1,1'-Diacetyl-1,1'-dihydro-4,4'-bipyridine and the Yellow and Colorless Modifications of 1,1'-Diacetyl-1,1',4,4'-tetrahydro-4,4'-bipyridine. The 1,1'-Diacetyl-4,4'-bipyridine Radical Cation

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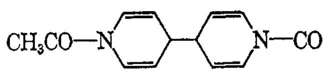
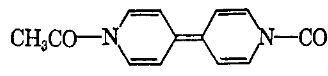
The properties of the yellow and colorless modifications of 1,1'-diacetyl-1,1',4,4'-tetrahydro-4,4'-bipyridine (I) have been carefully examined. The colorless form is shown to be pure I, and the yellow form (I-y), a mixture of I and 3-5% of 1,1'-diacetyl-1,1'-dihydro-4,4'-bipyridine (II). The existence of 1-acetylpyridinyl radicals (V) in samples of the yellow form, postulated by other workers, has been disproved by magnetic susceptibility and e.s.r. spectrum measurements on I-y. Evidence affirming structures I and II is presented. The n.m.r. spectrum of I indicates much double bond character in the amide C–N bond. Chemical behavior of II has been studied including its facile oxidation to 4,4'-bipyridine. The 1,1'-diacetyl-4,4'-bipyridine radical cation (XIV, green), an unstable intermediate in this oxidation process, has been prepared in solution and characterized by its visible and e.s.r. spectra.

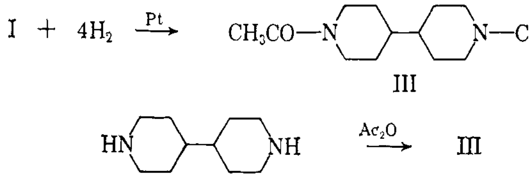
1,1'-Diacetyl-1,1',4,4'-tetrahydro-4,4'-bipyridine (I) is described as a product of reductive coupling and acetylation of pyridine with zinc dust and acetic anhydride.[3-5] The reaction, discovered by Dimroth and Heene,[3] leads to bright yellow crystals (I-y) having the molecular formula of I, $C_{14}H_{16}N_2O_2$. By crystallization of I-y from dilute methanolic potassium hydroxide solution,[3] a colorless modification is obtained having the same melting point and molecular formula. There is general agreement[3-6] that the colorless form is I, although its structure has not been rigorously established. The reason for the yellow color of I-y has been investigated by various workers.[3-6] It has been suggested that I-y is a mixture of I and pyridinyl radicals[6] or some colored diamagnetic impurity[3-5]; another suggestion is that I-y exists as a structural isomer of I.[3,6] We have carefully re-examined the problem and find that I-y contains no free radicals but is a mixture of I and small amounts of 1,1'-diacetyl-1,1'-dihydro-4,4'-bipyridine (II). Chemical behavior confirming structure assignments I and II is presented.


I


II

We have repeated the preparation of I-y according to the procedures of Dimroth and Heene[3] and Wibaut and Arens[5] and obtained yields similar to those reported previously (25–40%). Improved yields (45–47%) have been achieved by employing modifications in the procedure including a somewhat larger excess of zinc, a nitrogen atmosphere, and longer reaction time. Samples prepared by different procedures all appear to have closely similar properties. The colorless form (I) may be prepared by recrystallization of I-y in the manner described[3,5] in 70–82% yields, lit.[5] 73.5%.

Evidence presented previously[3-6] in support of structure I for the colorless form was found to be incomplete. Hydrogenation of I was reported to yield 1,1'-diacetyl-4,4'-bipiperidine (III)[6,7] by uniform absorption of 4 mole equiv. of hydrogen. By preparing an authentic sample of III by acetylation of 4,4'-bipiperidine and comparing it with the hydrogenation product obtained from I, we have now established this fact.



Since the location of double bonds in I had not previously been established, we have carefully examined the spectral properties of this substance. The infrared spectrum (potassium bromide) shows no O–H or N–H stretching bands, but strong amide C=O and olefinic C=C stretching bands at 1660 and 1620 cm.$^{-1}$, respectively. The ultraviolet spectrum (95% ethanol) reveals a broad band with maximum at 263 mμ (ϵ_{max} 24,000).[8] Structure I should have a spectrum roughly equivalent to two independently absorbing N-acetyl-1,4-dihydropyridine molecules. Published data on unsubstituted materials of this type appear to be lacking, but a reasonable model would be N-acetyl-9,10-dihydroacridine; its ultraviolet spectrum has the appearance of a broad band envelope with small protruding maxima of nearly equal intensity at *ca.* 252 and 258 mμ (ϵ_{max} ~19,000).[9]

The proton n.m.r. spectrum of I (*ca.* 20% in deuteriochloroform solution) is in agreement with structure I. The effect of rotational restriction about the amide C–N bond is observed in a large splitting of the

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[3] O. Dimroth and R. Heene, *Ber.*, **54**, 2934 (1921).

