

cyclopropyl), 1.67 (d, $J = 2$ Hz, 2, C-7 methylene), 1.50 (m, 4, C-3 and C-5 methylene), and its formation by hydrogenolysis of **4a**, **4b** over Pd/C. In addition, sulfone **6** has been synthesized independently from a mixture of **5a** and **5b** by a sequence consisting of oxymercuration–demercuration, mesylation of the alcohol mixture, and 1,3 elimination. Treatment of **2a** or **2b** with 2 *N* sodium hydroxide in the presence of isopropyl alcohol afforded not only **3**, **4a**, and **4b** but also **5a**, **5b**, and **6**. Since the rearranged bromo sulfones **4a** and **4b** are inert under these conditions, the three additional sulfones **5a**, **5b**, and **6** must arise directly from **2a** or **2b** via a free-radical intermediate and subsequent capture of hydrogen from isopropyl alcohol at C-2 or -5. The presence of 10 mol % iodine under reaction conditions employing 2 *N* sodium hydroxide inhibits the formation of **4a** and **4b**. Under these conditions, olefin **3**, the normal product of the Ramberg–Bäcklund rearrangement, is isolated in 80–90 % yield.

Although the stereochemistry of **2a** and **2b** may be deduced from chemical-shift data of the SO_2CH_3 moiety⁸ and the change in chemical shifts of the SO_2CH_3 absorptions upon saturation of the double bond⁹ we prefer to await the results of X-ray studies presently in progress for definitive stereochemical assignments for **2a**, **2b** and **4a**, **4b**.

We expect to report on further observations of the synthetic utility and mechanistic complexity of bromovinyl sulfone chemistry at a future date.

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(8) H. G. Kuivila and C. R. Warner, *J. Org. Chem.*, **29**, 2845 (1964), and references therein.

(9) R. R. Fraser, *Can. J. Chem.*, **40**, 78 (1962).

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Cleavage of Thymine Dimers Sensitized by Quinones. Chemically Induced Dynamic Nuclear Polarization in Radical Ions

Sir:

The photosensitized cleavage of thymine photodimers is being investigated in several laboratories¹ in order to provide guidelines for understanding the light-requiring step in photoreactivation,² the photoenzymatic reversal of pyrimidine dimer formation in DNA. Among the variety of sensitizers employed,

(1) (a) A. Wacker, H. Dellweg, L. Traeger, A. Kornhauser, E. Lodemann, G. Tuerck, R. Selzer, P. Chandra, and M. Ishimoto, *Photochem. Photobiol.*, **3**, 369 (1964); (b) A. A. Lamola, *J. Amer. Chem. Soc.*, **88**, 813 (1966); (c) I. Rosenthal and D. Elad, *Biochem. Biophys. Res. Commun.*, **32**, 599 (1968); (d) E. Ben-Hur and I. Rosenthal, *Photochem. Photobiol.*, **11**, 163 (1970); (e) C. Hélène and M. Charlier, *Biochem. Biophys. Res. Commun.*, **43**, 252 (1971); (f) A. A. Lamola, presented before 6th International Symposium on Photochemistry, Bordeaux, Sept 1971; *Mol. Photochem.*, in press; (g) D. Morton, R. Hautala, F. Pagano, N. J. Turro, and A. A. Lamola, unpublished results.

(2) C. S. Rupert in "Photophysiology," Vol. 2, A. C. Giese, Ed., Academic Press, New York, N. Y., 1964, pp 283–327.

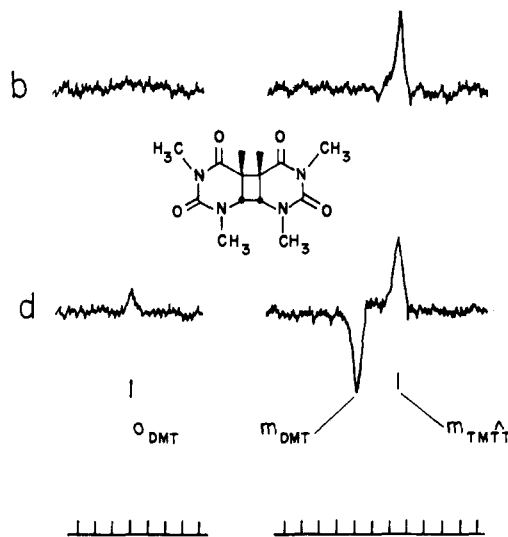


Figure 1. Pmr spectra (60 MHz) of 0.02 *M* solutions of A in D_2O containing 5 mg/ml TMTT before (b) and during (d) ultraviolet irradiation. The regions of the olefinic (o) and the C-methyl resonances (m_{DMT} , m_{TMTT}) are shown. The spectra obtained after irradiation were identical with spectrum b. The calibration marks are separated by 10.6 Hz.

quinones, e.g., 2-anthraquinone sulfonate (A), first suggested by Ben-Hur and Rosenthal,^{1d} were found to be particularly effective. For this group of sensitizers several experimental results^{1f,g} suggest a mechanism involving electron transfer as the initial step, i.e., the formation of quinone anions paired with substrate cations.

