The facility of the unsensitized photochemical transformation **1** → **2** is in marked contrast with the reported reduced rates of the di-π-methane to vinylcyclopropane rearrangements of benzonorbornadiene,[7] tetrafluorobenzobarrelene (**3**),[8] and various dibenzobarrelenes[9] on direct irradiation, and with the failure of benzobarrelene (**4**)[10] and 1,4-epoxy-1,4-dihydronaphthalene (**5**)[11] to undergo such rearrangement on direct irradiation.

These reduced rates might be viewed as a consequence of inefficient singlet to triplet intersystem crossing, as suggested for benzonorbornadiene.[7] Alternatively, if intersystem crossing is efficient in these systems,[12] retardation or total preclusion of the di-π-methane rearrangement may reflect the occurrence of an even more facile competing singlet process. Such a process has been suggested[10,11] to be the photochemically allowed concerted 2 + 2 intramolecular cycloaddition,[13,14] which is facilitated in all of the cited cases by the geometry imposed on [2.2.1] and [2.2.2] bicyclic systems. This intramolecular cycloaddition leads readily to the products observed on direct irradiation of **3, 4**, and **5**. In many of the cited cases, a light-wasting reversion of the cycloadduct to starting material may occur.[11]

(7) J. R. Edman, *J. Amer. Chem. Soc.*, **88**, 3454 (1966).

(8) J. P. N. Brewer and H. Heaney, *Chem. Commun.*, 811 (1967).

(9) E. Ciganek, *J. Amer. Chem. Soc.*, **88**, 2882 (1966).

(10) H. E. Zimmerman, R. S. Givens, and R. M. Pagni, *ibid.*, **90**, 6096 (1968).

(11) G. R. Ziegler, *ibid.*, **91**, 446 (1969).

(12) The quantum yield for solution-phase intersystem crossing of the phenyl excited singlet of 1-phenyl-2-butene has been estimated to be at least 0.36: H. Morrison and R. Peiffer, *ibid.*, **90**, 3428 (1968). Intersystem-crossing efficiencies of similar magnitude might be reasonably assumed for the systems in question here.

(13) R. Hoffmann and R. B. Woodward, *ibid.*, **87**, 2046 (1965).

(14) H. E. Zimmerman, *ibid.*, **88**, 1564 (1966).

In our system **1**, models indicate that geometry is not conducive to a 2 + 2 concerted process, since only one end of the isolated double bond π system can approach the benzene π cloud. However, that end is at least as close as comparable orbitals in benzonorbornadiene or benzobarrelene, and so the excited singlet state of **1** might directly initiate a di-π-methane rearrangement. On the other hand, intersystem crossing and triplet rearrangement could predominate in the absence of an efficient competitive singlet process.

A choice between these two pathways is not yet possibile and is under study.[15]

The photochemical behavior of **1** suggests the importance of competitive concerted 2 + 2 cycloaddition in many bicyclic di-π-methane systems by demonstrating the facility of the vinylcyclopropane rearrangement where cycloaddition is not favored.[16]

(15) The *a priori* possibility of forming 2 from 1 *via* a C-8 methylene bridge 1,2 shift has been ruled out by a deuterium labeling study; details will appear in our full paper. Such a shift has been suggested as an alternative to the di-π-methane rearrangement for bicyclo[3.2.1]-octa-2,6-diene: R. R. Sauers and A. Shurpik, *J. Org. Chem.*, **33**, 799 (1968).

(16) Very recently triptycene, nominally a bicyclic di-π-methane system, was reported to undergo a photochemical rearrangement on direct irradiation, suggested to proceed through an initial di-π-methane → vinylcyclopropane reaction.[17a,b] In this case, 2 + 2 cycloaddition again may be sufficiently less facile than the same process for the aryl-vinyl-di-π-methane systems discussed above to allow singlet–triplet intersystem crossing to become competitive.

(17) (a) T. D. Walsh, *J. Amer. Chem. Soc.*, **91**, 515 (1969); (b) N. J. Turro, M. Tobin, L. Friedman, and J. B. Hamilton, *ibid.*, **91**, 516 (1969).