[4] O. Dimroth and F. Frister, *ibid.*, **55**, 1223 (1922).

[5] J. P. Wibaut and J. F. Arens, *Rec. trav. chim.*, **60**, 119 (1941).

[6] R. L. Frank, F. Pelletier, and F. W. Starks, *J. Am. Chem. Soc.*, **70**, 1767 (1948).

[7] B. Emmert and A. Wolpert, *Ber.*, **74**, 1015 (1941).

[8] The ultraviolet spectrum of I previously reported[6] [λ_{max} 239 mμ (ϵ_{max} 5400) in 95% ethanol] would indicate that some oxidation to 4,4'-bipyridine had occurred; we find for 4,4'-bipyridine λ_{max} 239 mμ (ϵ_{max} 11,000) in the same solvent. In our hands ethanolic solutions of I, in a stoppered flask, were found to be quite stable (2% decrease in absorbance intensity at 263 mμ after 18 hr.).

[9] E. R. Blout and R. S. Corley, *J. Am. Chem. Soc.*, **69**, 763 (1947); measurement was made in 95% ethanol. Numbers, taken from a curve, are approximate.

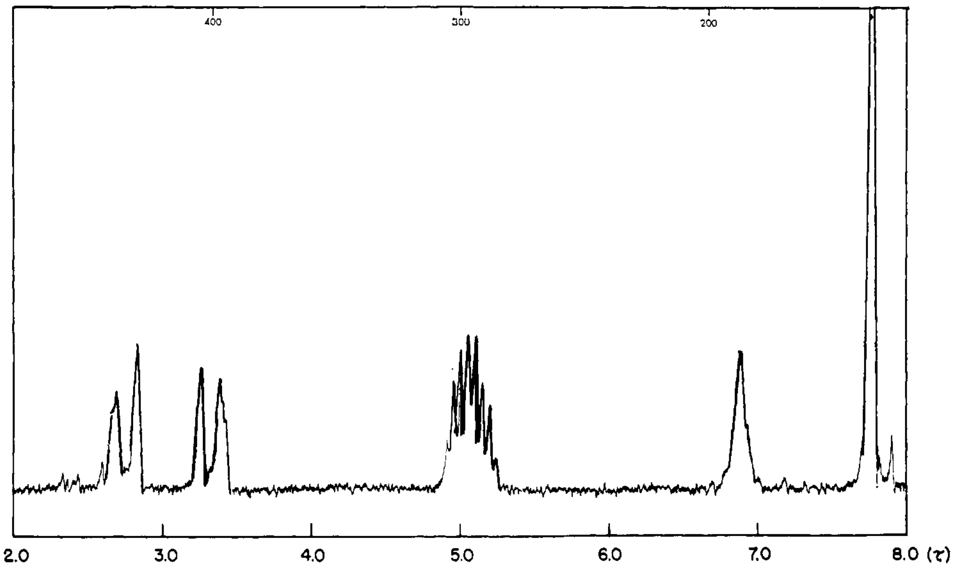
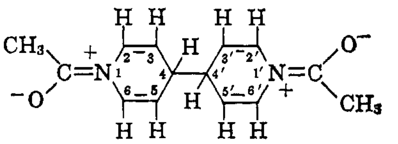


Fig. 1.—Proton n.m.r. spectrum of 1,1′-diacetyl-1,1′,4,4′-tetrahydro-4,4′-bipyridine (I) in deuteriochloroform at 10°: 60 Mc., tetramethylsilane internal reference.

adjacent ring proton signals indicating much p-orbital content of this C–N bond (contribution from resonance structures such as I′). Figure 1 shows the n.m.r. spectrum obtained at 10° with a Varian A-60 spectrometer. The group of four olefinic proton peaks which appear as doublets centered at τ 2.77 and 3.32 represent the protons in 2(2′)- and 6(6′)-positions.[10] [The chemical shift difference of 0.55 p.p.m. (33 c.p.s.) is much larger than the corresponding separation of *N*-methyl signals observed for dimethyl formamide (0.09 p.p.m.; chloroform).] The narrower 8-c.p.s. splitting of these two signals represents a *cis*-ethylenic coupling to adjacent ring protons in the 3(3′)- and 5(5′)-positions. These protons in turn appear as a complex multiplet at τ 5.08, in which the effects of rotational asymmetry as well as spin-coupling interactions contribute to the fine structure. A poorly resolved multiplet at τ 6.90 is assigned to the 4(4′)-position protons and appears to be broadened by spin coupling to all eight of the remaining ring protons. A sharp single acetyl methyl peak found at τ 7.78 completes the spectrum. Areas under the peaks correspond to the appropriate number of protons. Proton n.m.r. spectra of N-alkyl- and N-aryl-1,4-dihydropyridines have been reported.[11-13] These, however, do not show the peak splitting of the 2,6-olefinic protons observed in I.



