Figure 1. Circular dichroism spectra of *syn*-(1'S)-spiro[cyclo-butan-2-one-1,4'-(2'(a)-adamantane)] (1) (—) and *anti*-(1'S)-spiro[cyclobutan-2-one-1,4'-(2'(a)-adamantane (2) (------) in isopentane at 20° as determined on a JASCO Model J-20 ORD-CD spectrophotometer with photoelastic modulator. Corrections are made to 100% optical purity.

the cyclobutanone ring introduced by puckering does not place the methyl perturber in a back octant, and all possible back octant contributions located in such conformations are essentially canceling. Thus, we cite **1** with its strongly negative n–π* CE as compelling evidence for the existence of front octants and the validity of the octant rule. A "quadrant rule," wherein the predicted CE sign is (+) for **1** cannot be operating. The nature of the contour and location of the third octant surface remains to be discerned;[1,19] however, it seems likely at present that the so-named "anti-octant" effect found in a few saturated alkyl ketones is probably due to front octant contributions.

The isomeric *anti*-spiro ketone (**2**) exhibits the expected weak (−) CE due to the location of the lone dissymmetric methyl perturber in a lower left or upper right *back* octant. In fact, the location of the methyl group of **2** is almost identical with that in (1 S)-*endo*-2-methylbicyclo[2.2.1]heptan-7-one,[1] and their CE magnitudes are comparable.

(19) C. Coulombeau and A. Rassat, *Bull. Soc. Chim. Fr.*, **71**, 516 (1971).

(20) PRF Postdoctoral Fellow 1973–1974.

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Photorearrangements and Photosolvolyses of *syn*- and *anti*-7-Chloro- and -7-Bromobenzonorbornadienes[1]

Sir:

As photosolvolyses involving carbocationic intermediates are rare,[2] we were surprised to observe that direct or sensitized photoexcitation in methanol of either *anti*-7-(1-Br) or *syn*-7-bromobenzonorbornadiene (2-Br) gave the same solvolysis product, *syn*-7-methoxybenzonorbornadiene (2-OCH₃). Furthermore, in acetone or hexane, **1-Br** was quantitatively converted into **2-Br**. Similar irradiation of **2-Br** in acetone or hexane was without apparent effect. The naphthonorbornadienes, **3-Br** and **4-Br**, gave analogous results.
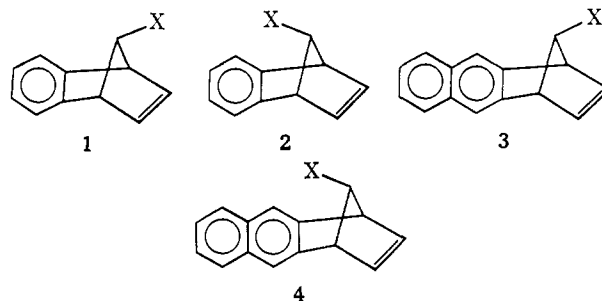
These results were interesting for several reasons. First, we knew that ground-state solvolyses of **1-Cl** lead[3] cleanly to **1** species, that **2-Cl** gives **2** species,[3] and that the bromides react analogously.[4] The inversion of configuration in the "photosolvolysis" experiment, compared with retention in ground-state solvolyses, was intriguing, as was the corresponding photoepimerization, assuming that carbocationic intermediates intervened. Further, our experience on irradiation of unsaturated and phenyl-substituted aliphatic halides[1,2f–h,5] suggested that photosolvolysis involving carbocationic intermediates occurs only in benzyl systems, even though rearrangements which can be ascribed to carbenium ion intermediates do occur in allylic and other systems. Additionally, all the literature reports on photosolvolyses are with benzyl systems.[2]

While our results could be accommodated to the idea that the photochemical process leads to a vibrationally excited cation[1,5] having enough energy to traverse the high barrier which undoubtedly separates **5** and **6** ions and analogous species,[3,6] an alternative path also suggested itself for consideration. Edman[7] has shown that benzonorbornadienes rearrange photochemically (by

(1) (a) Paper IX in series Photochemical Transformations, University of Colorado group. Paper VIII: S. J. Cristol, G. A. Lee, and A. L. Noreen, *J. Amer. Chem. Soc.*, **95**, 7067 (1973).