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Additions and Corrections

The Excess Free Energy and Related Properties of Solutions Containing Electrolytes [*J. Am. Chem. Soc.*, **90**, 3124 (1968)]. By GEORGE SCATCHARD, Department of Chemistry and Laboratory of Nuclear Science, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, and the Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830.

In eq 5, the last line should be $(\Sigma_i m_i'/2)^2 \Sigma_j \Sigma_k B_{jk} x_j x_k$.

Equation 8 should be $(G^n/RTW)_4 = \Sigma_i \Sigma_j \Sigma_k \Sigma_l m_i' m_j' m_k' m_l' f_{ijkl}$.

In the sixth line below, $ka/\sqrt{I} = a'$ should be $\kappa a/\sqrt{I} = a'$.

Equation 11 should be $G^{DH}/RT = WS\Sigma_a{}^+ \Sigma_f{}^- m_a' m_f' \cdot (\mathfrak{z}_a + \mathfrak{z}_f) X_{af}/2a_{af}' m'$.

In footnote 17, 289 should be 2898.

In eq 13 "ә" is omitted in the denominator of the second derivative.

In the twelfth line below eq 19, "and 1:2" should be omitted.

On page 3127, the paragraph beginning Young's rule should read as follows: Young's rule states that the free energy, the heat, and the volume changes of mixing at constant ionic strength of two 1:1 electrolytes with a common ion af and bf (or af and ag) is independent of the common ion, f (or a). It must hold for G^{DH}/RT and for $(G^n/RT)_2$, and it holds for $(G^n/RT)_3$ if $(2D_{abg} - D_{aag} - D_{bbg}) = (2D_{abf} - D_{aaf} - D_{bbf})$.

I had forgotten that H. E. Wirth, R. E. Lindstrom, and J. N. Johnson [*J. Phys. Chem.*, **67**, 2339 (1963)] had defined Young's rule as the special case in which the changes are zero, which is equivalent to Brønsted's Principle of the Specific Interaction of Ions or our extension of it.[3] They also applied it to mixtures without a common ion for which the earlier treatment is much superior.

On page 3127 in the first paragraph on the cross-square rule the quotation from Young should read "a sufficient but not a necessary condition." The last sentence of that paragraph should be deleted and

replaced by, "It holds for $(G^n/RT)_2$ and $(G^n/RT)_3$ and it holds for $(G^n/RT)_4$ if $4f_{abfg} - 2(f_{abff} + f_{abgg} + f_{aafg} + f_{bbfg}) + (f_{aaff} + f_{bbff} + f_{aagg} + f_{bbgg}) = 0$.

On page 3127, column 2, line 5, add "It is true that there is no asymmetry without interactions between three ions of the same sign."

The authors of ref 28 should be R. M. Rush and J. S. Johnson, Jr.

The last sentence of the paper should read: "This work was supported by the U. S. Atomic Energy Commission under Contract No. AT(30-1)-905 and by the Office of Saline Water, U. S. Department of the Interior under Union Carbide Corporation's contract with the U. S. Atomic Energy Commission."

Additional Studies Concerning the Existence of "O_3F_2" [*J. Am. Chem. Soc.*, **90**, 5408 (1968)]. By I. J. SOLOMON, J. N. KEITH, A. J. KACMAREK, and J. K. RANEY, IIT Research Institute, Chicago, Illinois 60616.

On page 5410, Table II, amend the data to read as follows.

0.94	71.0	29.0	0.9	2.40	2
1.49	89.1	16.5	0.4	5.40	6
1.96	62.9	1.4	2.3	45	∞

In the paragraph below the table, delete "The small amount of O_2 were entirely consistent with eq 4 and 5."

Electrogenerated Chemiluminescence. I. Mechanism of Anthracene Chemiluminescence in N,N-Dimethylformamide Solution [*J. Am. Chem. Soc.*, **90**, 6284 (1968)]. By LARRY R. FAULKNER and ALLEN J. BARD, Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712.