I′

To confirm the assumption that rotational restriction accounted for the doubling of ring-proton spectra, a series of spectra were determined at 10° intervals from 10 to 60°. The four-line group assigned to 2(2′)- and 6(6′)-protons showed the expected effect of increasing exchange rate, a steady line broadening that first obliterated the spin splitting near 50° followed by coalescence of the two remaining broad peaks above 60°. The fine structure of the multiplet assigned to the 3(3′)- and 5(5′)-protons behaved similarly, with line broadening at lower temperatures leaving two broad peaks about 7 c.p.s. apart which coalesced above 50°.

Further confirmation of restricted rotation appeared in the behavior of this material in other solvents. The n.m.r. spectrum observed for I in dimethylformamide showed the splitting of 2(2′)- and 6(6′)-protons reduced to 14 c.p.s., less than half that observed for a comparable deuteriochloroform solution. Gradual dilution of the deuteriochloroform solution with dimethylformamide resulted in intermediate reductions of the anisotropy splitting. This type of solvent dependence has been noted in n.m.r. spectra of amide solutions and correlated with associative interactions between the amide and the solvent.[14]

The properties of yellow I-y, except for the color, appear superficially to be identical with those of colorless I. Both substances have the same elemental analysis and melting point.[3,5,15] As with I, 1,4-diacetyl-4,4′-bipiperidine (III) is readily formed on hydrogenation with absorption of 4 mole equiv. of hydrogen at a uniform rate.[6] Only minor differences are noted in the spectra of I and I-y (infrared,[6] ultraviolet, and n.m.r.) and these suggest that I-y contains impurities. Thus the possibility is excluded that I-y exists as a double bond isomer of I.

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(10) The molecule I is symmetrical and the protons of the two halves have identical n.m.r. peaks. A closely similar olefinic proton spectrum has been observed for 1,4-diacetyl-1,4-dihydropyridine oxime,[7] indicating that the observed doubling of ring proton signals is not related to the bicyclic structure of I (unpublished results, this laboratory). A similar splitting of vinyl ring protons (quartet, τ 6.81–7.35) is observed with 2,6-di-*t*-butylbenzoquinone-4-oxime methyl ether: L. A. Cohen and W. M. Jones, *J. Am. Chem. Soc.*, **85**, 3397 (1963).

(11) R. F. Hutton and F. H. Westheimer, *Tetrahedron*, **3**, 73 (1958).

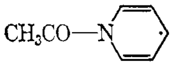
(12) E. M. Kosower and T. S. Sorensen, *J. Org. Chem.*, **27**, 3764 (1963).

(13) M. Saunders and E. H. Gold, *ibid.*, **27**, 1439 (1963).

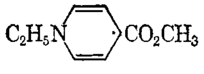
(14) J. V. Hatton and R. E. Richards, *Mol. Phys.*, **5**, 139 (1962).

(15) The melting points of I and I-y occur with some decomposition and depend on the rate of heating. Capillary melting points reported for I-y are 124–125°[3] and 130–131°.[5] We find melting ranges from 122–125° to 128–132° on various samples from different preparations. For colorless I melting points reported were 123–125°,[3] 130–131°,[6] and 132–132.8°[5]; our samples melted over the range 123–129°. Before melting, the colorless form is observed to turn yellow.

The suggestion has been made that I-y is yellow owing to the presence of 1-acetylpyridinyl radicals (V) as I-y was found to be paramagnetic while I was not.[6] The radical V probably has a certain stability[16] and a recent report[17] of the isolation of the 4-carbomethoxy-1-ethylpyridinyl radical (VI) as an emerald green liquid supports this idea. However, VI is extremely sensitive to oxygen and it appeared unlikely to us that V could exist as a trapped impurity in I for prolonged periods. We therefore repeated the magnetic susceptibility measurements on I-y ($K = -0.405 \times 10^{-6}$ g.$^{-1}$) and I ($K = -1.013 \times 10^{-6}$ g.$^{-1}$) and, contrary to the original report[6], found both substances to be diamagnetic.[18] Also, I-y showed no e.s.r. signal indicating absence of significant amounts of free radicals (calculated radical concentration less than 10^{-15} M). Thus the color of I-y must be due to some colored impurity other than radicals.



