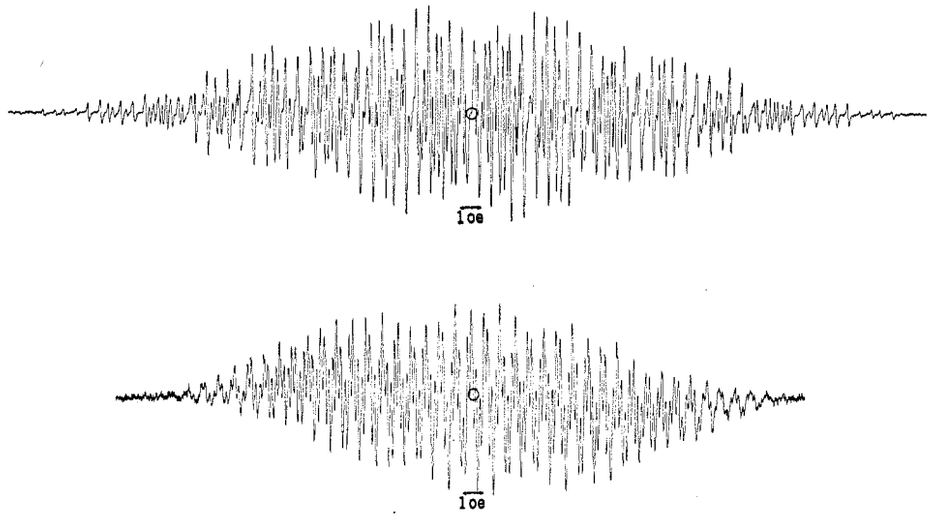
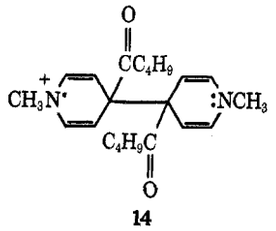


Figure 8.—Esr spectra of stable radicals generated from 4-acetylpyridine methiodide (**3**) (top) and its d_3 derivative **7** (bottom) in pyrrolidine–dimethoxyethylene solution.

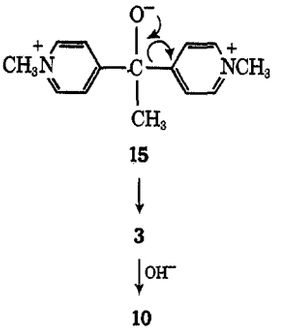
namely 6.51, one can easily verify that *there must be six deuterium atoms in the free radical derived from compound* **7**, *or two equivalent* CD_3 *groups*. That implies that there are two 4-substituted *N*-methylpyridine groups in the paramagnetic species and no other atoms with nuclear magnetic moment within the delocalized domain of the unpaired spin. The esr spectra also indicate that the presence of the two acetyl groups in radical **10** does not interfere sufficiently with the π through-space delocalization to prevent the equal time-distribution of the unpaired spin on each of the two pyridine rings. On the other hand, it seems quite reasonable that there should be no additional splitting in the esr spectrum caused by the CH_3 groups of the acetyls, since any hyperconjugative structures suggestive of unpaired-spin proximity to the H's of those CH_3 groups would represent highly improbable configurations. In addition we found that the esr spectrum of the radical derived from *N*-methyl-4-valeryl iodide (**4**) in hydroxide, presumably **14**,



14

was virtually identical with that of **10**. In contrast, the bulky derivative 4,4-dimethylvaleryl pyridyl ketone methiodide (**5**) yielded a totally different stable radical in deoxygenated 1 *N* aqueous sodium hydroxide. The intensely blue solution exhibited characteristic dimethyl viologen radical uv–visible absorption[4] and esr spectrum indistinguishable from that of viologen **2** prepared from different reagents.[5,6] The only tentative explanation for the difference in behavior of **5** compared to **3** is that the bulkiness of the dimethylvaleryl group sterically inhibits the formation of a radical retaining the two acyl groups analogous to **10**. To support this argument the unsubstituted valeryl analog **4** yielded uv–visible and esr spectra consistent with **14**, a radical similar to **10**.

We find it worth mentioning that di(4-pyridyl)-methylcarbinol (**6**), prepared by treatment of di(4-pyridyl) ketone with methylmagnesium iodide and then with excess methyl iodide, also generated radical **10** when treated with hydroxide. Immediately after mixing crystals of **6** with aqueous concentrated hydroxide an intense red color developed which persisted for several minutes only to change abruptly into a more stable deep blue color. Both uv–visible and esr spectra of this blue solution were identical with those derived from 4-acetylpyridine methiodide (**3**) with base under the same conditions. Whereas the uv–visible absorption is only moderately indicative of minor changes in alkyl substituent, the hyperfine



15

↓

3

↓ OH^-

10

splitting in the esr spectrum is extremely sensitive to even minor changes in the molecule. Therefore, the superimposable identity of the paramagnetic signals of the blue radicals derived from both **3** and **6** in hydroxide testifies to the formation of the same stable radical **10** and the necessary cleavage adjacent to the carbinol carbon of **6**. It is quite possible that the observed red intermediate is ion **15** which subsequently cleaves to form **3**, which, in turn, reacts with hydroxide to generate radical **10**.

