oxide followed by oxidation of the diol with lead tetra-acetate led to the keto aldehyde VI (80%), infrared max. 5.78, 5.87 μ, and this was cyclized by dilute base in ethanol to the unsaturated aldehyde VII (50% yield); infrared max. 3.67, 5.98, 6.17 μ; n.m.r. peaks at 0.75–1.10 δ (three methyls), 2.00 δ (C=C—CH$_3$), 4.47 δ (doublet, one acetal proton), and 9.90 δ (CHO), ultraviolet max. 266 mμ (ϵ 9900). Hydrolysis of the acetal function in VII was accomplished using 1.5% sulfuric acid in aqueous tetrahydrofuran to give synthetic helminthosporal (I), m.p. 55–58°, $[\alpha]^{18}$D $-47.8°$ (c 1.00, chloroform) having infrared, n.m.r., and ultraviolet spectra identical with those of the natural substance. Reduction of synthetic I with lithium aluminum hydride followed by reaction with 3,5-dinitrobenzoyl chloride afforded a bisdinitrobenzoate, m.p. 148–149.5°, alone or admixed with a sample, m.p. 148–149.5°, derived from natural helminthosporal.

Since the absolute configuration of (−)-carvomenthone is as shown in II (R$_1$ = R$_2$ = H), the absolute stereochemistry of helminthosporal (I) follows from the synthesis. The orientation of the formyl group at C-2 in helminthosporal as shown in I is indicated by n.m.r. data and the resistance of this substance to isomerization in acid solution.

An alternative approach to helminthosporal consists of the reaction of the ketone III (X = O) with the methylene transfer agent dimethylsulfonium methyl-ide[12] to give the oxirane VIII (95% yield, configuration at C-2 tentative), subsequent treatment with zinc bromide–benzene (30% yield) to form a mixture of C-2 epimeric aldehydes, and conversion to V (and the C-2 epimer) with ethylene glycol under acid catalysis.[13]

(12) E. J. Corey and M. Chaykovsky, *J. Am. Chem. Soc.*, **84**, 867 (1962).
(13) We thank Dr. Paul de Mayo for an authentic sample of tetrahydro-helminthosporal bis-3,5-dinitrobenzoate and for helpful discussions. This research was supported by the National Institutes of Health.

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The Rate of the Tris-(2,2′-dipyridine)-osmium(II)–Octacyanomolybdate(V) Electron-Transfer Reaction[1]

Sir:

The application of the temperature-jump method to the study of rapid bimolecular electron-transfer reactions requires that the equilibrium constant for the reaction be of the order of unity. Consequently, the standard entropy change for the electron-transfer reaction should be fairly large, so that the change in the equilibrium produced by the temperature jump may be readily measurable. One way in which this can be achieved is by the use of oppositely charged reactants. Halpern, Legare, and Lumry[2] have successfully used this method to measure the rate of electron transfer between tris-(4,7-dimethyl-1,10-phenanthroline)-iron-(II) and hexachloroiridate(IV). We report here the results of a study of the rate of the tris-(2,2′-dipyridine)-osmium(II)–octacyanomolybdate(V) reaction.

The temperature-jump apparatus is of similar design to that of Czerlinski and Eigen[3] and Diebler[4] except that we have used a single light beam instead of a dual beam. This modification improves the signal-to-noise ratio by a factor of two.[5] A Bausch and Lomb grating

(1) Research performed under the auspices of the U. S. Atomic Energy Commission.
(2) J. Halpern, R. J. Legare, and R. Lumry, *J. Am. Chem. Soc.*, **85**, 680 (1963).
(3) G. Czerlinski and M. Eigen, *Z. Elektrochem.*, **63**, 652 (1959).
(4) H. Diebler, Ph.D. Thesis, Georg-August-University, Göttingen, Germany, 1960.