V

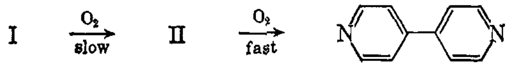


VI (green)

The presence of 1,1'-diacetyl-1,1'-dihydro-4,4'-bipyridine (II) as an impurity in I-y was suggested earlier.[3-5] The suggestion rested tentatively on the demonstration that low yields of II could be obtained by air oxidation of I in hot acetic anhydride solution.[3,4] Direct evidence of the presence of II in I-y has now been obtained by trituration of I-y with cold chloroform, in which I is very soluble but II is only slightly soluble; a 4.5% recovery of II (6% of material assaying 75% II by ultraviolet spectroscopy) was obtained in this manner. Also, the characteristic visible spectrum of II having a maximum at 428 mμ (95% ethanol) is found in I-y, but not in I. By comparison of absorbances at 428 mμ (calculated at zero time by extrapolation) it is estimated that I-y contains *ca.* 3–5% II. The maximum in the ultraviolet spectrum at 263 mμ in I ($\epsilon_{\max}$ 24,000) is also found in I-y but of slightly lowered extinction coefficient ($\epsilon_{\max}$ 23,200 after the rapid conversion of II to 4,4'-bipyridine VII[4] is complete). By correcting for the absorbance of VII at 263 mμ, the amount of II present in I-y is calculated to be 4.6%. The infrared spectrum of I-y suggests very small amounts of II to be present, but no significant amounts of other impurities except possible trace amounts of VII. However, an accurate assay cannot be made from the appropriate characteristic infrared absorbances because of the low concentrations of impurities. It is concluded that samples of I-y contain II as the major (and only colored) impurity and 93–97% I.

Structure II was established by its hydrogenation to 1,4-diacetyl-4,4'-bipiperidine (III) (platinum catalyst, 1 atm., ethanol, 25°), 5 mole equiv. of hydrogen being rapidly and uniformly absorbed.

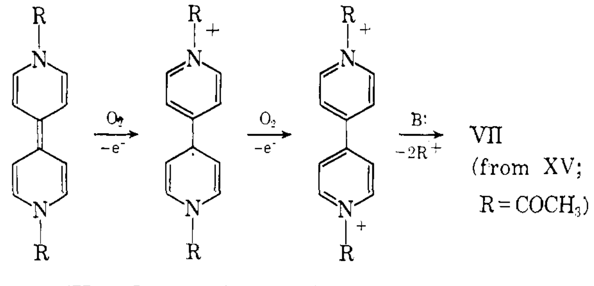
4,4'-Bipyridine (VII) has been obtained by air oxidation of I or II[3,4,19] in various solvents, the oxidation of II occurring quite rapidly.[4] Oxidation of I to II has been demonstrated,[3,4] and in our opinion is the cause, rather than radical formation,[6] for color changes observed with I in solution. The appearance of a yellow color when ethanolic solutions of I (colorless) are warmed in a stoppered flask and the disappearance of the yellow color on exposure to air[6] are believed due to rapid oxidation of II (yellow in solution) to VII (colorless). The intermediate steps in the oxidation, II → VII, are discussed below. (Dilute solutions of I in ethanol are much more stable[8] than those of II.) The rate of conversion of II to VII has been followed spectrophotometrically in 95% ethanol solution by observing the decrease in intensity of absorption at 428 mμ (by extrapolation to zero time, $\epsilon_{\max}$ 32,500). Excellent first-order plots of log A (absorbance) against time are obtained, $k = 2.8 \times 10^{-3}$ sec.$^{-1}$ at 25°. The band at 428 mμ found in I-y due to presence of II disappears at the same average rate, although the range of rate constant values is larger. The disappearance of the 428-mμ band is accompanied by the appearance of a strong 4,4'-bipyridine band at 239 mμ in the ultraviolet region ($\epsilon_{\max}$ 10,300 after destruction of II is 98% ocmplete; 4,4'-bipyridine $\epsilon_{\max}$ 11,000 at 239 mμ). The rate of disappearance of II in ethanol solution is more rapid in the presence of dilute sodium hydroxide and is also hastened by exposure to strong incandescent light.



VII

The chemical behavior of I and II finds close analogy in that of colorless 1,1'-dibenzyl-1,1',4,4'-tetrahydro-4,4'-bipyridine (VIII), m.p. 83–87°, and the corresponding brown dihydro compound (IX), m.p. 140° with decomposition.[20] Compound VIII in solution is oxidized to IX by air and becomes yellow-brown as its melting point is approached. 1,1'-Dibenzyl-4,4'-bipiperidine is formed by hydrogenation of VIII and IX (4 and 5 mole equiv. of hydrogen absorbed, respectively).[21]

Another property to be predicted for II, which is characteristic of IX, is its one-electron oxidation to a deeply colored radical cation (XIV, R = $COCH_3$). This radical is an intermediate in the oxidation process leading to 4,4'-bipyridine (II → VII). Radical X (R = $CH_2C_6H_5$) and XI (R = H, derived from 4,4'-bi-



II, IX, XII X, XI (blue) XV, XVI,
XIII, XIV XVII, XVIII
(green)

XI, XVIII, R = H II, XIV, XV, R = $COCH_3$
IX, X, XVI, R = $CH_2C_6H_5$ XII, XIII, XVII, R = C_6H_5

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[16] Arguments have been advanced explaining the stability of V; *cf.* R. A. Barnes in "Pyridine and Its Derivatives," Part I, E. Klingsberg, Ed., Interscience Publishers, Inc., New York, N. Y., 1960, p. 56.

