$Mo(CN)_8{}^{4-}$–$Mo(CN)_8{}^{3-}$ 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(13) R. Campion, unpublished observations.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
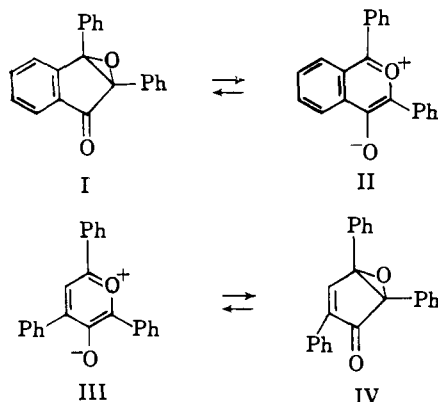

obtained to permit its isolation.[2] The recent report[3] of the preparation of the stable 2,4,6-triphenylpyrylium oxide (III) has now permitted a more direct study of the photochemistry of these interesting dipolar molecules.

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 ⇌ 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.
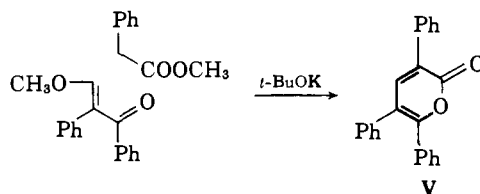
In contrast, in the absence of hydroxylic solvents, the oily photorearrangement product of III retained its photochromic property and displayed absorption at $\lambda_{max}^{C_6H_{12}}$ 231 mμ (ε 23,000) and 288 (7100), and $\lambda_{max}^{CHCl_3}$ 5.78 μ, which was not inconsistent with its formulation 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 (OCH₃), 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
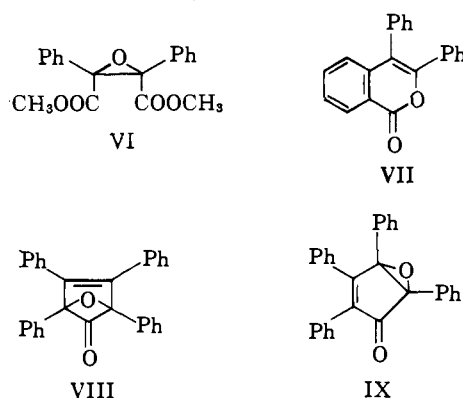
undergoes a related rearrangement to VII in strong acids.[6] Similarly, a compound tentatively formulated by Dilthey as the keto oxide (VIII), but which by virtue of its photochromic properties is probably the epoxide (IX), can be recrystallized unchanged from methanol but rearranges on strong heating, 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., **1:9**, 183 (1937); **150**, 40 (1938). We are indebted to Professor P. Yates for bringing this reference to our attention.

In a nonhydroxylic solvent such as benzene several hours of refluxing were required to carry out the conversion.

This observation was of value in the examination of the thermal equilibrium process III $\rightleftharpoons$ IV. Thus, while the thermal equilibration between I and II sets in, albeit slowly, even at room temperature,[8] the pyrylium oxide (III) in methanol at 150° for 5.5 hr. failed to yield a detectable amount of the pyrone (V). The pyrylium oxide (III) must, therefore, not be thermally isomerized to the epoxyketone (IV), since the latter would have rapidly rearranged under these conditions.

Interestingly, the much higher activation energy for the thermal reaction III → IV compared to that for the reaction II → I is reflected in the photochemical process. Thus, while photochemical interconversion between I and II and conversion of the epoxyketone (IV) to the pyrylium oxide (III) occur readily in a hydrocarbon glass at 77°K., visible light fails to reconvert III to IV under these conditions. We tentatively interpret these results as indicative of a photochemical tautomerization process involving a vibrationally excited ground state. The excited singlet state of III is of considerably lower energy than that of IV and thus cannot be thermally converted to it. A mechanism involving a temperature-dependent interconversion of excited singlet states at least for the process III → IV therefore is unlikely. However, temperature dependence may be explained if the vibrationally excited ground state of III arising from internal conversion of excited singlet III (or an excited nonspectroscopic singlet common to III and IV) has an energy lower than the thermal transition state barrier between III and IV, for no photoreaction could then occur without additional thermal activation. Alternatively, thermal interconversion of similarly energetic triplet states cannot be excluded, although intervention of triplet states appears unlikely because of the absence of phosphorescence and of quenching by heavy metals.

Additional evidence concerning these questions will be described in a later publication.

(8) W. A. Henderson, Jr., and E. F. Ullman, unpublished observation.

