

conic Acid Violet": UV (H₂O) 534 (ϵ 89 200), 447 (sh, ϵ 13 000), 314 (ϵ 5900), 281 (sh, ϵ 8200), 254 (ϵ 17 800), 238 (sh, 13 100), 228 (sh, ϵ 10 800) nm. Aqueous solutions of either the salt or the acid **4** absorb at the same region in the visible spectrum. Cyclic voltammetry (water) of **4** gave an irreversible oxidation potential at +0.3 V and an irreversible reduction potential at -1.1 V. The IR spectrum (KBr) showed strong bands at 1774 and 1720 (C=O), 1662, 1608 (C=O + C=C), and 1570 and 1512 cm⁻¹ (CC(CN)₂), indicating possible existence of a hybrid structure. The acid **4** is one of the strongest oxocyanocarbon acids ($pK_1 = 0.32 \pm 0.02$, $pK_2 = 1.02 \pm 0.02$) thus far discovered; it is twice as strong as acid as croconic acid (**3**, R = H; R¹ = R² = O¹³ ($pK_1 = 0.80 \pm 0.01$, $pK_2 = 2.24 \pm 0.01$ ¹⁶)). The high acidity constant of the oxocyanocarbon acid **4** is considered to be due to the considerable delocalization of π electrons in the substantially planar ring of its dianion **2**, as is also observed for the oxocarbon acids and their anions.² The acid **4** was readily reconverted into the dipotassium salt of **2** by careful neutralization (CH₃OK-CH₃OH or aqueous K₂CO₃ at 60–70 °C for 5–15 min), and this procedure is the best way found for preparing the other alkali salts of type **2** Cs, Li, Na, Rb); the lithium salt, extremely soluble in water, was recrystallized from methanol-ether. The acid **4** is a potential electron acceptor.

The direct interaction of croconic acid (**3**, R = H, R¹ = R² = O) with malononitrile in warm water gives another oxocyanocarbon acid.¹⁷

Treatment of dimethyl, diethyl, or dipropyl croconates (**3**, R = CH₃, R¹ = R² = O;¹⁸ R = C₂H₅, R¹ = R² = O;¹⁸ R = C₃H₇, R¹ = R² = O) (mp 54–56 °C, m/e 226 (M⁺) (75% yield), or diisopropyl croconate R = *i*-C₃H₇, R¹ = R² = O) (mp 215–225 °C dec, m/e 226 (M⁺) (80% yield)¹⁹) in *N,N*-dimethylformamide with malononitrile produces golden plates of **5** (R = CH₃) (2-(dicyanomethylene)-4,5-dimethoxy-4-cyclopentene-1,3-dione; mp 183–184 °C; m/e 213 (M⁺); UV (CH₃OH) 482 (sh), 410, 320, 258 nm; 86% yield) or the corresponding 4,5-dialkyl derivatives of **5**: R = C₂H₅, mp 124–125 °C, m/e 246 (M⁺) (85% yield); R = C₃H₇, mp 114–115 °C, m/e 274 (M⁺) (82% yield); R = *i*-C₃H₇, mp 145–146 °C, m/e 274 (M⁺) (86% yield).²⁰ 2-Dicyanomethylenealkyl croconates **5** are efficient electron acceptors (e.g., in regard to the formation of salts with tetrathiafulvalene, TTF); chemically, they react readily with aniline in warm alcohol to give deep red dyes of structure similar to that described for the product of reaction of 2-(dicyanomethylene)-1,3-indandione with the reagent.²¹

Careful alkaline hydrolysis (CH₃OK-CH₃OH, 60 °C, 1 min) of **5** (R = CH₃, R = C₂H₅, or R = C₃H₇) caused a substantial change in color, to give a new, violet dianion (**6**) (UV (CH₃OH), 540 (ϵ 82 500), 444 (sh, ϵ 11 500)), to which a bond-delocalized structure is assigned.