Experimental Section

Spectrograde solvents were used throughout. Alkoxide solutions were freshly prepared by dissolving metallic sodium in alcohol. Degassed solutions were prepared by repeated freeze–thaw cycles under high vacuum in either silica absorption cells or esr tubes provided with side reservoirs and constrictions for flame sealing. Degassing was carried out with the solvent in the side bulb and the crystals of solute in the sample compartment. Because of dielectric loss in the solvent, aqueous esr samples were placed in 1-mm i.d. quartz tubes and those in alcohol in 1-, 2-, or 3-mm i.d. tubes.

Uv–visible absorption spectra were recorded on the Cary spectrophotometer Model 15 in double-beam mode. Esr spectra were recorded on a modified Varian V-4502 spectrometer with 10-kHz modulation. The microwave bridge of the spectrometer consisted of a circulator in the sample arm and a precision attenuator and phase shifter in the bucking arm. Computer simulations were carried out on an IBM 360/91 computer and drawn by the Cal-Comp Associates Plotter; other calculations were performed on an IBM 360/50 computer.

Nmr spectra were recorded on a Hitachi Perkin-Elmer nmr spectrometer, Model R-20, with internal and in some cases external TMS standard. Infrared spectra were taken on a Perkin-Elmer 221 infrared spectrometer. Mass spectra were run on a Perkin-Elmer 270 GC mass spectrograph.

The preparation of di(4-pyridyl) ketone (**1**) and di(4-pyridyl)-methylcarbinol dimethiodide (**6**) was described previously.[4]

4-Acetylpyridinium Methiodide (3).—Treatment of 10 g (82.6 mmol) of 4-acetylpyridine (Aldrich) with excess CH_3I gave 19 g of orange, crystalline methiodide: yield 87%; mp 172–173°; ir (KBr) ν 1690 cm^{-1} (C=O); nmr (DMSO-d_6) δ 9.26 (2 H, doublet, 2,6-pyridinium H's), 8.47 (2 H, doublet, 3,5-pyridinium H's), 4.50 (3 H, singlet, NCH_3), 2.79 (3 H, singlet, acetyl H's).

Anal. Calcd for $C_8H_{10}NOI$: C, 36.5; H, 3.80. Found: C, 36.3; H, 3.90.

4-(4′,4′-Dimethylvaleryl)pyridine.—To a stirred solution of dry 4-cyanopyridine (41.0 g, 0.39 mol) dissolved in 300 ml of anhydrous ether under an N_2 atmosphere was added dropwise 1 *M* *tert*-butyllithium in *n*-pentane (200 ml, 0.39 mol). The dark red-brown solution was stirred for 8 hr, then hydrolyzed with dilute HCl. The organic layer was extracted with five 60-ml portions of dilute HCl; the combined aqueous extracts were made basic with concentrated NaOH and extracted with eight 50-ml portions of chloroform, which were then dried over $MgSO_4$. The $CHCl_3$ was evaporated off, leaving a red oil which was distilled at reduced pressure. The fraction of bp 96–98° (0.5 mm) showed only one peak upon vpc analysis and was identified as 4-(4′,4′-dimethylvaleryl)pyridine: yield 5 g (9.3%); ir (neat) ν 1685 cm^{-1} (C=O); nmr (neat) δ 8.35 (2 H, doublet, 2,6-pyridyl H's), 7.32 (2 H, doublet, 3,5-pyridyl H's), 2.60 (2 H, triplet, methylene adjacent to C=O), 1.22 (2 H, triplet, methylene adjacent to *tert*-butyl), 0.55 ppm (9 H, singlet, *tert*-butyl group); mass spectrum *m/e* (rel intensity) 191 (19, M^+), 176 (23), 135 (41), 134 (14), 122 (31), 107 (26), 106 (100), 79 (28), 78 (42), 57 (61), 51 (23), 41 (28).

4-Valerylpyridine was obtained by treatment of dry 4-cyanopyridine (10.4 g, 0.1 mol) with 2.67 *M* *n*-butyllithium in *n*-hexane (60 ml) followed by hydrolysis with dilute HCl and similar work-up as with 4-(4′,4′-dimethylvaleryl)pyridine: yield 5 g (30%); bp 94–96° (0.5 mm); ir (neat) ν 1694 cm^{-1} (C=O); nmr (neat) δ 8.20 (2 H, complex doublet, 2,6-pyridyl H's), 7.14 (2 H, complex doublet, 3,5-pyridyl H's), 2.51 (2 H, triplet, methylene adjacent to C=O), 1.07 and 0.50 ppm (7 H, multiplet, *n*-propyl group).

