discrete high-spin Mn(III) complexes and for a pronounced tetragonal distortion of the coordination polyhedron.

In the case of manganese(III) porphyrins, the structural data for two crystalline forms of Mn(TPP)Cl[9, 10] and the results reported herein lead to the expectation of stable six-coordinate complexes when high-spin manganese(III) porphyrins of the general formula Mn(Por)(X) are in the presence of, or crystallized from, strongly coordinating solvents and five-coordinate species when in the presence of, or crystallized from, weakly coordinating solvents. In the latter case the coordination polyhedron would be characterized by having the Mn atom displaced from the porphine skeleton toward the anionic X ligand and a Mn–X bond of "normal" length. In the former case the distinguishing characteristics would be "long" bonds from the axial ligands to a Mn atom which might be more nearly in the porphine plane.

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## Trapping of the Carbene Intermediates in the Photolysis of Triptycenes

*Sir:*

The photochemical isomerization of triptycene (tribenzobarrelene) (1)[1] is unique among barrelene derivatives[2, 3] in that the single product (2) which is neither the expected semibullvalene (3) nor a cyclooctatetraene derivative is formed smoothly in inert as well as in photosensitizing solvents. On the assumption that the pathway for triptycene photoisomerization should not be drastically different from that elucidated for barrelene,[2] the photoproduct 2 was considered as being formed by a 1,5-sigmatropic rearrangement of 3 which might be initially formed by way of the di-$\pi$-methane rearrangement of 1 (path a in Scheme I).[1, 4]

We have been advocating for a couple of years the carbene mechanism for the photolytic rearrangement of 1 to 2 (path b in Scheme I)[5] and wish to report here on

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

(2) H. E. Zimmerman and G. L. Grunewald, *J. Amer. Chem. Soc.*, **88**, 183 (1966); H. E. Zimmerman, R. W. Binkley, R. S. Givens, and M. A. Sherwin, *ibid.*, **89**, 3932 (1967).

(3) H. E. Zimmerman, R. S. Givens, and R. M. Pagni, *J. Amer. Chem. Soc.*, **90**, 4191, 6096 (1968); P. W. Rabideau, J. B. Hamilton, and L. Friedman, *ibid.*, **90**, 4465 (1968); E. Ciganek, *ibid.*, **88**, 2882 (1966); R. S. H. Liu, *ibid.*, **90**, 215 (1968).

(4) The molecular frameworks of these compounds require that the 1,5-sigmatropic rearrangement of 3 to 2 should be the suprafacial shift with inversion of configuration at the migrating center. The process is symmetry-forbidden in the ground state, and reexcitation of 3 is necessary for path a to be an energetically favorable reaction. Since the photoisomerization is rather efficient,[1] a two-photon process cannot be highly likely.

two trapping experiments of the carbene intermediates **4** and **4a**.

Irradiation of a 0.003 $M$ solution of **1** in methanol under nitrogen for 2 hr with a Vycor filtered Ushio UM-452 500-W high-pressure mercury source in an immersion apparatus resulted in 85% consumption of the starting material. The photoproduct isolated by tlc on silica gel was not the reported **2**[1] but was identified as 9-(2-methoxymethylphenyl)fluorene (**5**): colorless needles; mp 120–121°; in 75% isolated yield based on the unrecovered **1**; nmr (CDCl$_3$) $\delta$ 3.51 (s, CH$_3$O), 4.84 (s, OCH$_2$), 5.46 (s, C$_9$–H), 6.39 (dd, $J$ = 8.1, 2.0 Hz, C$_{6'}$–H), 7.1–7.5 (m, 9 aromatic H's), and 7.6–7.9 (m, 2 aromatic H's).[6–8] An authentic sample for comparison was prepared by methanolysis of 9-(2-iodomethylphenyl)fluorene.[5b] A preliminary result on the quantum efficiency ($\phi$ = 0.3) of formation of **5** was not different from that of **2** in inert solvents.[1] Photoproduct **2** is also not stable in methanol under irradiation.[9] However, the main product is 8,12$b$-dihydrobenz[$a$]aceanthrylene: colorless prisms, mp 139–140°,[10] in 57% yield.[11]