The dianions **2** and **6** and the dianions reported^{5–11} may be regarded as members of a new class of nonbenzenoid, aromatic, pseudooxocarbons with the general formula C_{*n*}O_{*n-m*}X_{*m*}¹⁻ where X = N, S, Se, P, =C-.

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References and Notes

- (1) K. Yamada, M. Mizuno, and Y. Hirata, *Bull. Chem. Soc. Jpn.*, **31**, 543 (1958). For more on the molecular structure of the croconate dianion C₅O₅²⁻, see M. Iijima, Y. Udagawa, K. Kaya, and M. Ito, *Chem. Phys.*, **9**, 229 (1975); S. Skujins and G. A. Webb, *Spectrochim. Acta, Part A*, **25**, 917 (1970); K. Sakamoto and Y. T. Haya, *Theor. Chim. Acta*, **13**, 220 (1969); J. C. Berg, *J. Chim. Phys. Physicochim. Biol.*, **67**, 586 (1970); *Chem. Abstr.*, **73**, 44693 (1970).
- (2) R. West, H. Y. Niu, D. L. Powell, and M. A. Evans, *J. Am. Chem. Soc.*, **82**, 6204 (1960).
- (3) R. West and J. Niu, "Nonbenzenoid Aromatics", Vol 1, J. P. Snyder Ed., Academic Press, New York, N.Y., 1969, Chapter 6; R. West and J. Niu, "The

Chemistry of the Carbonyl Group", Vol. 2, J. Zabicky, Ed., Interscience, New York, N.Y., 1970, Chapter 4.