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Reactions of Metal–Ammonia Solutions. IV. Kinetics of Potassium–Liquid Ammonia Reaction at Room Temperature

Sir:

As a prelude to the study of the kinetics of reactions in liquid ammonia at room temperature between alkali metals and certain organic reductants, we have examined the rate of the reaction of potassium with liquid ammonia in Pyrex. The sodium reaction has been studied under similar conditions by Ebert,[1] the potassium reaction by Stirand.[2] Our findings appear to differ considerably from those of Stirand, who reported that the reaction was not first order, but that indeed the rate (as measured by the time for half the metal to react) increased as the initial concentration of metal decreased over the range 0.2 to 0.04 M.[3] By an extrapolation from Stirand's data, the half-time of reaction for solutions in our concentration range is calculated to be of the order of 5 min. and less. We find it to be

(1) G. Ebert, Z. anorg. allgem. Chem., 294, 129 (1958).
(2) O. Stirand, Czech. J. Phys., B, 12, 207 (1962).
(3) See also the theoretical treatment of Stirand's data by M. Podlaha, ibid., B, 11, 627 (1961).

over 100 times this long, and we find the reaction to be first order, with a rate constant of 0.065 ± 0.012 hr.$^{-1}$.

A plot of our data shows the reaction to be first order until approximately 75% of the metal has reacted. Initial concentrations and half-times for four runs at $23 \pm 1°$ are, respectively: 1.13×10^{-3} M, 11 hr.; 7.5×10^{-4} M, 10 hr.; 3.7×10^{-4} M, 13 hr.; and 2.0×10^{-4} M, 9 hr.

We have used a two-compartment Pyrex reaction cell, one end being a 1-cm. × 1-cm. × 4-cm. optical cuvette, the other end being a 3.2-cm. i.d. round tube about 10 cm. long. These ends were separated by an internal fragile glass diaphragm. The cells were cleaned with aqua regia, rinsed, and baked at 400° and $<1 \times 10^{-5}$ mm. for 24 hr. prior to filling *in vacuo*.[4] According to Warshawsky, even this treatment may leave water on the cell wall, but we have been able to detect no evidence of adsorbed water to date.

With triply-distilled potassium *in vacuo* in one end and about 35 ml. of purified liquid ammonia and a heavy glass breaker in the other, the cells were shaken to break the diaphragms and initiate the reactions. Details of construction of a cell[5] and its steel sheath will be published later.

The progress of the reaction was followed with a Cary Model 14 spectrophotometer by making periodic scans of the spectrum from 8000 to 3000 Å. The absorbance at 6500 Å. was taken as a measure of the unchanged metal,[6] while the peak that developed at about 3520 Å. was taken as a measure of the amide ion concentration. During much of the reaction, a plot of one of these absorbance values *vs.* the other is linear. This indicates that Beer's law holds over the range of concentrations and that the electron is being used in the expected reaction

$$K^+ + e^-(NH_3)_x \longrightarrow K^+ + NH_2^- + (x-1)NH_3 + {}^1/{}_2H_2$$
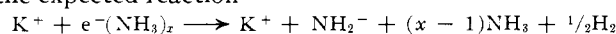
It was noted that, on standing prior to periodic mixing during a run, the reaction appeared to be taking place slightly more rapidly in the cuvette than in the body of the cell. This behavior indicates that the reaction is taking place at the cell wall; if so, reactions in different cells and in cells of different sizes would have different rates. Differences in cell treatment,[7] type of glass, and wall-to-volume ratios may account for the differences between Stirand's results and ours.

We have made one run with lithium. The initial concentration was approximately 0.001 M; the reaction was first order for 75 hr., with a calculated half-life of about 120 hr. After 75 hr., the rate of reaction decreased[8]; for the next 140 hr., the half-life was about 140 hr. At about the same time the rate of the reaction changed, the plot of absorbance at 6500 Å. *vs.* amide peak showed a deviation from linearity which indicated the amount of dissolved amide was remaining constant. It is possible that the precipitation of lithium amide on the glass affected the reaction rate;

(4) In this work we have striven to maintain standards of purity and procedure similar to those of J. F. Dewald and G. Lepoutre, J. Am. Chem. Soc., 76, 3369 (1954); I. Warshawsky, J. Inorg. Nucl. Chem., 25, 601 (1963).
(5) We are indebted to Labglass of Tennessee, Kingsport, Tennessee, for perfecting the breakable diaphragm and for helping us design our reaction cells.
(6) At lower temperatures Beer's law is reported to hold for alkali metal–ammonia solutions at this wave length by M. Gold and W. L. Jolly, Inorg. Chem., 1, 818 (1962); under similar conditions, negative deviation from Beer's law for potassium solutions was reported by R. C. Douthit and J. L. Dye, J. Am. Chem. Soc., 82, 4472 (1960).
(7) Stirand's solutions were made up in equipment described by J. Moc and M. Podlaha, Cesk. casopsis. fys., 10, 534 (1960). These authors state that their cells were simply heated for 6 to 8 hr. in an oven, then evacuated to 10^{-5} mm. prior to being filled in vacuo with potassium solutions.
(8) It is doubtful that precipitation of lithium amide on the walls of the cuvette caused an increase in absorbance to begin at this point. The absorbance of the solution at 6500 Å. at the conclusion of the reaction was the same as for pure ammonia.