(2) (a) H. E. Zimmerman and V. R. Sandel, *J. Amer. Chem. Soc.*, **85**, 915 (1963); (b) H. E. Zimmerman and S. Somasakhara, *ibid.*, **85**, 922 (1963); (c) A. L. Maycock and G. A. Berchtold, *J. Org. Chem.*, **35**, 2532 (1970); (d) M. A. Ratcliff and J. Kochi, *ibid.*, **36**, 3112 (1971); (e) V. L. Ivanov, V. B. Ivanov, and M. G. Kuz'min, *Zh. Org. Khim.*, **8**, 6 (1972); (f) S. J. Cristol and G. C. Schloemer, *J. Amer. Chem. Soc.*, **94**, 5916 (1972); (g) G. C. Schloemer, Ph.D. Thesis, University of Colorado, 1972; (h) B. E. Greenwald, M.S. Thesis, University of Colorado, 1973.

(3) S. J. Cristol and G. W. Nachtigall, *J. Amer. Chem. Soc.*, **90**, 7132, 7133 (1968).

(4) (a) J. W. Wilt and P. J. Chenier, *J. Amer. Chem. Soc.*, **90**, 7366 (1968); (b) *J. Org. Chem.*, **35**, 1571 (1970); (c) P. D. Bartlett and W. P. Giddings, *J. Amer. Chem. Soc.*, **82**, 1240 (1960).

(5) (a) S. J. Cristol, G. O. Mayo, and G. A. Lee, *J. Amer. Chem. Soc.*, **91**, 214 (1969); (b) S. J. Cristol and G. A. Lee, *ibid.*, **91**, 7554 (1969); (c) R. Micheli, M.S. Thesis, University of Colorado, 1973.

(6) R. K. Lustgarten, M. Brookhart, and S. Winstein, *J. Amer. Chem. Soc.*, **94**, 2347 (1972).

(7) J. R. Edman, *J. Amer. Chem. Soc.*, **88**, 3454 (1966); **91**, 7103 (1969).

di-π-methane rearrangements) to derivatives of 4-benzo-tricyclo[4.1.0.0^{3,7}]heptene, 7-H (or 8-H). Furthermore, Tufariello and Rowe[8] showed that photorearrangements of 1-X isomers give exo 2-tricyclic compounds 7-X, while those of 2-X give endo 2-epimers 8-X. It was known[3,9] that 8-X species rearrange thermally to 2-X isomers, but, more pertinent to this work, Tufariello and Rowe showed that exo isomers 7 also rearrange to the syn (2-X) derivatives, when cationic processes are involved. Thus 9 (or a variant thereof) which presumably is formed from 7-X leads, before capture of the cation, to 6, which gives[3,4] syn-2-X products (either of rearrangement or solvolysis).

5   6   7

8   9
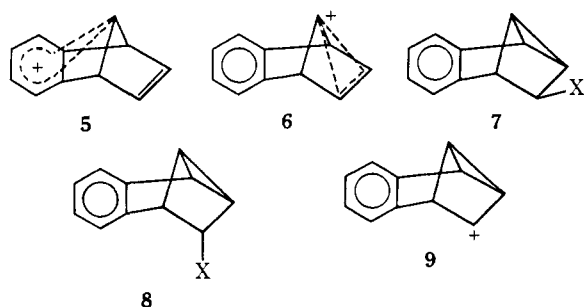
Such a mechanism could be demonstrated (or rejected) by carrying out the irradiation under conditions where 7 isomers are stable. Indeed 1-Cl, when irradiated at 35° directly[10] in hexane, or with photosensitization in acetone, gave a mixture of 2-Cl and 7-Cl. That the primary photoproduct was 7-Cl was established by following the disappearance of 1-Cl and the production of 2-Cl and 7-Cl. During irradiation, 7-Cl appeared immediately (pmr analysis[11-13]), followed by slower appearance of 2-Cl. The 7-Cl to 2-Cl transformation was a thermal reaction, occurring equally well in the dark or light, while the disappearance of 1-Cl and formation of 7-Cl required photoexcitation.[14]

When 1-Br was irradiated at room temperature, only 2-Br was noted. However, irradiation in acetone-d_6 at −70° led to a mixture comprising mainly 7-Br with some 2-Br, which upon warming isomerized completely to 2-Br. Addition of methanol at −70° to a partially photoisomerized sample of 1-Br in n-pentane gave 2-

OCH$_3$ from 7-Br but did not affect the unrearranged 1-Br.

In addition, photoisomerization of 1-Cl at 5° in acetone–benzene, followed by treatment with 4 M sodium methoxide in methanol, gave an 83:17 mixture of 8-OCH$_3$ and 2-OCH$_3$. As this mixture was identical with that[3,9] produced by the ground-state solvolysis of 2-Cl in a comparable medium, the intermediacy of the cation 6 in the thermal portion of these "photosolvolyses" is confirmed.