monochromator equipped with a 30-w. tungsten filament lamp was used as the light source. The temperature jump of about 10° was produced by discharging a 0.02 μf. condenser, charged to 80 kv., through the solution, and the resulting change in the equilibrium was measured by recording the absorbance of Os(dipy)$_3^{2+}$ at 480 mμ as a function of time. The values of k_f and k_r defined by the equation

$$Os(dipy)_3^{2+} + Mo(CN)_8^{3-} \underset{k_r}{\overset{k_f}{\rightleftharpoons}} Os(dipy)_3^{3+} + Mo(CN)_8^{4-}$$
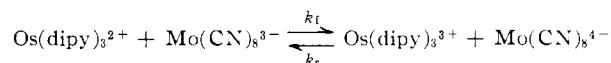
were found to be 2.0×10^9 F^{-1} sec.$^{-1}$ and 4.0×10^9 F^{-1} sec.$^{-1}$, respectively, at 10° and ionic strength 0.50 (0.45 F KNO$_3$ + 0.05 F HNO$_3$). These rate constants are even somewhat higher than those found for the Fe(DMP)$_3^{2+}$–IrCl$_6^{2-}$ system under comparable conditions.[2]

The diffusion-limited rate constants for the Os-(dipy)$_3^{2+}$–Mo(CN)$_8^{3-}$ and Os(dipy)$_3^{3+}$–Mo(CN)$_8^{4-}$ reactions calculated from the Debye equation[6] are 1 $\times 10^{10}$ F^{-1} sec.$^{-1}$ and 2×10^{10} F^{-1} sec.$^{-1}$, respectively, at 10° and zero ionic strength. The values will be somewhat lower at the ionic strength used in these studies. It will be seen that the observed rate constants lie within one order of magnitude of the diffusion-controlled limits, as do the rate constants obtained by Halpern, Legare, and Lumry.[2]

Since the observed rates are close to the diffusion-controlled limits, the energy required to reorganize the inner and outer coordination shells of the reactants and products cannot be very large. The Marcus theory[7] may be used to calculate the rate constants for the electron-exchange reactions related to this oxidation–reduction reaction, and one may then compare these calculations with the observed rates. According to this theory the rate constant for an electron-transfer reaction is given by

$$k = Ze^{-(w + m^2\lambda)/RT} \qquad (1)$$

where Z is the collision frequency between two uncharged molecules in solution (10^{11} 1. mole^{-1} sec.$^{-1}$), w is the work required to bring the two reactants together, and $m^2\lambda$ is the energy required to reorganize the inner and outer coordination shells of the reactants. Substitution of $k = 2.0 \times 10^9$ F^{-1} sec.$^{-1}$ in eq. 1 gives $m^2\lambda = 3 \pm 1$ kcal. mole^{-1} at 10°.[8] The energy required to reorganize the coordination shells of Os-(dipy)$_3^{2+}$ and Mo(CN)$_8^{3-}$ prior to the electron transfer thus appear to be much lower than the values calculated for many other reactants.[9,10] Since the reorganization energies are small and probably not too different in other electron-transfer reactions involving Os(dipy)$_3^{2+}$, Mo(CN)$_8^{3-}$, Os(dipy)$_3^{3+}$, and Mo(CN)$_8^{4-}$ (provided $K \approx 1$), the rate constants for the Os(dipy)$_3^{2+}$–Os-(dipy)$_3^{3+}$ and Mo(CN)$_8^{4-}$–Mo(CN)$_8^{3-}$ exchange reactions may be estimated from the rate constant for the Os(dipy)$_3^{2+}$–Mo(CN)$_8^{3-}$ reaction merely by correcting for the differences in the electrostatic work required to bring the various pairs of reactants together, and assuming the reorganization terms to be the same, for all three reactions in the first approximation. When these corrections are made, estimates of 1×10^7 F^{-1} sec.$^{-1}$ and 3×10^4 F^{-1} sec.$^{-1}$ are obtained for the rate constants for the Os(dipy)$_3^{2+}$–Os(dipy)$_3^{3+}$ and

(5) G. G. Hammes and J. I. Steinfeld, *J. Am. Chem. Soc.*, **84**, 4639 (1962).
(6) P. Debye, *Trans. Electrochem. Soc.*, **82**, 265 (1942).
(7) R. A. Marcus, *J. Phys. Chem.*, **67**, 853 (1963).
(8) The upper and lower limits of $m^2\lambda$ were calculated on the assumption that $w = z_1 z_2 e^2/DR$ and $w = z_1 z_2 e^2$ [exp $(-\kappa R)$]/DR, respectively. The mean value of w was used in calculating the electron-exchange rates.
(9) N. Sutin, *Ann. Rev. Nucl. Sci.*, **12**, 285 (1962).
(10) B. M. Gordon, L. L. Williams, and N. Sutin, *J. Am. Chem. Soc.*, **83**, 2061 (1961).