[17] E. M. Kosower and E. J. Poziomek, *J. Am. Chem. Soc.*, **85**, 2035 (1963).

[18] Compound II is also diamagnetic ($K = -0.298 \times 10^{-6}$ g.$^{-1}$). Measurements were performed by Mr. Kenneth Kneip, Tulane University.

[19] A. E. Arbuzov, *Bull. acad. sci. URSS Classe sci. chim.*, 451 (1945); *Chem. Abstr.*, **42**, 5912 (1948).

[20] R. Weitz, T. König, and L. V. Wistinghausen, *Ber.*, **57**, 153 (1924).

[21] R. Weitz, *Angew. Chem.*, **66**, 658 (1954).

pyridine itself) are blue,[21–24] and XIII (R = C_6H_5) from 1,1′-diphenyl-1,1′-dihydro-4,4′-bipyridine (XII) is green.[21] A dilute chloroform solution of II, to which trifluoroacetic acid had been added, was oxidized immediately upon exposure to air or treatment with iodine to a deep green substance (blue-green in concentrated solutions), λ_{max} 637 and 707 mμ, assigned the radical cation structure XIV (R = $COCH_3$). The visible spectrum of XIV resembles that of 1-carbomethoxy-4-ethylpyridinyl radical (VI, $\lambda_{max}^{CH_3CN}$ 632.5, shoulders at 690 and 775 mμ).[17] The e.s.r. spectrum of XIV was determined at −15° in degassed chloroform solution containing a few drops of trifluoroacetic acid (1% solution of II). At this temperature the green color persisted for 45 min. A single sharp line centered at 2.003 gauss, width ~7–10 gauss between inflection points, was obtained. By double integration of the spectrum curve area, the conversion to radical is calculated to be very high (roughly quantitative), and would suggest the narrow single-line spectrum without resolved hyperfine structure to be due to exchange narrowing due to high radical concentration.[25] Attempts to observe hyperfine structure by decreasing concentration failed because solutions were unstable.

Further oxidation of XIV occurs rapidly in air leading to a light yellow solution presumed to contain the dication XV, analogous to known dications XVI, XVII, and XVIII derived from X, XI, and XIII, respectively. Addition of II to the solution of XV regenerates the green color. Deacylation of XV (by treatment with water or other base) produces 4,4′-bipyridine (VII).

Experimental[26]

1,1′-Diacetyl-1,1′,4,4′-tetrahydro-4,4′-bipyridine (Yellow Modification, I-y).—The original procedure of Dimroth and Heene[1] was followed with certain modifications. To a mixture of 200 ml. (194 g., 2.46 moles) of pure pyridine, 1 l. of acetic anhydride, 20 ml. of acetic acid, and 1.0 g. of ferric chloride contained in a 3-l. three-necked flask was added, with vigorous stirring, a 75-g. portion of powdered zinc (99.9% assay). The mixture was stirred vigorously until a temperature rise to 40° occurred (0.5–1.5 hr.).[27] The temperature was then maintained at 30–40° by occasional ice-bath cooling and nitrogen was passed through the system; zinc (265 g. more, total 340 g.) was added in *ca.* 30-g. portions at regular intervals during 4.5–5 hr. Vigorous stirring was continued for 15 hr. (25–30°) after addition of the zinc was complete (nitrogen atmosphere maintained). The flask was then surrounded by a large container of boiling water to heat the stirred mixture to 90° within 5 min. The mixture was then filtered immediately through a Büchner funnel and the filter cake was washed three times with acetic anhydride (100-ml. portions). The clear yellow filtrate was chilled immediately in an ice bath and kept at 0–5° for 4 hr. while shaking and stirring vigorously at intervals. The bright yellow crystals were filtered and washed first with acetic anhydride and then several times with water and finally dried in a vacuum desiccator over sodium hydroxide; yield 135–140 g. (45–47%), m.p. 125–128°.[15,26] Alternatively, the acetic anhydride filtrate may be poured directly into a large amount of ice and water and filtered (47% yield). When the procedure of Dimroth and Heene[3] was followed on the above scale (90% assay zinc, air atmosphere), yields of 23–34% were obtained; m.p. 122–127° to 128–132° on different runs, lit. m.p. 124–125°[3] and 130–131°.[5]

1,1′-Diacetyl-1,1′,4,4′-tetrahydro-4,4′-bipyridine (Colorless Modification, I).—A 50.0-g. sample of the yellow form I-y was dissolved in 500 ml. of hot methanol. A solution of 2 g. of potassium hydroxide in 20 ml. of methanol was added and the mixture was heated to boiling for 5–10 min. After filtering, the filtrate was chilled quickly in an ice bath and shaken vigorously. The crystals were filtered immediately and washed with ice-cold methanol to yield 35–41 g. (70–82%) of colorless I, m.p. 126–129°,[15,26] lit. m.p. 123–125°[3] and 132–132.8°.[5] The melting point depends on the rate of heating and values determined on a Kofler hot stage were 5–10° lower.[26] As observed previously[6] samples of I and I-y when exposed to air at room temperature occasionally decompose spontaneously, and rapidly form a viscous brown oil. Samples placed in a well-sealed container in a refrigerator have never been observed to decompose after storage for periods of several months.

