yield; ^{19}F NMR −133.4 (m, $W_{h/2}$ = 110 Hz); **72**, 15% yield; ^{19}F NMR −153.7 (m, $W_{h/2}$ = 100 Hz); **73**, 15% yield; ^{19}F NMR −165.1 (br t, J_{HF} = 40 Hz).

Fluorination of *trans*- and *cis*-1-*tert*-Butyl-4-methylcyclohexane (74 and 75). These compounds were obtained from 4-*tert*-butylcyclohexanone treated with MeMgI. The resulting alcohol was dehydrated and the formed olefin dihydrogenated. A mixture of **74** and **75** was obtained in a corresponding ratio of 3:1 and separated by HPLC using cyclohexane as an eluent. Both isomers were separately fluorinated by using 1.5% F_2 in N_2. In both cases a mixture of two isomers were obtained which we were unable to completely separate. Thus **74** gave a mixture of **76** and **77** in 6:1 ratio: combined yield 70%; ^{19}F NMR (for **76**) −172.5 (m, $W_{h/2}$ = 90 Hz), (for **77**) −153.0 (m, $W_{h/2}$ = 95 Hz). The cis alkane **75** gave **78** and **79** in 65% combined yield in a 4.4:1 ratio. ^{19}F NMR (for **78**) −176.0 (m, $W_{h/2}$ = 88 Hz), (for **79**) −156.9 (m, $W_{h/2}$ = 96 Hz).

Dehydrofluorination Procedures. Three methods were employed for the described HF eliminations. Method A: 1.0 mmol of the corresponding fluoroderivative was dissolved under nitrogen in dry benzene and cooled down to about 10 °C. Freshly distilled $BF_3 \cdot OEt_2$ (8 mL) was added in one portion, the reaction mixture allowed to warm to room temperature and stirred for additional 4 h. Cold diluted HCl solution was added and the organic layer washed with bicarbonate and worked up as usual. The resulting olefins were usually chromatographed on HPLC. Method B: 1.0 mmol of the fluoro compound was dissolved in dry ether and cooled to 0 °C under nitrogen. About 3 mmol of MeMgI solution in ether was added, and the reaction mixture was stirred at room temperature overnight. Workup was as above. Method C: 1.0-mmol of the corresponding fluoride was dissolved in ethylene glycol to which 2 g of aqueous NaOH was added. The reaction mixture was stirred overnight at 105 °C, poured into water, extracted with several portions of CH_2Cl_2, and worked up as usual. The obtained olefins are known compounds, and their physical and spectroscopic data are in excellent agreement with the literature. When a mixture of olefins was obtained we have not separated them. In all cases, including the isomeric mixtures, the empirical formulas were established also by microanalysis fully confirming the purity and the assigned structure.

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Registry No. **1**, 75350-69-5; **2**, 75350-71-9; **3**, 75350-73-1; **4**, 75350-75-3; **5**, 75350-70-8; **6**, 75350-74-2; **7**, 75350-72-0; **8**, 75350-76-4; **9**, 107742-88-1; **11**, 1900-69-2; **12**, 107742-89-2; **13**, 20298-72-0; **14**, 107742-90-5; **16**, 107742-91-6; **17**, 107742-92-7; **18**, 107742-93-8; **19**, 107742-94-9; **20**, 107742-95-0; **22**, 98-53-3; **23**, 107742-96-1; **24**, 589-92-4; **25**, 82953-31-9; **26**, 51113-52-1; **27**, 82953-32-0; *cis*-**35**, 107742-97-2; *trans*-**35**, 107742-98-3; *cis*-**36**, 107742-99-4; *trans*-**36**, 107743-00-0; **37**, 97865-17-3; **38**, 97845-33-5; **39**, 107743-01-1; **40**, 107768-21-8; **41**, 97845-31-3; **42**, 97845-32-4; **43**, 92709-07-4; **44**, 107743-02-2; **45**, 97845-29-9; **46**, 97845-30-2; **47**, 4277-14-9; **48**, 75350-80-0; **49**, 75350-81-1; **50**, 2225-93-6; **51**, 107743-04-4; **52**, 107743-03-3; **53**, 20777-41-7; **54**, 107743-05-5; **55**, 54289-26-8; **56**, 22222-30-6; **57**, 90304-28-2; **58**, 107768-22-9; α-**59**, 107743-06-6; β-**59**, 107743-07-7; **60**, 107743-08-8; **61**, 107743-09-9; **62**, 3178-22-1; **63**, 90304-26-0; **64**, 92-51-3; **65**, 493-01-6; **66**, 493-02-7; **67**, 107743-10-2; **68**, 90304-27-1; **69**, 82823-26-5; **70**, 1678-82-6; **71**, 107743-11-3; **72**, 107743-12-4; **73**, 107743-13-5; **74**, 4001-94-9; **75**, 3325-80-2; **76**, 90304-29-3; **77**, 65199-17-9; **78**, 107743-14-6; **79**, 65199-18-0; **80**, 75350-77-5; **82**, 107743-15-7; **83**, 107743-16-8; **84**, 107743-17-9; **85**, 107743-18-0; **86**, 107743-19-1; **87**, 58045-40-2; **88**, 86905-77-3; **90**, 3282-54-0; **91**, 4233-18-5; **92**, 493-03-8; **93**, 1194-95-2; F_2, 7782-41-4.