$Mo(CN)_8{}^{4-}$–$Mo(CN)_8{}^{3-}$ exchange reactions at $10°$ and zero ionic strength. The agreement of these estimates with the observed values of $>1 \times 10^5\ F^{-1}$ sec.$^{-1}$ and $\sim3 \times 10^4\ F^{-1}$ sec.$^{-1}$, respectively, at essentially zero ionic strength[11-13] is encouraging. They are in agreement with the Marcus theory and also, it would appear, support the electrostatic calculation of the work terms, within the limit indicated, in dilute media.

Acknowledgment.—We wish to thank Dr. H. Diebler for valuable advice concerning the construction of the temperature-jump apparatus and Drs. R. W. Dodson and R. A. Marcus for valuable discussions.

(11) E. Eichler and A. C. Wahl, J. Am. Chem. Soc., **80**, 4145 (1958).

(12) M. W. Dietrich and A. C. Wahl, J. Chem. Phys., **38**, 1591 (1963).

(13) R. Campion, unpublished observations.

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Photochemical Valence Tautomerization of 2,4,6-Triphenylpyrylium 3-Oxide

Sir:

The thermochromic behavior of 2,3-diphenylindenone oxide (I) was recently shown to involve the reversible formation of the red benzopyrylium oxide (II).[1] It was also found that these compounds may be photochemically interconverted, the photostationary state concentration of II being dependent on the exciting wave lengths, but a sufficient concentration of II could not be

I   II

III   IV
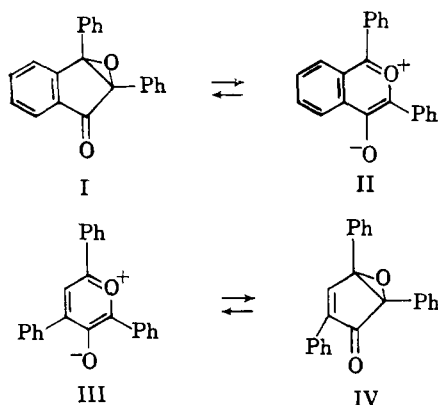
obtained to permit its isolation.[2] The recent report[3] of the preparation of the stable 2,4,6-triphenylpyrylium oxide (III) has now permitted a more direct study of the photochemistry of these interesting dipolar molecules.

A deep red acetonitrile solution of III, prepared by a modification of the reported procedure,[3] was found to be bleached to a pale yellow by irradiation with light from a 500-watt projector lamp filtered to remove wave lengths shorter than 4500 Å. Irradiation of the resulting solution with 3200–3930 Å light from a B-H6 high pressure mercury arc produced an instantaneous recoloration which is attributed to the reformation of III by the reappearance of characteristic absorption at 311 mμ, 524 mμ, and 6.52 μ. After the intensities of the 311 and 524 mμ peaks had increased to about 27% of their original values little further change occurred on prolonged irradiation. Re-irradiation with visible light (>4500 Å.) again bleached the solution and the process could be repeated.

(1) E. F. Ullman and J. E. Milks, J. Am. Chem. Soc., **84**, 1315 (1962).

(2) E. F. Ullman and J. E. Milks, unpublished observation.

(3) G. Suld and C. C. Price, J. Am. Chem. Soc., **83**, 1770 (1961); **84**, 2094 (1962).