- (4) D. Eggerding and R. West, *J. Am. Chem. Soc.*, **98**, 3641 (1976).
- (5) S. Hunig and H. Putter, *Angew. Chem., Int. Ed. Engl.*, **12**, 149 (1973).
- (6) D. Coucouvanis, F. J. Hollander, R. West, and D. Eggerding, *J. Am. Chem. Soc.*, **96**, 3006 (1974).
- (7) G. Seitz, K. Mann, R. Schmiedel, and R. Matusch, *Chem.-Ztg.*, **99**, 90 (1975).
- (8) A. H. Schmidt, W. Ried, and P. Pustoslemsek, *Chem.-Ztg.*, **101**, 154 (1977); *Chem. Abstr.*, **86**, 189 258 (1977).
- (9) H. E. Sprenger and W. Ziegenbein, *Angew. Chem., Int. Ed. Engl.*, **6**, 553 (1967); **7**, 530 (1968).
- (10) B. Lunelli, C. Corvaja, and G. Farna, *Trans. Faraday Soc.*, **67**, 1951 (1975); C. Corvaja, G. Farina, and B. Lunelli, *J. Chem. Soc., Faraday Trans. 2*, **71**, 1293 (1975).
- (11) G. Seitz, K. Mann, and R. Matusch, *Arch. Pharm. (Weinheim)*, **308**, 792 (1975).
- (12) T. Fukunaga, *J. Am. Chem. Soc.*, **98**, 610 (1976); U.S. Patent 3 963 769 (1976); *Chem. Abstr.*, **86**, 55 052 (1977).
- (13) A. J. Fatiadi, H. S. Isbell, and W. F. Sager, *J. Res. Natl. Bur. Stand., Sect. A*, **67**, 153 (1963).
- (14) The complete, x-ray crystal structure of the dipotassium salt of **2** will be described in a separate publication.
- (15) Aqueous or alcoholic solutions of salts of **2** or acid **4** impart adherent stains to the skin; consequently, all operations require the use of rubber or plastic gloves.
- (16) L. M. Schwartz, R. I. Gelb, and J. O. Yardly, *J. Phys. Chem.*, **79**, 2248 (1975); R. I. Gelb and L. M. Schwartz, *J. Chem. Soc., Perkin Trans. 2*, 930 (1976).
- (17) A. J. Fatiadi, *Synthesis*, 165 (1978). Unlike the reaction of the croconic salts (e.g., their dianions) with malononitrile (to give Croconate Violet of type **2**), the direct interaction of croconic acid (**3**, R = H, R¹ = R² = O) with malononitrile in warm water gives another oxocyanocarbon acid, a new, solvatochromic dye (caution: strongly skin-staining) called "Croconic Acid Blue", the intense color of which is dependent on the polarity of the solvent; for example, its solution in alcohol or acetone is red (UV (Me₂CO) 475 nm); in water, it is deep blue (UV (H₂O) 595–600 nm).
- (18) R. Malachowski and S. Pröbendowski, *Ber.*, **71**, 2241 (1938).
- (19) Prepared by stirring silver croconate¹⁸ with propyl or isopropyl iodide in ether (or ether-tetrahydrofuran) for 18–20 h. The esters of croconic acid (**3**, R = CH₃, C₂H₅, C₃H₇, *i*-C₃H₇; R¹ = R² = O) form conducting salts following reaction with tetrathiafulvalene.
- (20) All new compounds gave satisfactory elemental analyses. Calcd for C₁₁H₄N₄O₆K₂, **3** (R = K, R¹ = C(CN)₂, R² = O) (2H₂O): C, 37.71; H, 1.15; N, 15.99; K, 22.32; 2H₂O, 10.28. Found: C, 37.51; H, 1.25; N, 15.88; K, 22.10; 2H₂O, 10.12. Calcd for C₁₁H₆N₄O₆Na₂, **3** (R = Na, R¹ = C(CN)₂, R² = O) (3H₂O): C, 39.30; H, 1.80; N, 16.66; Na, 13.68. Found: C, 39.22; H, 1.64; N, 16.78; Na, 13.48. Calcd for C₉H₄N₂O₆K₂, **6** (R = K, R¹ = O, R² = C(CN)₂) (2H₂O): C, 31.78; H, 1.33; N, 9.27. Found: C, 31.59; H, 1.15; N, 9.18. Calcd for C₁₁H₂N₄O₃, **4** (R = H, R¹ = C(CN)₂, R² = O): C, 55.47; H, 0.84; N, 23.52. Found: C, 55.35; H, 0.77; N, 23.44. Calcd for C₁₁H₄O₅, **3** (R = *i*-C₃H₇, R¹ = R² = O): C, 58.42; H, 6.23. Found: C, 58.36; H, 6.12. Calcd for C₁₄H₁₄N₂O₄, **3** (R = *i*-C₃H₇, R¹ = O, R² = C(CN)₂): C, 61.13; H, 5.14; N, 10.21. Found: C, 61.07; H, 5.02; N, 10.10.
- (21) H. Junek, H. Aigner, and H. Fischer-Colbrie, *Monatsh. Chem.*, **103**, 639 (1972).

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On the Mechanism of the Rubrene-Enhanced Chemiluminescence of α -Peroxy lactones¹

Sir:

A few years ago we reported² that the mechanism of the rubrene-enhanced chemiluminescence of α -peroxy lactones involved energy transfer by the triplet donor (chemienergized carbonyl product from the α -peroxy lactone) producing a triplet acceptor (rubrene), followed by triplet-triplet annihilation to afford singlet excited rubrene which emits efficiently. This mechanism was defended on the facts that rubrene gave rise to a ~100-fold greater light intensity than DPA (9,10-diphenylanthracene), but the decay rate constants of the enhanced chemiluminescence intensities were within the experimental error, the same as those for the direct chemiluminescence. That is, up to enhancer concentrations of $\sim 5 \times 10^{-4}$ M no induced decomposition of the α -peroxy lactone by the enhancer could be detected.