4-Valerylpyridinium Methiodide (4).—Treatment of 4-valerylpyridine (2.2 g, 13.5 mmol) with CH_3I (5 ml) in benzene gave the orange-red methyl iodide: yield 3.7 g (89%); mp 87–89°; ir (KBr) ν 1680 cm^{-1} (C=O); nmr (DMSO-d_6) δ 9.10 (2 H, doublet, 2,6-pyridinium H's), 8.36 (2 H, doublet, 3,5-pyridinium H's), 4.49 (3 H, singlet, NCH_3), 3.15 (2 H, triplet, methylene H's adjacent to carbonyl group), 1.41 and 0.90 ppm (7 H, multiplet, *n*-propyl group).

Anal. Calcd for $C_{11}H_{16}NOI$: C, 43.29; H, 5.28. Found: C, 42.77; H, 5.38.

4′,4′-Dimethylvalerylpyridine Methiodide (5). Treatment of 4-(4′,4′-dimethylvaleryl)pyridine (1.0 g, 5.24 mmol) with CH_3I (3 ml) in methyl ethyl ketone formed orange methyl iodide: yield 1.4 g (81%); mp 177.5–178.5°; ir (KBr) ν 1695 cm^{-1} (C=O); nmr (DMSO-d_6) δ 9.16 (2 H, doublet, 2,6-pyridinium H's), 8.42 (2 H, doublet, 3,5-pyridinium H's), 4.38 (3 H, singlet, NCH_3), 3.12 (2 H, triplet, methylene H's adjacent to carbonyl), 1.47 (2 H, triplet, methylene H's adjacent to *tert*-butyl group), 0.89 ppm (9 H, singlet, *tert*-butyl H's).

Anal. Calcd for $C_{13}H_{20}NOI$: C, 46.85; H, 6.05. Found: C, 46.23; H, 6.22.

***N*-Methyl-d_3-4-acetylpyridinium iodide (7)** was prepared with CD_3I (ICN Corp., 99.5%) by a procedure[16–18] similar to that described for **3** as orange crystals: yield 68%; mp 172.5–173.5°; ir (KBr) ν 1690 cm^{-1} (C=O); nmr (DMSO-d_6) δ 9.22 (2 H, doublet, 2,6-pyridinium H's), 8.49 (2 H, doublet, 3,5-pyridinium H's), 2.79 ppm (3 H, singlet, acetyl H's).

1,1′-Dimethyl-4,4′-diacetyl-1,1′-dihydro-4,4′-bipyridinium Dihydrochloride (8).—Radical cation **10** (1.1 g, 3.8 mmol) was suspended at room temperature in 30 ml of 0.5 *M* HCl. The green crystals turned red immediately. Within 25 min the crystals were completely dissolved. After the yellow solution was filtered, 5 ml of 1 *N* NaOH was added dropwise to pH ~9. The solution turned purple, violet, and then blue. The red crystals were reprecipitated with 37% HCl to pH 2. The crystals were suction filtered and washed with ethyl ether: yield 1.3 g (96.15%); mp 296–297°; uv (H_2SO_4) λ_{max} 390 nm (ϵ 16,900), 372 (14,600), 355 sh (8300), 316 (3000), 305 (2900), 295 sh (2600), 285 sh (2500), 262 sh (3400), 250 (5900), 244 (5800); ir (KBr) 1640 cm^{-1} (C=O); the nmr spectrum is shown in Figure 6.

Anal. Calcd for $C_{16}H_{22}N_2O_2Cl_2$: C, 55.62; H, 6.42; N, 8.11; O, 9.26; Cl, 20.53. Found: C, 55.92; H, 5.59; N, 8.29; O, 9.04; Cl, 20.96.

Preparation of 1,1′-Dimethyl-4,4′-diacetyl-1,1′-dihydro-4,4′-bipyridyl (12).—Work was done under N_2 atmosphere. *N*-Methyl-4-acetylpyridinium iodide (**3**) (5 g, 0.019 mol) was introduced into a 250-ml three-necked flask equipped with pressure-equalizing addition funnel and magnetic stirrer. Freshly prepared aqueous 2 *N* NaOH (30 ml) previously deaerated for 20 min by N_2 bubbling, was added dropwise at room temperature. A green solution developed and within 10–15 min a green precipitate appeared. After 2 hr the apparatus was transferred to a nitrogen glove box, and the precipitate was filtered off by suction and washed with ethyl ether, yield 1.5 g (54.74%); uv and nmr spectra are given in text.

Registry No.—**3**, 7630-04-8; **4**, 39833-34-6; **5**, 39833-35-7; **7**, 39833-36-8; **8**, 39833-37-9; **8** di-2,4-DNP, 39833-38-0; **10**, 39833-39-1; **12**, 39833-40-4; **13**, 39833-41-5; CH_3I, 74-88-4; CD_3I, 865-50-9; 4-acetylpyridine, 1122-54-9; 4-(4′,4′-dimethylvaleryl)pyridine, 39833-42-6; 4-cyanopyridine, 100-48-1; 4-valerylpyridine, 1701-73-1.

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