These results suggest the existence of a photoequilibrium between III and a tautomer tentatively assumed to be the epoxyketone (IV) based on the indenone oxide analogy (I $\rightleftarrows$ II). Concentration of a freshly bleached benzene solution of III left an oil, which rapidly crystallized on addition of methanol to give a yellow solid V[4] isomeric with III, which was neither photo- nor thermochromic, m.p. 146–148°, $\lambda_{max}^{C_6H_{12}}$ 238 mμ (ϵ 16,200) and 358 (15,200), $\lambda_{max}^{CHCl_3}$ 5.82 μ (C=O). The spectral features of the product,[5] its failure to form ketone derivatives, and the formation of benzoic acid on treatment with alkali support structure V. Confirmation was obtained by the synthesis shown.

V
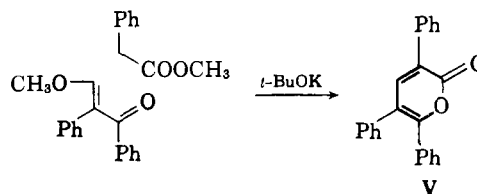
In contrast, in the absence of hydroxylic solvents, the oily photorearrangement product of III retained its photochromic property and displayed absorption at $\lambda_{max}^{C_6H_{12}}$ 231 mμ (ϵ 23,000) and 288 (7100), and $\lambda_{max}^{CHCl_3}$ 5.78 μ, which was not inconsistent with its formulation as the epoxide IV. Ozonolysis of IV in ethyl acetate followed by treatment with alkaline hydrogen peroxide gave benzoic acid plus an oily acid. The latter on diazomethane esterification gave the crystalline epoxyester VI,[4] m.p. 129–130°, $\lambda_{max}^{CHCl_3}$ 5.73 μ (C=O) and 12.13 (epoxide); n.m.r. 2.70 τ (ArH), 6.17 (OCH$_3$), intensities 5:3; m/e 312 (parent). The isolation of this epoxide strongly supports structure IV for the photobleached product.

The very facile rearrangement in hydroxylic solvents of the epoxide (IV) to the pyrone (V) is unexpected. The indenone oxide (I) is stable toward alcohols but

VI   VII

VIII   IX
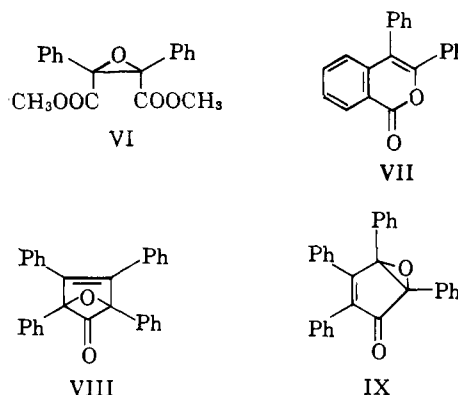
undergoes a related rearrangement to VII in strong acids.[6] Similarly, a compound tentatively formulated by Dilthey as the keto oxide (VIII), but which by virtue of its photochromic properties is probably the epoxide (IX), can be recrystallized unchanged from methanol but rearranges on strong heating, irradiation, or acid treatment to tetraphenyl-2-pyrone.[7] In contrast, the epoxyketone (IV) is converted in methanol to V in fair yield ($>50\%$) in several minutes at room temperature. The reaction is not inhibited by triethylamine but is strongly catalyzed by hydroxylic solvents.

(4) Satisfactory combustion analyses were obtained.

(5) Compare 3,6-diphenyl-2-pyrone: $\lambda_{max}^{CH_3OH}$ 245 mμ (ϵ 17,800), 360 (28,800); λ_{max}^{KBr} 5.84 μ; [R. H. Wiley, C. H. Jarboe, and F. N. Hayes, J. Am. Chem. Soc., **79**, 2602 (1957)].

(6) E. Weitz and A. Scheffer, Ber., **54**, 2327 (1921); C. F. H. Allen and J. W. Gates, Jr., J. Am. Chem. Soc., **65**, 1230 (1943).

(7) R. Pütter and W. Dilthey, J. prakt. Chem., **159**, 183 (1937); **150**, 40 (1938). We are indebted to Professor P. Yates for bringing this reference to our attention.