This mechanistic interpretation was recently criticized on energetic grounds.³ We also were alarmed by the fact that the triplet excited-state yield from the dimethyl α -peroxy lactone

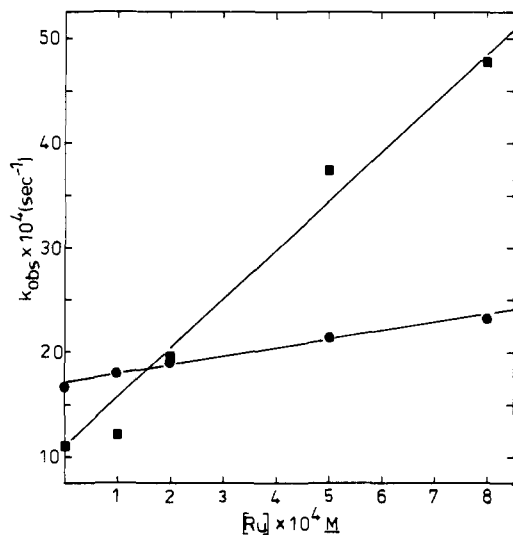


Figure 1. Dependence of k_{obsd} on $[\text{Ru}]$ for *tert*-butyl (**1a**) (●) and dimethyl (**1b**) (■) α -peroxylactones in CH_2Cl_2 at 27 °C: $[\mathbf{1a}] = 2.1 \times 10^{-4} \text{ M}$ and $[\mathbf{1b}] = 2.0 \times 10^{-4} \text{ M}$.

(**1b**), determined by DBA (9,10-dibromoanthracene) counting,⁴ was considerably lower than that estimated by our triplet-triplet annihilation mechanism.² We dispensed with this discrepancy by suggesting that at high fluorescer concentration induced decomposition was operating.⁵ Similarly, when we attempted to assess by the DBA method the triplet yield for *tert*-butyl carboxaldehyde, chemienergized by *tert*-butyl α -peroxylactone (**1a**), we found⁶ that it was again much lower than that estimated in the rubrene-enhanced chemiluminescence.² We confirmed the very low triplet yield of aldehyde from the *tert*-butyl α -peroxylactone by chemical titration with *trans*-1,2-dicyanoethylene.⁷ Under conditions at which *cis*-*trans* isomerization should have occurred even if only $\sim 1\%$ triplet aldehyde had been formed, no *cis*-1,2-dicyanoethylene could be detected by GC analysis. Control experiments confirm that photoenergized *tert*-butyl carboxaldehyde did sensitize *cis*-*trans* isomerization of 1,2-dicyanoethylene.⁸

Clearly, our original mechanism is in conflict. Not enough triplets are being formed to account for the large rubrene-enhanced chemiluminescence intensity.

In view of the fact that the principal mechanism of the enhanced chemiluminescence exhibited by diphenyl peroxide³ and by the reaction of 3,6-diphenyl-3,5-cyclohexadiene-1,2-*trans*-dicarboxylic acid and diisopropylethylamine in the presence of hydrogen peroxide⁹ involves "chemically initiated electron exchange luminescence" (CIEEL mechanism), we decided to reinvestigate the enhanced chemiluminescence exhibited by α -peroxylactones at high concentrations of the fluorescer. Presently we report our results for the *tert*-butyl (**1a**) and dimethyl (**1b**) α -peroxylactones using rubrene (Ru), tetracene, perylene, and 9,10-diphenylanthracene (DPA) as fluoroscres.

In Figure 1 the overall rate constant, k_{obsd} , for the rubrene-enhanced chemiluminescence decay is exhibited for the α -peroxylactones **1a** and **1b** as a function of $[\text{Ru}]$.¹⁰ In the $[\text{Ru}]$ range examined, both α -peroxylactones reveal a direct reaction with the fluorescer following the relationship shown in

$$k_{\text{obsd}} = k_1 + k_2[\text{Ru}] \quad (1)$$

where k_1 (intercept) represents the unimolecular decomposition of **1a** or **1b** and k_2 (slope) the bimolecular decomposition by rubrene. The extrapolated k_1 values are 17.6×10^{-4} and $10.2 \times 10^{-4} \text{ s}^{-1}$, respectively, for **1a** and **1b**. These, within the experimental error ($\sim 10\%$), agree well with the k_1 values obtained by direct chemiluminescence, i.e., respectively, 16.7×10^{-4} and $10.2 \times 10^{-4} \text{ s}^{-1}$ for **1a** and **1b**.⁶ The k_2 values are