Methyl Viologen Neutral MV:. 1. Preparation and Some Properties

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The highest reduction product of 1,1′-dimethyl-4,4′-bipyridinium dichloride (methyl viologen dichloride, $MVCl_2$), methyl viologen neutral MV:, was obtained by magnesium reduction in acetonitrile and sodium reduction in tetrahydrofuran. The optical spectrum [λ_{max} 396 nm (ϵ 27 000 in MeCN)] and NMR spectra [δ 5.536 and 5.509 (H_2 H_6), 5.317 and 5.290 (H_3, H_5), 2.096 (CH_3)] were recorded. MV: was not found to be a diradical, nor was it found to possess a large dipole moment. It was found to undergo photoassisted reaction with water.

1,1′-Dimethyl-4,4′-bipyridinium dichloride (I), also known as methyl viologen (MV^{2+}) dichloride or paraquat, is an interesting and important member of the viologen family.[1] Some of the members of the family exhibit herbicidal activity.[2] Besides, these compounds have been investigated for electrochromic properties.[3] Methyl viologen dichloride itself has been used as a probe to investigate the structure and dynamics of clay and polymer electrodes, catalytic production of hydrogen, and micelle formation.[4]

Generally, investigations and studies have been confined to the first reduction product, the methyl viologen cation radical (eq 1). The higher reduction product (eq 2) was indicated by some workers,[1a,2c] but its importance was pointed out by Mohammad and co-workers,[5] and a sys-

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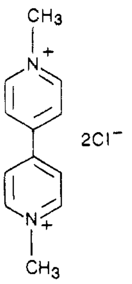

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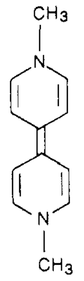

II

tematic study was undertaken by them. The relevance of this species—methyl viologen neutral MV:—in some physicochemical processes is now being accepted by other workers.[6] Since very little is known about this chemical species, except for its existence and some chemical reactions,[7] it was thought proper to attempt to isolate MV: and study some of its properties. In this report, its method of preparation and optical and NMR spectra are reported.

Preparation of MV:. The existence of MV: II had been known through electrochemical studies of MV^{2+}. It can be produced by direct electrochemical reduction (eq 1 and 2)[1,2,5] or through disproportionation[5] (eq 3), where K in

$$MV^{2+} + e^- \rightleftharpoons MV^{\bullet +} \tag{1}$$

$$MV^{\bullet +} + e^- \rightleftharpoons MV\colon \tag{2}$$

water is of the order of 10^{-5}, while in MeCN it is of the order of 10^{-7}.

$$2MV^{\bullet +} \overset{K}{\rightleftharpoons} MV\colon + MV^{2+} \tag{3}$$

Chemically, MV: can be produced through suitable reducing agents. Magnesium metal (acetonitrile solvent) and sodium metal (tetrahydrofuran solvent) are suitable reducing agents and are employed here. In both cases, the optical spectra of the final product are the same, confirming the production of the same species by the two different methods.