1,1′-Diacetyl-1,1′-dihydro-4,4′-bipyridine (II) was prepared according to the procedure of Dimroth and Frister[4] by heating equivalent amounts of I and 4,4′-bipyridine in acetic anhydride under nitrogen on the steam bath for 30 min. The crude product was recrystallized from hot acetic acid as bright orange leaflets (30% yield), m.p. 260–264° dec.,[26] lit. m.p. 248°[3] and 284°[4]; the melting point depends on the rate of heating. The substance has very limited solubility in all solvents tested and a suitable n.m.r. spectrum could not be obtained. The infrared spectrum (Nujol) showed split carbonyl absorption at 1660 and 1640 and a C=C stretching band at 1560 cm.$^{-1}$ (absent in I but present in 4,4′-bipyridine at 1580 cm.$^{-1}$); strong bands at 893 and 750 present in I and at 815 cm.$^{-1}$ present in 4,4′-bipyridine were absent.

The ultraviolet spectrum was determined in 95% ethanol solution (c 2.1 × 10^{-4} M) using a Cary Model 11 MS recording spectrophotometer. Absorbance of the yellow solution (λ_{max} 428, shoulder 415 mμ) decreased with time and absorbance readings were taken at intervals at 428 mμ: 429 sec., A 1.95; 520, 1.48; 611, 1.11; 756, 0.71; 847, 0.55; 942, 0.43. By plotting log A against time the points were found to lie on a straight line and extrapolation to zero time gave A = 6.8 (ϵ_{max} 32,400). From the slope a first-order rate constant could be calculated, k = 2.93 × 10^{-3} sec.$^{-1}$. Values obtained in another run were ϵ_{max} 32,600 and k = 2.72 × 10^{-3} sec.$^{-1}$; average 2.8 × 10^{-3} sec.$^{-1}$ ϵ_{max} 32,500 (for shoulder at 415 mμ, ϵ 28,200, calculated in the same manner). The disappearance of the band at 428 mμ is accompanied by an increase in intensity of a band at 239 mμ in the ultraviolet region: 540 sec., A 1.90; 780, 2.05; 899, 2.08; 1238, 2.17; 1490, 2.20. At 1490 sec., ϵ_{max} was 10,300 at 239 mμ and 560 at 428 mμ (when destruction of II is 98% complete). The band at 239 mμ is believed to be that of 4,4′-bipyridine which was found to have an absorption maximum at this wave length (ϵ_{max}^{239} 11,000), lit.[28] λ_{max} 237 mμ (ϵ_{max} 13,000) in hexane.

Addition of dilute sodium hydroxide to saturated ethanolic solutions of II (100 ml. in volumetric flask) hastened the transformation to a colorless solution (25°); 1.0 ml. of 1.0 N aqueous sodium hydroxide caused decolorization in 45 min. and 0.1 ml. caused decolorization in 80 min. A control solution containing no additives was decolorized in 200 min. Exposure of ethanolic solutions of II to ultraviolet or incandescent lamps hastens destruction of the yellow color two- to threefold.

1,1′-Diacetyl-4,4′-bipyridine Radical Cation (XIV).—Saturated solutions of II in chloroform (*ca.* 0.7 g./100 ml., deep yellow) when treated with a few drops of trifluoroacetic acid produced a deep blue-green color when shaken in air (λ_{max} 637 and 707 mμ). Within a few minutes the solution became light yellow in color; addition of more II regenerated the green color. The transformation could also be carried out with iodine (nitrogen atmos-

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[22] E. Müller and K. A. Bruhn, *Ber.*, **86**, 1122 (1953).

[23] F. Bruin, F. W. Heineken, M. Bruin, and A. Zahlan, *J. Chem. Phys.*, **36**, 2783 (1962).

[24] The deep blue color produced by prolonged heating of ethanolic solutions of I was shown by Dimroth[2] to arise from the 4,4,-bipyridine formed by decomposition. Later,[22] the blue color was shown to be that of the cation radical XI (R = H).

[25] R. L. Ward and S. I. Weissman, *J. Am. Chem. Soc.*, **79**, 2086 (1957).

[26] Melting points reported for I-y, I, and II were determined in capillary tubes, others on a Kofler hot stage.

[27] An induction period of 0.5–1.5 hr. was noted before a temperature rise and the appearance of a bright yellow-green color occurred. Maintenance of an air atmosphere during this time (rather than nitrogen) and the additions of acetic acid and a small amount of ferric chloride were found to shorten this induction period.