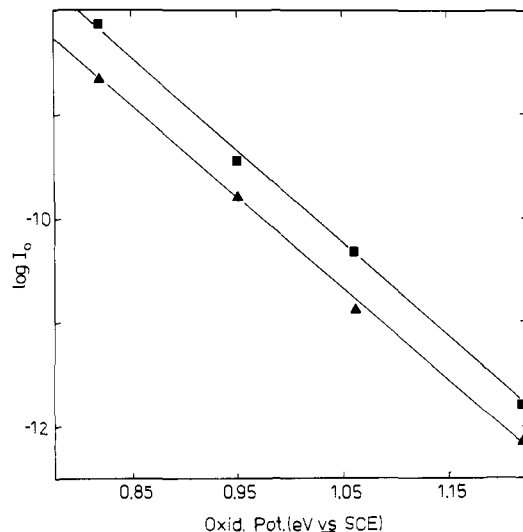


Figure 2. Dependence of total intensity ($\log I_0$) on oxidation potential (OP) of fluorescer (Fl) for *tert*-butyl (**1a**) (■) and dimethyl (**1b**) (▲) α -peroxylactones in CH_2Cl_2 at 27 °C: $[\mathbf{1a}] = 2.1 \times 10^{-4} \text{ M}$, $[\mathbf{1b}] = 2.0 \times 10^{-4} \text{ M}$, and $[\text{Fl}] = 10 \times 10^{-4} \text{ M}$. The fluoroscres are from left to right rubrene, naphthacene, perylene, and 9,10-diphenylanthracene.

0.73 and $5.4 \text{ M}^{-1} \text{ s}^{-1}$, respectively, for **1a** and **1b**. Analogous direct reaction between the α -peroxylactones and tetracene was observed, but perylene and 9,10-diphenylanthracene were quite ineffective. As expected from the CIEEL mechanism the k_2 values are dependant on the fluorescer structure, but the k_1 values are all constant and within the experimental error equal to those derived from direct chemiluminescence measurements.

The most convincing confirmation of the CIEEL mechanism is brought out in Figure 2 in which the initial intensities¹¹ of the enhanced chemiluminescence of the four fluoroscres is plotted semilogarithmically against their oxidation potentials.³ For both α -peroxylactones perfectly straight lines with identical slopes are observed. Thus, the bimolecular process (CIEEL) is a sensitive function of the fluorescer structure, i.e., the more readily the fluorescer is oxidized the more pronounced the CIEEL process. As expected, the α -peroxylactone structure is not critical. We are in the process of exploring this mechanism in more detail.

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References and Notes

- (1) Paper No. 59 in the Cyclic Peroxide Series.
- (2) W. Adam, G. A. Simpson, and F. Yany, *J. Phys. Chem.*, **78**, 2559 (1974).
- (3) J.-Y. Koo and G. B. Schuster, *J. Am. Chem. Soc.*, **99**, 6107 (1977), and references cited therein.
- (4) N. J. Turro, P. Lechtken, G. Schuster, J. Orell, H.-C. Steinmetzer, and W. Adam, *J. Am. Chem. Soc.*, **96**, 1627 (1974).
- (5) Reference 2, footnote 36.
- (6) F. Yany, Doctoral Dissertation, University of Puerto Rico, Aug 1977.
- (7) N. J. Turro and P. Lechtken, *J. Am. Chem. Soc.*, **94**, 2886 (1972).
- (8) J. C. Dalton, M. W. Gelger, and J. J. Snyder, *J. Am. Chem. Soc.*, **98**, 398 (1976).
- (9) G. B. Schuster, *J. Am. Chem. Soc.*, **99**, 651 (1977).
- (10) The rate measurements were performed as described in ref 2. All reagents were rigorously purified, the solvents were freshly distilled from EDTA, and the Parker scintillation vials and other glassware were rinsed prior to use thoroughly with an aqueous EDTA solution and dried in a vacuum oven. Consistently reproducible results were obtained irrespective of the α -