An all-glass apparatus (with a quartz optical cell) was used for the production of MV: by the magnesium metal reduction in acetonitrile (see paragraph at the end of paper about supplementary material). About 30 mg of $MV^{2+},2Cl^-$ was taken with about 1 g of magnesium turnings. The apparatus, *containing an* ampule of purified degassed acetonitrile (25–30 mL) and another of purified degassed *n*-heptane (25–30 mL), was connected to a high-vacuum line. After being degassed for several hours at pressure 10^{-5} mm or less, the apparatus was sealed off from the vacuum line. Acetonitrile was distilled into the reaction vessel (the empty MeCN ampule was sealed off). The mixture was stirred for about 48 h, and the progress of reaction was monitored with the optical cell. The solution first turned blue-purple, giving the characteristic spectrum of the methyl viologen cation radical. After the completion of the reaction, as evidenced by the development of a yellowish red color, the absence of the long-wavelength absorption (of $MV^{\bullet +}$), and no further change in the optical density at λ_{max} (290 nm), acetonitrile was distilled off and heptane was distilled in. MV: was extracted by heptane. Finally, the ampule containing MV: in heptane, with the provision of a break-seal, was sealed off.

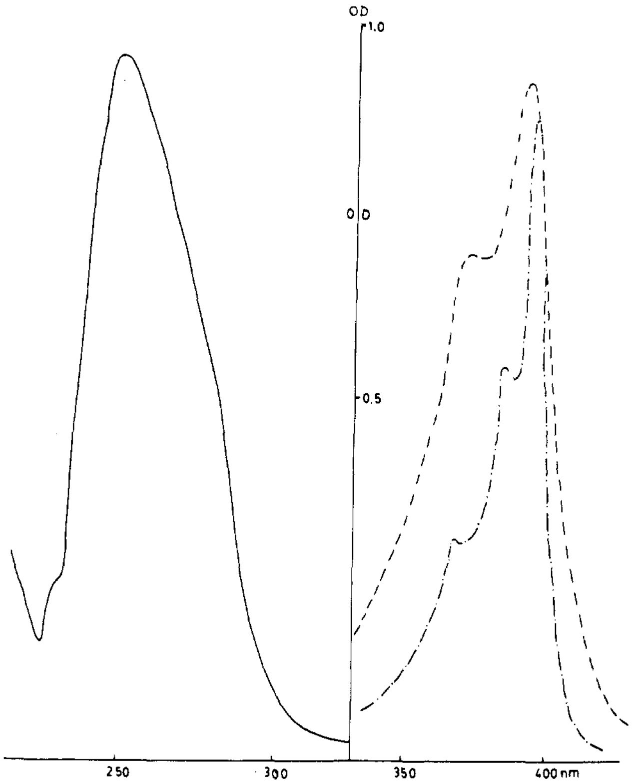

Figure 1. Optical spectra of $MV(PF_6)_2$ (—), $MV^{\bullet +}$ (-··-), and MV: (- -) in MeCN. The absorption scale is in OD units and wavelengths are in nanometers.

Preparation of MV: in THF by sodium reduction followed the standard procedure of reducing $MVCl_2$ (in THF) by sodium mirror under high-vacuum conditions. A feature of minor interest is that because $MVCl_2$ was almost insoluble in THF, the reduction of the dication is very slow, and because the solubility of MVCl is also very low, the absorption spectra of $MV^{\bullet +}$ could not be recorded. The final optical spectrum of the reduction product was, however, more or less the same as that of MV: in MeCN and heptane (see later text).

When the solution of MV: in heptane was slowly concentrated, long dark needle-shaped crystals separated, which redissolved on dilution and warming of the solution.

The solution of MV: in benzene was made by distilling off *n*-heptane (from MV: in heptane) and distilling in benzene. In all these solvents, the color of the dilute solution is yellow, while that of the concentrated solution is orange-red.

Optical and NMR Spectra. (i) Optical Spectra. The optical spectra of the final reduction product in MeCN, *n*-heptane, benzene, and THF are quite close to each other, differing sightly in details. These are shown in Figures 1–4. For comparison, the spectra of MV^{2+} and $MV^{\bullet +}$ are also given. The optical spectra of MV: can also be compared with those of 1-ethyl-4-carbomethoxypyridinyl and 1,1′-*N*-methylenebis(4-carbomethoxypyridinyl)[1a] (1:*n*:1; *n* = 3–5) diradicals. All these radicals have absorption bands around 400 nm, as does MV: neutral. However, in dilute solutions, unlike 1:3:1 and 1:4:1 diradicals or the $MV^{\bullet +}$ cation radical, methyl viologen neutral MV: does not have long-wavelength absorptions; i.e., the characteristic blue color considered to be associated with an odd electron is absent. The long wave-length, however, does appear in the concentrated solution of MV:.