Since chemical processes involving radical pairs can give rise to nuclear spin polarization (CIDNP),³ we sought direct support for the electron-transfer mechanism in pmr experiments, investigating the photo-reactions of several quinones with the cis-syn dimer (TMTT) of 1,3-dimethylthymine (DMT). In this communication we present the CIDNP effects we found in these systems, to our knowledge the first report of CIDNP arising from pairs of radical ions.⁴

When deoxygenated solutions of A (0.02 *M*) containing low concentrations of TMTT were photolyzed in the probe of an nmr spectrometer,⁵ two enhanced signals were observed (Figure 1): a broad absorption signal (~ 5.1 ppm) and a stronger signal in emission (~ 1.4 ppm). The chemical shifts of the enhanced signals match those of the olefinic proton and the allylic methyl group of the monomer DMT. We were unable to detect any enhancement of TMTT signals. The CIDNP signals of the monomer disappeared very quickly after the light was extinguished and reappeared upon resumed irradiation. During the brief irradiation periods (< 10 sec) required for recording these signals only a small fraction ($< 10\%$) of the dimer was monomerized. No enhanced resonances were observed in the

(3) (a) J. Bargon, H. Fischer, and U. Johnson, *Z. Naturforsch.*, **A**, **22**, 1551 (1967); (b) H. R. Ward and R. G. Lawler, *J. Amer. Chem. Soc.*, **89**, 5518 (1967).

(4) Nuclear spin polarization induced in pairs of radical ions was independently found during the quenching of excited aromatic hydrocarbon singlets by electron acceptors: G. N. Taylor, private communication.

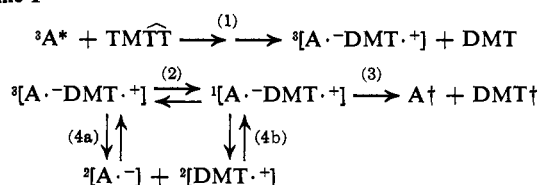
(5) With a 2500-W high-pressure mercury lamp, Corning filter 052 (cut-off, 340 nm).

absence of the sensitizer even if the sample was irradiated with light of wavelengths which cause direct splitting of the dimer.

We explain the enhanced signals on the basis of the CKO (radical pair) theory.⁶ An analysis of the signal directions is straightforward, if one assumes a polarizing encounter of quinone radical anion ($A^{\cdot-}$) and monomer radical cation ($DMT^{\cdot+}$). Kinetic studies and quenching experiments^{1f,g} suggest that the triplet state of A is involved in the primary step so that the geminate radical pair should be generated as a triplet (in Kaptein's notation,^{6e} +). The product-forming reaction, *i.e.*, reverse electron transfer, has to occur in the encounter cage (+); the *g* value of $DMT^{\cdot+}$ ⁷ is smaller (-) than that of $A^{\cdot-}$.⁹ Given these parameters the signal direction of a proton in the product should be opposite to the sign of the hyperfine coupling constant of the same proton in the parent radical ion; emission (-) is expected (and observed) for the methyl group ($a_{CH_3} = +20$ G),⁸ absorption (+) for the olefinic proton ($a_H \approx -4$ G).⁸ Additional support for the involvement of $DMT^{\cdot+}$ is derived from the fact that the intensity enhancement of the signals is proportional to the magnitude of the hyperfine coupling constants of $DMT^{\cdot+}$.

On the basis of the CIDNP results we propose the following mechanism for the A-TMTT photoreaction (Scheme I).

Scheme I^a



^a A dagger denotes nuclear spin polarization; an asterisk denotes an excited state; arabic numerals indicate electron spin multiplicity.