peroxylactone batch, the operator, and the fluorescer source. Occasionally a "wild run" was observed, but this was immediately obvious and discarded.

- (11) Initial intensities (I_0) were obtained by extrapolation of the enhanced chemiluminescence intensity decay plots, standardized with the POPOP scintillation cocktail, and corrected for photomultiplier response and fluorescer reabsorption as detailed in ref 2.
- (12) NIH Career Development Awardee, 1975–1980.

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Organic Photochemistry with High Energy (6.7 eV) Photons: Cis \rightleftharpoons Trans Isomerism in Cyclooctene

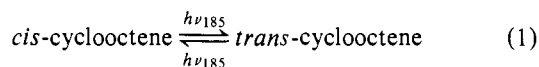
Sir:

In contrast to the numerous studies which have been conducted on the photochemical cis \rightleftharpoons trans isomerism in olefins at wavelengths longer than 200 nm,¹ there have been only a few reports of such investigations in the far-ultraviolet region. A recent study² of the direct photolysis of cyclooctene at 185 nm in solution drew attention to the high value (~ 1) of the ratio of the trans to cis isomer at the photostationary state. It was also observed that, in the initial stages of the reaction, there was negligible loss of the olefin by side reactions. No quantum yields were reported and the results were interpreted in terms of the $\pi \rightarrow \pi^*$ singlet state of the olefin.

We wish to report our results on a quantitative investigation of this system at the same wavelength which allows a more detailed examination of the excited state which may be involved in this process.

The strong absorption of *cis*-cyclooctene has a maximum at 185 nm and its extinction coefficient at 185 nm (1.0×10^4 L/(mol cm)) is almost exactly as large as that of *trans*-cyclooctene at this wavelength. The latter has a broad maximum in its ultraviolet absorption at ~ 196 nm.³ At longer wavelengths, both molecules exhibit the weaker $\pi \rightarrow 3s$ Rydberg absorption.⁴ Weak absorption extends down to 254 nm (*cis*, $\epsilon_{254} \sim 16$; *trans*, $\epsilon_{254} < 1$).

Irradiations were carried out in pentane solution (2×10^{-2} M) using a 50-W mercury resonance lamp. To measure quantum yields, the light intensity at 185 nm was calibrated by using the gas phase conversion of oxygen to ozone ($\Phi = 2$) as the actinometer.⁵ The rate of ozone formation was measured by standard iodimetry.⁶ Quantum yields for both forward and reverse reactions in the photoequilibrium



were extrapolated to zero conversion from the data in Figure 1. At $t = 0$, the quantum yields were equal to each other within experimental error ($\pm 5\%$) and equal to unity ($\pm 20\%$). Since there were small amounts of other products^{2,7} which amounted to 5% of the *cis*-cyclooctene which disappeared, it is probable that the actual quantum yield for the forward reaction (1) is 0.95. We propose that this reaction can serve as a practical actinometer for solution phase photochemistry at 185 nm. The reaction is easy to follow by gas chromatography, the reactant (*cis*-cyclooctene) is readily available and inexpensive, and the solvent can be any saturated hydrocarbon of sufficient purity. Below concentrations of 4×10^{-2} M, no effect of concentration was evident.