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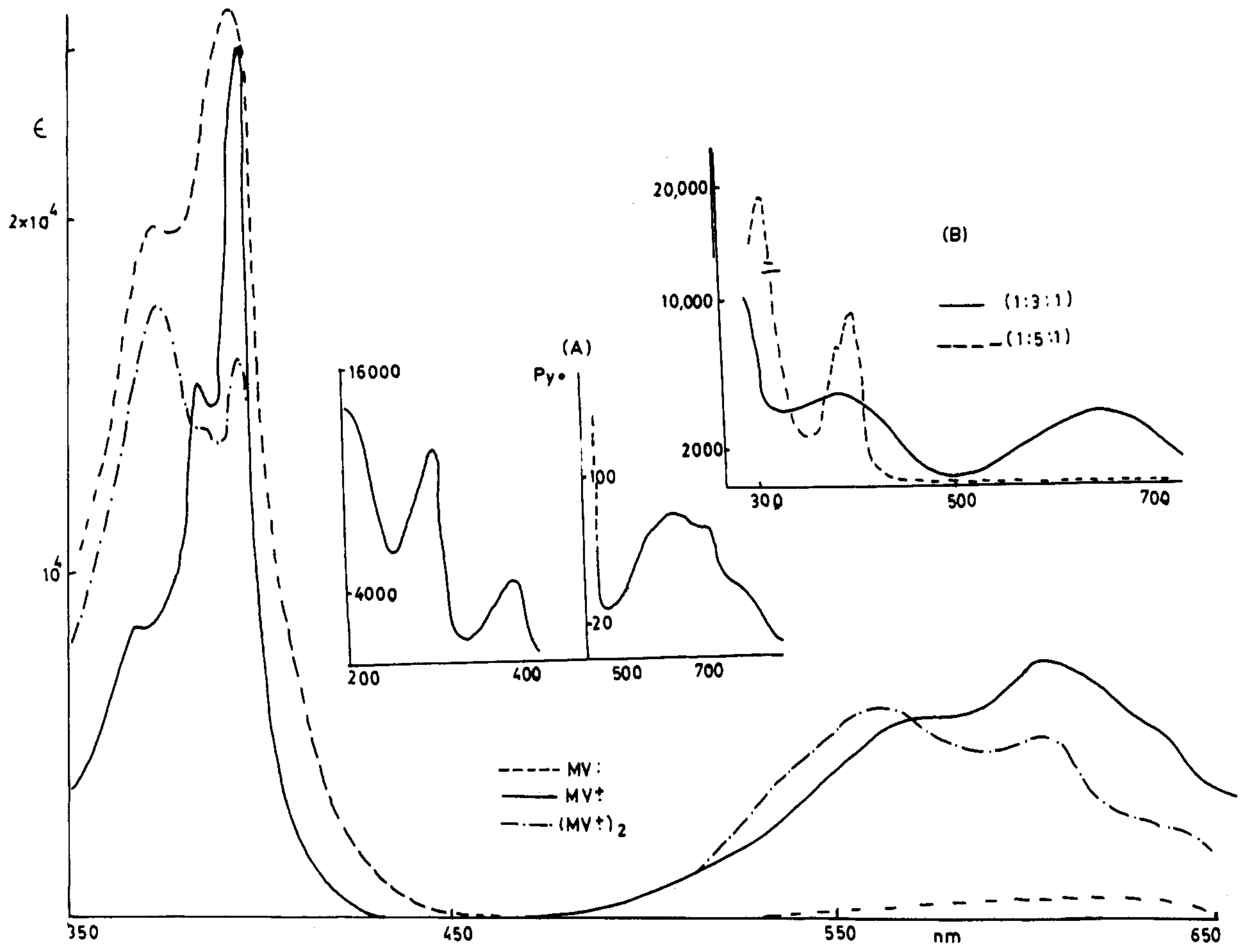

Figure 2. Optical spectra: MV:, $MV^{\bullet+}$ and $(MV^{\bullet+})_2$ in MeCN; *N*-methylenebis(pyridinyl) diradicals $(1{:}3{:}1)_2$ and $(1{:}5{:}1)_2$; py. The insets are taken from the work of E. M. Kosower (ref 1a), M. Mohammad (unpublished work), and J. Hajdu (Ph.D. Thesis, State University of New York, Stony Brook, 1974).