The fate of the radical ion pairs, after their excess energy is dissipated, should be spin dependent, *i.e.*, only pairs of singlet multiplicity should undergo reverse electron transfer (3). This spin selection principle is closely analogous to the one generally accepted for pairs of neutral radicals⁶ and appears equally sound energetically, at least for the system discussed here. Electron return in a triplet pair requires that either A or DMT be generated in the triplet state which appears energetically unfavorable under the reaction conditions.¹⁰ Therefore, we assume that aside from inter-system crossing triplet pairs can only diffuse apart (4a).

If Scheme I is correct, in particular if the formation of the triplet ion pair is fast and essentially irreversible and if the combined energies of ${}^3A^*$ and DMT are higher than the energy of the $A^{\cdot-}$ - $DMT^{\cdot+}$ pair, the

(6) G. L. Closs and A. D. Trifunac, *J. Amer. Chem. Soc.*, **92**, 2183, 2186, 7227 (1970); (b) G. L. Closs, C. E. Doubleday, and D. R. Paulson, *ibid.*, **92**, 2185 (1970); (c) R. Kaptein and L. J. Oosterhoff, *Chem. Phys. Lett.*, **4**, 195, 214 (1969); (d) S. H. Giarum, Abstracts, 159th National Meeting of the American Chemical Society, Houston, Texas, Feb 1970, No. ORGN 040; (e) R. Kaptein, *Chem. Commun.*, 732 (1971).

(7) We assume that $DMT^{\cdot+}$ has a similar *g* value as the thymine radical cation ($g_{T^{\cdot+}} = 2.0038$).⁸

(8) M. D. Sevilla, *J. Phys. Chem.*, **75**, 626 (1971); *cf.* L. C. Snyder, R. G. Shulman, and D. B. Neumann, *J. Chem. Phys.*, **53**, 256 (1970).

(9) $g_{A^{\cdot-}} = 2.0040$; we are indebted to Mr. J. H. Marshall for determining this value.

(10) The triplet state of A lies at 2.7 eV, that of DMT at 3.2 eV. We estimate the energy of the ion pair $[{}^3A^{\cdot-}DMT^{\cdot+}]$ to be ≤ 2.5 eV.

identical pair should be formed in the reaction of ${}^3A^*$ with monomeric DMT, and subsequent electron return should yield spin-polarized DMT. Indeed, when A was irradiated in aqueous solutions containing low concentrations of DMT, CIDNP spectra were observed which showed the same features as the spectra obtained in the dimer reaction.

This result might suggest that the CIDNP spectra observed in dimer samples arise from the reaction of ${}^3A^*$ with DMT previously produced from the dimer. We deem this unlikely since the signals were recorded within seconds after starting the irradiation, when the concentrations of DMT were still negligible.

The CIDNP data cannot establish the detailed mechanism leading from the dimer to the $A^{\cdot-}$ - $DMT^{\cdot+}$ pair. However, it appears that the cleavage sequence is essentially irreversible since a limiting quantum yield of 1 was found for this reaction.^{1f,g} This observation would explain why we did not observe spin-polarized TMTT.

Further work is in progress to elucidate the photochemistry of similar systems by using the CIDNP technique.

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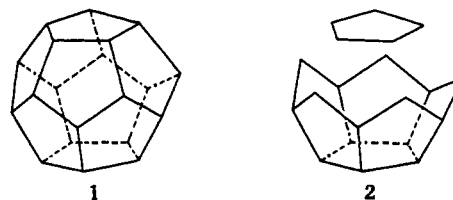
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The Peristylane System¹

Sir:

We are pursuing the synthesis of dodecahedrane (1). For the purpose of synthetic design we view dodecahedrane as made up of two subunits, cyclopentane and the C-15 fragment 2, as illustrated. We have



named the larger fragment "peristylane" from the Greek *περιστύλον*, a group of columns arranged about an open space and designed to support a roof.

We report now the preparation of the first members of the peristylane family. Our synthesis proceeds by elaboration of *cis*-bicyclo[3.3.0]octane-2,8-dione (6), preserving the mirror plane symmetry element. The *cis* ring fusion in bicyclo[3.3.0]octane is 6 kcal/mol more stable than the *trans*;² this large difference is of great help in maintaining stereochemical control while manipulating derivatives of the system.

(1) Taken in large part from the Ph.D. Thesis of R. H. M., The University of Chicago, 1971. A referee from the American Chemical Society Nomenclature Committee has informed us that the correct systematic name for peristylane is tetradecahydro-3,4-methanocyclopenta[*cd*]pentaleno[6.1.2-*fg*h]pentalene.

(2) J. W. Barrett and R. P. Linstead, *J. Chem. Soc.*, 611 (1936).