Irradiation of either 7-bromonaphthonorbornadiene in inert solvents led to pure syn bromide 4-Br, and irradiation of 3-Br in methanol gave pure syn ether 4-OCH$_3$. Thus these followed the same pattern as the benzonorbornadienes.

Our experiments lead us to conclude that it is likely that the "photosolvolyses," the photoepimerization, and the "photostability" of 2 and 4 in inert solvents are all manifestations of one primary photoprocess, a di-π-methane rearrangement. Subsequent ion pair formation precedes either internal return to 2-X or 4-X or solvolysis to 2-OCH$_3$ or 4-OCH$_3$. While we have not demonstrated that the "photostability" of the syn isomers is due to the reversible 2 ⇌ 8 transformation or that other diradical or homoallyl to cyclopropylcarbinyl transformations do not occur in the 1 to 7 isomerization, the ubiquitousness of the di-π-methane rearrangement[17] make alternative formulations highly speculative. Appropriate labeling experiments can distinguish such alternatives, as the di-π-methane rearrangement leads to carbon-scrambling of a predictable nature.[7,8,17,18]

(8) J. J. Tufariello and D. W. Rowe, *J. Org. Chem.*, **36**, 2057 (1971).

(9) G. W. Nachtigall, Ph.D. Thesis, University of Colorado, 1968.

(10) Edman[7] gave convincing evidence that his photorearrangements involved triplets, and we assume that this is true for our compounds, even under direct irradiation. The heavy atom (chlorine or bromine) may promote rapid intersystem crossing.

(11) The pmr spectrum of 7-Cl, isolated pure by irradiation of 1-Cl at 5° in 3:1 benzene–acetone, lacked olefinic absorptions and had two aromatic peaks (ratio 3:1), indicating an unsymmetrical tetracyclic skeleton. Comparison of this spectrum to those of other 7 and 8 derivatives confirmed the structure assignment. The exo stereochemistry of the chlorine atom at C-2 was assigned by noting that the exo C-2 proton in compounds of the general structure 8 appear in pmr spectra as four-line patterns,[2,8,12] whereas the endo C-2 protons in compounds 7 appear as doublets[7,8,13] (7-Cl, CCl$_4$, δ 3.41, d, J = 3.5 Hz).

(12) S. J. Cristol and J. I. Maxwell, *J. Org. Chem.*, **39**, 228 (1974).

(13) J. I. Maxwell, unpublished results.

(14) While 2-Cl appeared to be photoinert upon direct irradiation in hexane, or upon photosensitization in acetone or in acetone–benzene mixtures, its photoisomerization would give 8-Cl, which can be anticipated[2,15,16] to be unstable at room temperature and to rearrange rapidly to 2-Cl. The photomethanolysis of 2-Br is consistent with this.

(15) J. J. Tufariello and R. J. Lorence, *J. Amer. Chem. Soc.*, **91**, 1546 (1969); J. J. Tufariello and D. W. Rowe, *J. Chem. Soc., Chem. Commun.*, 1066 (1972).

(16) J. Lhomme, A. Diaz, and S. Winstein, *J. Amer. Chem. Soc.*, **91**, 1548 (1969).

(17) H. E. Zimmerman and P. S. Mariano, *J. Amer. Chem. Soc.*, **91**, 1718 (1969), and references therein.

(18) H. E. Zimmerman, R. W. Binkley, R. S. Givens, and M. S. Sherwin, *J. Amer. Chem. Soc.*, **89**, 3933 (1967); H. E. Zimmerman, R. S. Givens, and R. M. Pagni, *ibid.*, **90**, 4191, 6096 (1968); H. E. Zimmerman and C. O. Bender, *ibid.*, **92**, 4366 (1970); H. E. Zimmerman and D. R. Amick, *ibid.*, **95**, 3977 (1973).

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The Structure of "Titanocene." Clarification by Carbon-13 Nuclear Magnetic Resonance

Sir:

It has been known for some time that reduction of (η^5-C$_5$H$_5$)$_2$TiCl$_2$[1] or (η^5-C$_5$H$_5$)$_2$Ti(CH$_3$)$_2$[2] yields a green dimeric compound conforming to the stoichiometry required for "titanocene." The structure of this green dimeric form of "titanocene" has been the subject of

(1) G. W. Watt, L. J. Baye, and F. O. Drummond, Jr., *J. Amer. Chem. Soc.*, **88**, 1138 (1966), and references therein.

(2) K. Clauss and H. Bestian, *Justus Liebigs Ann. Chem.*, **654**, 8 (1962).