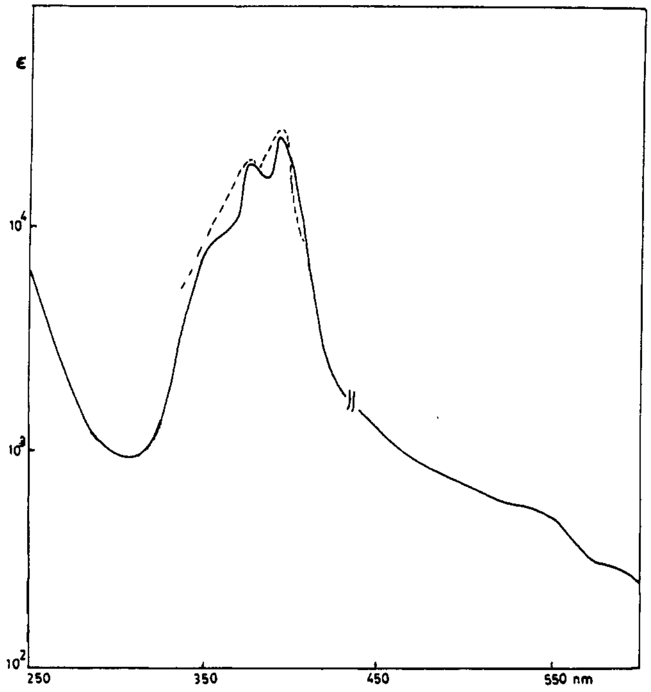

Figure 3. Optical spectra of MV: in heptane (—) and MeCN (- -).

Thus, a concentrated solution of MV: in heptane shows distinct shoulders, but no peaks (around 600, 540, and 500 nm).

Thus, to interpret the optical spectra of MV:, one has to consider its spectra in the context of the ones of other (mono-, cation, di-) radicals, the solvent effect, and the dilution effect. It is quite obvious that the second electron put into the highest partially filled molecular orbitals of $MV^{\bullet+}$ should move this and unoccupied (antibonding) molecular orbitals to higher levels of energy (electrostatic repulsion). The absorption around 550 nm (sh) is most probably due to dimerization of MV:. There is some solvent effect on the optical spectra of (dilute-solution) MV:. The lower wavelength (near-UV) absorption spectra in a low-polarity solvent, heptane, exhibit distinct peaks at λ 360 and 370 nm. The same effect is also visible, but to lesser extent, in THF, but in MeCN, there is a shoulder and a peak. Interestingly, one notices that the dimer of $MV^{\bullet+}$ cation radical also has similar characteristics (sharp peaks) in the near-UV region.

There are interesting questions, e.g., the geometry of the dimer of MV: giving rise to long-wavelength absorptions (sh) and the solvent effect on the near-UV spectra of MV:. These questions will be taken up some other time.

The extinction coefficients for the various λ_{max} in the optical spectra of MV: were obtained by straightforward titration of MV: with MV^{2+}. The reaction (eq 4) produced $MV^{\bullet+}$ (see eq 3, *K*), the extinction coefficients of the various absorption bands of which are known.

$$MV{:} + MV^{2+} \rightarrow 2MV^{\bullet+} \qquad (4)$$

Thus the extinction coefficients of the absorption bands in MeCN are given as ϵ 27 000 at 396 nm and as ϵ 20 000 at 370 nm (sh).

(ii) NMR Spectra. No ESR signal was observed for dilute solutions of MV: in MeCN, THF, heptane, or benzene, and because, as reported below, sharp lines were

