Registry No.—**4a**, 26958-30-5; **4b**, 26958-31-6; **4c**, 26958-32-7; **4d**, 26958-33-8; **4e**, 27039-92-5; **5a**, 26958-34-9; **5b**, 26958-35-0; **5c**, 27006-05-9; **5d**, 26958-36-1; **7**, 26958-37-2; **8**, 26958-38-3.

Viologen Radical from Di(4-pyridyl) Ketone Methiodides in Hydroxide[1]

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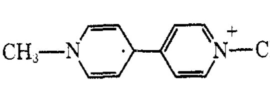
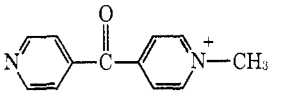
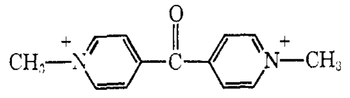
The stability of pyridinyl radical cations has made them subject to intense investigations.[3-8] Kosower and Cotter reported an interesting formation of dimethylviologen radical **1** from 4-cyanopyridinium methiodide and sodium dithionite, presumably *via* dimerization of the neutral 4-cyanopyridinyl radical intermediate.[6] We report here on the unusual formation of the same viologen radical from di(4-pyridyl) ketone mono- and dimethiodides (**2** and **3**) in aqueous hydroxide solution.



1



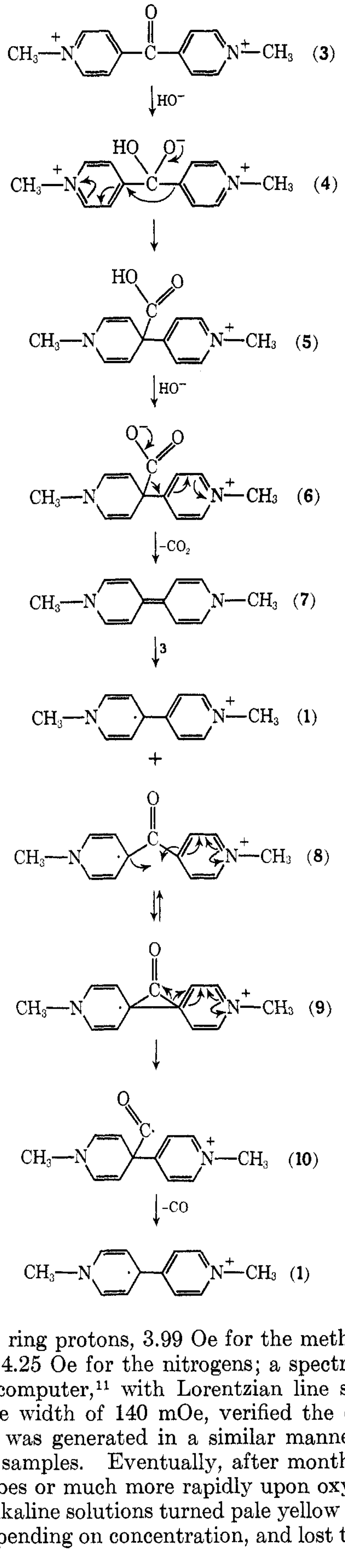
2



3

When 1 *M* NaOH solutions, thoroughly degassed by numerous freeze–thaw cycles, were mixed under vacuum with crystals of either **2** or **3**, the resulting mixture turned deep blue immediately and remained so indefinitely (months). As the color developed, the near-uv–visible absorption showed a parallel increase in the two structured bands characteristic[6] of **1**, namely, in the visible at $\lambda_{\max}$ (ϵ) 560 (7450), 602 (10,400), 660 (5500), and 730 nm [1650 l./(mol cm)] and in the uv at 367 (12,300), 384 (22,300), and 395 nm [34,200 l./(mol cm)]. The blue solutions gave strong esr signals whose presence or absence paralleled that of the color. Examination of high-resolution esr spectra clearly indicated that the blue paramagnetic species formed from both **2** and **3** was dimethylviologen cation radical.[6,9,10] The experimental splitting constants for **1** in water, which differ only slightly from those in ethanol,[9] are 1.33 and 1.59 Oe for the ring protons, 3.99 Oe for the methyl hydrogens, and 4.25 Oe for the nitrogens; a spectrum simulated by computer,[11] with Lorentzian line shape and with a line width of 140 mOe, verified the constants. Radical **1** was generated in a similar manner in nondeaerated samples. Eventually, after months in open sample tubes or much more rapidly upon oxygenation, the blue alkaline solutions turned pale yellow or reddish brown, depending on concentration, and lost their para-

Scheme I



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[1] Taken in part from work done by C. L. T. in partial fulfillment of the Ph.D. requirements at The George Washington University.

[2] To whom correspondence should be directed at The George Washington University.