[28] C. W. F. Spiers and J. P. Wibaut, *Rec. trav. chim.*, **56**, 573 (1937). The lower value of ϵ_{max} found in 95% ethanol (compared with hexane) may be due to formation of pyridinium ions. P. Krumholz [*J. Am. Chem. Soc.*, **73**, 3487 (1951)] reported for VII λ_{max} *ca.* 238 mμ (ϵ_{max} 15,000) in methanol containing ammonia (0.02 M); numbers taken from published curve are approximate. At low concentrations such as those employed here (1.4 × 10^{-4} M anhydrous VII) some 4,4,-bipyridinium mono ion may be produced (λ_{max} 256 mμ) causing a broadening of the band envelope and lowering of ϵ_{max}.

phere), traces of which produced a deep green color while an excess produced a light yellow solution. The green solutions were stable in air for only a few minutes and stable under nitrogen for only slightly longer periods. By careful addition of glycerol as a floating layer over the chloroform solutions,[23] the green color remained for 15–20 min. The green solutions, believed to contain 1,1'-diacetyl-4,4'-bipyridyl radical cation (XIV) could also be prepared in acetonitrile and less readily in benzene, ethanol, acetone, or acetic acid; solutions of XIV prepared in these solvents were much less stable than the chloroform solutions.

The e.s.r. spectrum of the radical cation XIV was obtained with a Strand Model 600 x-band spectrometer and a Harvey Wells L-128 magnet. The magnetic field (nominally 3400 gauss) was calibrated by monitoring the frequency of a Harvey Wells F-502 NMR oscillator with a Hewlett Packard HP-524C frequency counter. Field sweep rates of 1 gauss/min. were used. Microwave power was kept low, although no saturation was observed up to 10 mw. of klystron power.

Solutions were prepared in pure chloroform in quartz e.s.r. tubes equipped with Teflon stopcocks and then degassed using the triple freeze-thaw technique.[29] The stopcock was opened briefly to allow the addition of a few drops of trifluoroacetic acid to generate the radical. All spectra were obtained at −15° using a glass flow cryostat. At this temperature the green color was found to persist for *ca.* 45 min. if degassed chloroform and fresh trifluoroacetic acid were used. On a 1% solution (0.1 g./10 ml.) a single sharp line was obtained, centered at 2.003 gauss (width ~7–10 gauss measured between inflection points). Attempts to observe hyperfine structure by decreasing concentration failed because solutions were unstable. The lowest stable concentration was *ca.* 0.1% with spectrum parameters the same as for the 1% solution.

Radical concentrations were measured by using a chromium-doped ruby crystal mounted within the microwave cavity as an internal standard.[30] The crystal was oriented in such a manner as to give a single line well resolved from the radical signal. The two signals thus obtained were compared on the basis of a double integration of the area under each curve. The intensity of the ruby signal was calibrated with a series of diphenylpicrylhydrazide–asphaltene standards. The estimated radical concentration of the 1% solution (containing *ca.* 2.5 × 10^{19} molecules/ml.) was 5 × 10^{18}/ml. In a single line spectrum of the type observed, intensity measurements are reliable to about one order of magnitude. Thus the conversion to radical is roughly quantitative.

Properties of Yellow Modification I-y.—The infrared spectrum (potassium bromide) was practically identical with that of I; no OH or NH bands but strong amide C=O and olefinic C=C stretching bands at 1660 and 1620 cm.$^{-1}$, respectively. Slight lowering of intensities of certain bands present in I and absent in II (893 and 750 cm.$^{-1}$) was noted. Also present was a very weak band near 810 cm.$^{-1}$, absent in I and II but present in 4,4'-bipyridine (813 cm.$^{-1}$) as a very strong broad band.

The visible spectrum was determined in 95% ethanol by the procedure described for II, the characteristic maximum at 428 mμ and shoulder at 415 mμ were observed. A 1.95 × 10^{-3} *M* solution (employing mol. wt. 244.3) had an absorbance of 2.0 at zero time at 428 mμ (ϵ_{max} 1030) corresponding to 3.2% II; another sample contained 4.3% II. The decrease in absorbance at 428 mμ was followed as with pure II and plots of log *A* against time gave a straight line from which rate constants could be calculated from the slopes; values of 1.23, 2.26, and 3.55 × 10^{-3} sec.$^{-3}$ were observed with different samples (rate for pure II, 2.8 × 10^{-3} sec.$^{-1}$). The variation in rates may possibly be attributed to variable amounts of trace impurities present in each sample.

In the ultraviolet spectrum a broad band was observed at 262 mμ (ϵ_{max} 23,200 after solution became colorless in spectrophotometer, *ca.* 30 min.); after standing 18 hr., ϵ_{max}^{262} was 22,800 (employing mol. wt. 244.3). The measurement at 30 min. was determined after the impurity II had been completely converted into 4,4'-bipyridine (VII). At 262 mμ, VII has ϵ 5900 and, assuming no impurity other than VII to be present, the amount of VII is calculated to be 4.4% from the equation $\epsilon_{obsd} = \epsilon^{I}(1 - c) + \epsilon^{VII}c$, where ϵ^{I} and ϵ^{VII} are the extinction coefficients of I and VII at 262 mμ, *i.e.*, 24,000 and 5900, respectively, and *c* is the fraction of VII in the mixture. Since VII arises quantitatively from II, the amount of VII originally present in I-y is probably very small (<1%).