The mercury resonance lamp that was used emitted radiation at 254 nm as well as at 185 nm. The light intensity at the former wavelength was ~ 6 times the value at the latter.⁸ However, the effect of any parallel reaction due to absorption of 254-nm light during irradiation at 185 nm can be discounted

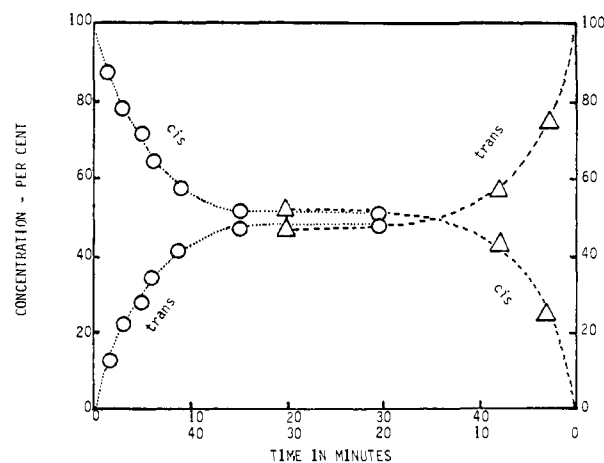


Figure 1. Composite diagram of percent interconversion of cyclooctene stereoisomers as function of time: 185-nm radiation; solvent pentane; concentration 10^{-2} to 10^{-3} M. Left ordinate and circles refer to reaction starting from 100% *cis* isomer. Right ordinate and triangles refer to reaction starting from 100% *trans* isomer.

since, at the concentrations and pathlengths that were used, the optical density for the *cis*-cyclooctene solution at 254 nm was ~ 0.05 . Published work^{2,9,10} indicates a highly unfavorable ratio of trans to *cis* isomer on irradiation (direct, sensitized, or catalyzed) at long wavelengths.

The significant point of interest in the present work is that $\Phi_{c \rightarrow t} + \Phi_{t \rightarrow c} \sim 2$ which indicates that a common excited state or intermediate is not reached during irradiation of either isomer at 185 nm. It further suggests that, for each isomer, from its excited state that is initially reached at this energy, a favorable path without barriers leads to the other isomer from which the latter can internally convert to the ground state, all steps being highly efficient. With this picture in mind, one can examine the energy diagram of olefins with a view to identify the source of these isomerizations.

Discussions of the photochemical reactions of olefins are invariably based on the mapping of the torsion coordinate as a function of energy for ethylene as given by Merer and Mulliken.¹¹ In the region from 200 to 175 nm, not only is there less than general agreement on anything but the most general features,⁴ but shifts in the energy levels through alkyl substitution have also to be taken into account.

Both the $\pi \rightarrow \pi^*$ singlet and triplet states have similar energy profiles with a minimum at 90° of twist with the result that equilibration between the two isomers in their excited states seems unavoidable. Therefore, the present results cannot be accommodated by initial excitation to the $\pi \rightarrow \pi^*$ singlet as previously proposed.² The *R* states in the energy diagram of ethylene do have the profile stipulated before. The problem lies in locating these states in the spectrum of *cis* and *trans* cyclooctene.

A detailed analysis of the spectrum of *cis*-cyclooctene has not been carried out. Both the optical absorption and circular dichroism spectra of *trans*-cyclooctene have been analyzed in detail.³ The band with a maximum at 196 nm has been assigned to the $\pi \rightarrow \pi^*$ singlet state. On the short wavelength side of it, at ~ 178 nm, a Rydberg absorption is clearly present as revealed in the circular dichroism spectrum. From a recent ab initio theoretical calculation on the circular dichroism spectrum of this compound, Liskow and Segal¹² have computed the energy levels of the Rydberg states in this region as $\pi \rightarrow 3P_y$, 6.62 eV, and $\pi \rightarrow 3P_x$, 6.39 eV, respectively. The geometry of the former state would be well suited to undergo the isomerization reaction studied here and its energy level would be accessible with the photon energy used.

Preliminary results⁷ show that such an efficient *cis* \rightarrow *trans*