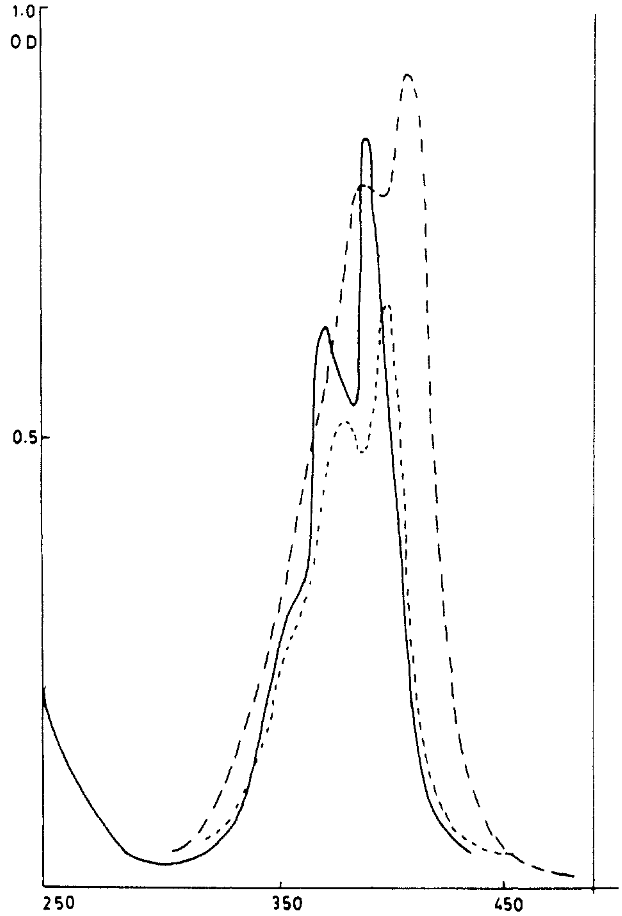

Figure 4. Optical spectra of MV: in heptane (—), benzene (- -), and THF (···) (dilute solutions). The absorption scale is in OD units.

observed in the proton NMR spectrum, it can be concluded that MV: in the ground state is not a diradical.

NMR spectra of MV: were recorded in C_6D_6, the chemical shifts being δ 5.536 and 5.509 (H2, H6), 5.317 and 5.290 (H3, H5), and 2.096 (CH_3), while the chemical shifts for MV^{2+} in methanol[11] were δ 9.21 (H2, H6), 8.68 (H3, H5), and 4.56 (CH_3). The charges due to the two electrons have tremendous effect on the positions of the proton resonance lines. The lines shifted upfield due to screening of proton through charges on carbon and nitrogen atoms. It is interesting to note that $\Delta\delta$ for the 2,6 and 3,5 protons is smaller (δ 0.3) for MV: compared with that for MV^{2+} ($\delta \geq 0.5$). The integration gives 4,4 and 6 protons (corrected for the base line) for (2,6), (3,5), and (1,1) positions, which should be so for MV:.

Some interesting work on the tetrabenzo analogue (lucigenin) has been carried out by Evans and Bush.[8] They concluded that the two-electron-reduction product of lucigenin is planar, which precludes a diradical structure.

Some Interesting Properties. The chemistry of methyl viologen neutral MV: is under investigation; however, some preliminary studies have established that MV: is an extremely reactive species. Its preparation under high vacuum and rigorous exclusion of impurities reflect its high reactivity. Nevertheless, it is stable in solvents like acetonitrile, tetrahydrofuran, heptane, and benzene. Earlier (electrochemical) studies[5] established that MV: is about 1000 times more reactive (toward protonating agent and oxygen) than the cation radical $MV^{\bullet+}$. Thus, MV: reacts with protonating agents (acids) and oxygen.[5] A recent study on the reduction of carbon dioxide[9] shows that MV: reacts with CO_2.

Though MV: does not show much reactivity toward water, an interesting observation was made about the reaction of MV: with water present as an impurity in acetonitrile. During the preparation of MV: by magnesium reduction of MV^{2+}, MV: was found to react with water under the influence of light. A deep blue color of $MV^{\bullet+}$ develops when MV: in MeCN, with water as impurity, is separated from magnesium turnings and kept exposed to light. The reaction does not take place in the dark, nor is there any photoassisted reaction of MV: with aprotic solvents. It was noted that the photoassisted reaction of MV: with water was not a simple electron-transfer reaction, since MV: (and hence MV^{2+}) was slowly destroyed.

MV: is neutral and has a small dipole moment, since it is highly soluble in such nonpolar solvents as *n*-heptane.

Experimental Procedures. For the preparation of MV:, solvents have to be extremely pure and oxygen has to be rigorously excluded. These conditions were realized by purifying the solvents by standard methods and working under high vacuum.[10] An all-glass apparatus was used and mixing was done through break-seals. Optical spectra were recorded on a Cary 14 spectrophotomer, while NMR spectra were recorded on 400-MHz NMR spectrometer.

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Registry No. I, 1910-42-5; II, 25128-26-1.

Supplementary Material Available: Figure of the apparatus used for the preparation of MV: by the magnesium metal reduction in acetonitrile (1 page). Ordering information is given on any current masthead page.

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[11] Ross, J. H.; Kreiger, R. L. *J. Agric. Food Chem.* **1980**, *28*, 1026.