Several figure captions in the article have been transposed. The figures themselves have been numbered correctly, and they appear in the proper order. The corrections are as follows.

Figure 5. Cyclic voltammetric curves: (a) Scan for 2 mM anthrone plus anthranol at a platinum disk electrode in DMF and 0.1 M TBAP; (b) scan for 10 mM anthracene in DMF and 0.1 M TBAP at a platinum electrode following a double potential step.

Figure 6. Sensitization of anthranol fluorescence at 457 mμ by anthracene.

Figure 7. Quenching of anthracene fluorescence at 404 mμ by anthranol.

Figure 8. ECL emission spectrum of a solution 1.2 m M in anthrone plus anthranol.

Transition Metal Carbonyl Anions. I. The Course of the Reduction of Chromium Hexacarbonyl [*J. Am. Chem. Soc.*, **90**, 6340 (1968)]. By WILLIAM C. KASKA, Department of Chemistry, University of California, Santa Barbara, California 93106.

On page 6341, column 1, the equations should read $[(C_2H_5)_4N][Cr_2(CO)_{10}H]$ instead of $[(C_2H_5)_4N]$-$[Cr(CO)_5H]$.

Chelation of Uranyl Ions by Adenine Nucleotides. II. Proton Magnetic Resonance Investigation of the Uranyl Nitrate–Adenosine 5'-Monophosphate Chelate in D_2O at Basic pD [*J. Am. Chem. Soc.*, **90**, 6635 (1968)]. By RAGHUNATH P. AGARWAL and ISAAC FELDMAN, Department of Radiation Biology and Biophysics, University of Rochester School of Medicine and Dentistry, Rochester, New York 14620.

The sentence beginning on page 6637, line 25, *viz.*, "Most of the difference..... to phosphate," erroneously implies that the uranium-induced downfield shift of the H_8 signal (decreased shielding) is due to the elimination of the specific phosphate deshielding of H_8. The latter change is, of course, a shielding effect. Our intention, however, was to note that the chelation of uranium by the phosphate causes the phosphate to move considerably away from its previous position adjacent to H_8, thereby eliminating the electrostatic attraction of phosphate for H_8 and allowing the torsion angle to adopt a more negative value to give the molecule minimum potential energy. In addition, chelation of the uranium by the ribose hydroxyl oxygens and phosphate causes a considerable change in the ribose ring conformation, as is evident from the fact that this chelation increases $J_{2'-3'}$ from 4.8 cps to 8.0 cps and the fact that the $H_{4'}$ signal becomes a sharp singlet. Using Dreiding stereomodels and the Karplus plot relating vicinal coupling constants to the dihedral angles, one sees that in the chelate the ribose ring oxygen atom should be considerably out of plane, either *endo* or *exo*. In the latter case, the distance between H_8 and the ribose ring oxygen would be lengthened considerably and significant deshielding of H_8 should result. This *exo* case is also consistent with the suggestion on page 6639 that the U–$O_{3'}$ bond might be longer than the U–$O_{2'}$ bond.

The abstract should, therefore, be corrected in lines 5 and 6 by substituting "attraction of phosphate for H_8" in place of "specific phosphate deshielding of H_8."

The Alkylation of Diazoacetonitrile and Ethyl Diazoacetate by Means of Organoboranes. A New Synthesis of Nitriles and Esters [*J. Am. Chem. Soc.*, **90**, 6891 (1968)]. By JOHN HOOZ and SIEGFRIED LINKE, Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada.

The last entry in the first column of Table I should read *trans*-3-Hexene[e].

Evernitrose, a Naturally Occurring Nitro Sugar from Everninomicins [*J. Am. Chem. Soc.*, **90**, 7129 (1968)]. By A. K. GANGULY, OLGA Z. SARRE, and HANS REIMANN, Natural Products Research Department, Schering Corporation, Bloomfield, New Jersey 07003.

On page 7130, column 2, line 5 should read "of the 3,4-di-O-methyl derivative X and the 4-O-methyl"