The n.m.r. spectrum of I-y in deuteriochloroform solution was practically indistinguishable from that of I.

The e.s.r. spectrum of I-y showed no signal. In various runs the spectrometer setting was varied such that line widths up to 100 gauss would have been detected if the spin concentration were greater than 10^{-15} *M*. In all cases, the results were negative. The absence of an e.s.r. signal is not conclusive proof that the material is diamagnetic, but this point was covered by the magnetic susceptibility measurements. Compounds I and II and substance I-y were all found to be diamagnetic[18]; see discussion for numerical values.

Trituration of a 4.0-g. sample of yellow I-y with 10 ml. of chloroform produced an orange solid which was filtered and washed with water to yield orange crystals, 0.24 g., m.p. 176–180° dec. A 2.06 × 10^{-4} *M* solution (employing mol. wt. 242.3) of this substance in 95% ethanol was calculated to have ϵ_{max} 24,300 at 428 mμ by extrapolation to zero time as described above, corresponding to 75% II in the crude product. The recovery of pure II corresponds to 4.5%. The decrease in absorbance at 428 mμ occurred uniformly as with pure II, $k = 2.54 \times 10^{-3}$ sec.$^{-1}$. The loss of II due to solubility in the concentrated solution of I is believed to be small since the solubility of II would be less in such a solution than in pure chloroform where it is only *ca.* 1.0–0.7 g./100 ml. at 25°.

4,4'-Bipiperidine.—A 1.56-g. sample of 4,4'-bipyridine (anhydrous, m.p. 111–112°) in 50 ml. of absolute ethanol was hydrogenated with 1.0 g. of 10% palladium–charcoal catalyst at 50 p.s.i. and 25° in a Parr apparatus until hydrogen uptake ceased (6 mole equiv. absorbed after 60 hr.). The catalyst was filtered and the filtrate was concentrated and triturated with acetone to yield 1.39 g. (83%) of 4,4'-bipiperidine, m.p. 168–170°[26]; recrystallization from acetone did not change the melting point; lit. m.p. 170–171°[31] and 171–172°.[32] The substance readily absorbs water and carbon dioxide from the atmosphere. When the hydrogenation procedure employed with I and II (see below) was applied to 4,4'-bipyridine (700 mm., 25°, platinum catalyst), essentially no hydrogen uptake was observed after 19 hr.

1,1'-Diacetyl-4,4'-bipiperidine (III). A. **From 4,4'-bipiperidine.**—A 0.9-g. sample of 4,4'-bipiperidine in 15 ml. of acetic anhydride was heated under reflux for 2 hr.; concentration of the mixture to near dryness followed by addition of acetone led to 0.19 g. of crude 1,1'-diacetyl-4,4'-bipiperidine, m.p. 174–175° after recrystallization from acetone (lit.[7] m.p. 174°); infrared spectrum (potassium bromide) had a strong amide carbonyl band at 1640 cm.$^{-1}$, NH and OH bands absent.

B. **From II by Hydrogenation.**—A 0.0798-g. sample of 1,1'-diacetyl-1,1'-dihydro-4,4'-bipyridine (II) partly suspended in 10 ml. of acetic acid was hydrogenated in the presence of platinum oxide catalyst (10 mg.) at 702 mm., 25°, until hydrogen uptake essentially ceased (2.3 hr., 5.0 mole equiv. of hydrogen absorbed uniformly); near the end of the reaction the deep yellow color of the solution changed to colorless. The platinum was filtered and the filtrate was concentrated to dryness *in vacuo* to yield 0.08 g. of material, m.p. 158–159°; recrystallization from acetone raised the melting point to 174.5–175.5°; when mixed with the authentic sample (m.p. 174–175°) the melting point was not depressed; infrared spectrum (potassium bromide) identical with that of the authentic sample.

C. **From I by Hydrogenation.**—The procedure employed above with II was applied to 1,1'-diacetyl-1,1',4,4'-tetrahydro-4,4'-bipyridine (I) dissolved in ethanol. Four mole equivalents of hydrogen were absorbed uniformly before uptake ceased (1.5 hr.). The product was isolated as above in 78% yield, m.p. 169–174°; recrystallization from dioxane gave m.p. 174°; when mixed with an authentic sample the melting point was not depressed; infrared spectrum was identical with authentic sample.

Anal. Calcd. for $C_{14}H_{24}N_2O_2$: C, 66.63; H, 9.59; N, 11.10; mol. wt., 252.35; sapon. equiv., 126.17. Found: C, 66.93; H, 9.84; N, 11.10; mol. wt., 257; sapon. equiv., 126.

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