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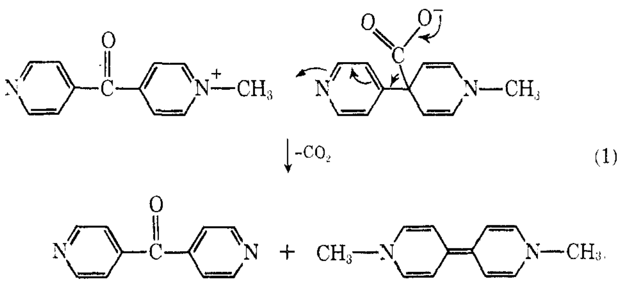
magnetism. Preparative scale solutions of either **2** or **3** purposely decolorized with CO_2-free oxygen produced copious amounts of carbon dioxide upon acidification. An approximate gravimetric evaluation indicated 30 mol % CO_2 yield with respect to original dimethiodide. Furthermore, carbon monoxide was detected with the I_2O_5 test for both **2** and **3**. The liberated iodine in the case of **3** was determined both colorimetrically and by titration to be about 12 mol %. These observations were useful in the formulation of a reaction mechanism. When the base concentration was lower than ~0.1 *M*, no blue color developed. On the other hand, when the base concentration was very high (~10 *M*), the methiodides were no longer soluble and only a very weak blue color developed.

Unlike those of its methiodides, sodium hydroxide solutions of the parent dipyridyl ketone remained colorless and diamagnetic under similar conditions.[12]

A plausible mechanism for viologen radical formation from **3** is shown in Scheme I. Although the hydroxide ion could abstract protons from the methyl groups activated by the pyridinium nitrogens, it seems to attack preferentially the carbonyl group, followed by a 1,2 "push-pull" migration of a 4-pyridinium group to generate cation **5**. One can easily visualize proton abstraction from **5** and subsequent facile decarboxylation of zwitterion **6** with formation of the powerful reducing agent[10,13,14] *N,N'*-dimethyldihydro-4,4'-bipyridyl (**7**), which is rapidly oxidized by dimethiodide **3** to viologen radical **1**. It is known that such molecules as **7**, which have also been called "alkali-metal analogs," are capable of generating viologen radicals in reaction even with common solvents.[13,14] We found that radical cation **8** formed by metal reduction of **3** has a long lifetime in degassed acetonitrile.[15] Apparently, however, in aqueous hydroxide it undergoes rapid decarbonylation *via* **9** and **10**, as shown in Scheme I, with ultimate formation of another viologen radical. It is conceivable that radical **8** leads reversibly to **9** with slow leakage over an energy barrier to **10**. Presence of both carbon monoxide and carbonate among products together with viologen-radical yields of roughly 50 mol %[16] tends to confirm the postulated mechanism. A reaction path for viologen-radical formation from monomethiodide **2** requires decarboxylation, decarbonylation, and either fission at the carbonyl site with subsequent coupling of *N*-methylpyridine moieties or acquisition of a second methyl group at the nonmethylated nitrogen. This latter alternative can be visualized as shown in eq 1. However, this possibility should be considered only tentative, since further analytical work may be necessary to substantiate such a mechanism.



(1)

Registry No.—**1**, 26985-31-9; **2**, 26988-47-6; **3**, 26988-48-7.

Acknowledgment.—We thank Professor E. M. Kosower for helpful suggestions and the Atomic Energy Commission for partial support on Contract AT-(40-1)-3797.

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[16] The conversion of the methiodides to viologen radical was evaluated spectroscopically in degassed samples of known concentrations from maximum absorbance at 395 and 602 nm.

A Stereoselective Synthesis of *trans*-Isobornylcyclohexanol

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The long-recognized value of sandalwood oil as a perfume essential to the formulation of a variety of fine soap fragrances has prompted us to consider syntheses for other materials reputed to possess sandalwood-like odors. The curious discovery that a mixture of terpene cyclohexanols, formed by catalytic reduction of the condensation products of camphene and guiacol or camphene and phenol, provides a sandalwood odor first appeared about 20 years ago.[1] Although there has been some use of this material in perfumery, it was some years before Demole[2] isolated and synthesized the one material responsible for the sandalwood-like odor, *trans*-3-(*exo*-5-isocamphyl)cyclohexanol. Meanwhile, Russian workers reported[3] that the somewhat simpler system, *trans*-3-isobornylcyclohexanol (**7**), also possessed a "strong sandalwood" odor.

The reported odor properties for trans isomer **7** seemed to mark it as a unique member in a family of similar compounds. Each of the 2- and 4-isobornylcyclohexanols, prepared by others,[4] and 4-bornylcyclohexanol, prepared in these laboratories,[5] were characterized as almost odorless. Furthermore, the *cis*-3-isobornylcyclohexanol (**8**) was claimed to possess a cedar note. Because of what appeared to be very unique and strict structural requirements for the sandalwood odor, we wished to validate this observation through independent synthesis.

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