When a solution of 1-acetyltriptycene (**6**) was irradiated similarly in methanol, no trace of the normal isomerization products, **7**, was detected as evidenced by lack of the characteristic uv absorption at 350 nm due to the chromophore of **2**[1, 5] in the crude reaction mixture. The photoproduct, mp 115–116°,[6] was separated in 68% yield from the starting material by tlc on silica gel and has been identified as **8** on the basis of spectral analysis. The mass spectrum shows a molecular ion at $m/e$ 328 (M) with other prominent peaks at 296 (M − CH$_4$O), 268 (M − C$_2$H$_4$O$_2$), 253 (M − C$_3$H$_7$O$_2$; base peak), and 241 (M − C$_4$H$_7$O$_2$). The infrared spectrum (KBr disks) indicates the presence of an aliphatic ester group at 1738 and 1210 cm$^{-1}$. The uv absorptions $\lambda_{max}$, nm (log $\epsilon$) in methanol are 255 (3.81), 267 (4.15), 292 (3.57), and 303 (3.81). The nmr spectrum is essentially first order and shows the presence of two conformers in a ratio of 2.2:1. The dominant conformer shows a three-proton doublet at $\delta$ 1.73 ($J$ = 7.1 Hz), an OCH$_3$ singlet at 3.77, a methine quartet at 4.55 ($J$ = 7.1 Hz), a C$_9$–H singlet at 5.46, a characteristic double doublet due to C$_{6'}$–H at 6.35, and aromatic

(5) The circumstantial evidences in support of the carbene mechanism found in these laboratories are (a) lack of interconversion of the atropisomeric 1,6-bis(1-cyano-1-methylethyl)triptycenes under irradiation (rotation of the pivot bonds extending from the bridgehead to the substituents in the intermediates for the di-$\pi$-methane rearrangement followed by decay to the starting material would result in mutual isomerization of the meso and $dl$ isomers of the recovered triptycenes: H. Iwamura, The 4th IUPAC Symposium on Photochemistry, Baden-Baden, Germany, July 16–22, 1972, abstracts of contributed papers, p 104; *J. Chem. Soc., Chem. Commun.*, 232 (1973)), (b) formation of **2** from **4** generated independently from the corresponding diazo compound (H. Iwamura, *Chemistry Lett.*, 5 (1974)), and (c) unique product distribution of a series of substituted triptycenes (to be published elsewhere).

(6) All new compounds have satisfactory analytical data.

(7) The nmr signals are relatively broad because the averaging of the chemical shifts between the conformers due to the restricted rotation around the aryl–C$_9$ bond is incomplete at 34° under 60 MHz. In a probe heated at 50° the signals are reasonably sharp. A precedent can be found in 9-($o$-tolyl)fluorene.[8]
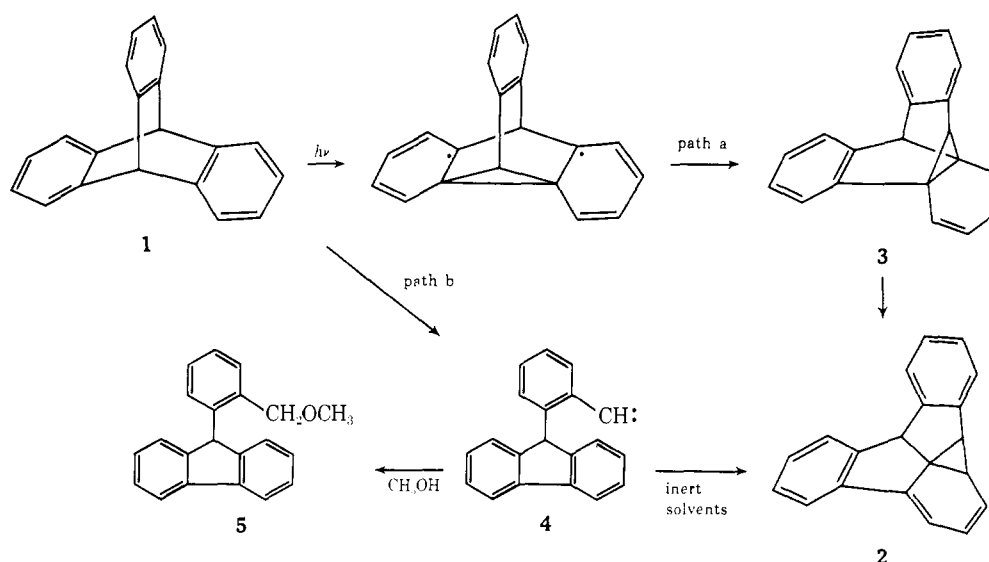
(8) T. H. Siddall, III, and W. E. Stewart, *J. Org. Chem.*, **34**, 233 (1969).

(9) We are grateful to the referees for pointing out this possibility. Except for the quantum efficiency data, an operational test to rule out the remote possibility of **3** fragmenting under reaction conditions to give carbene **4** could not be designed.
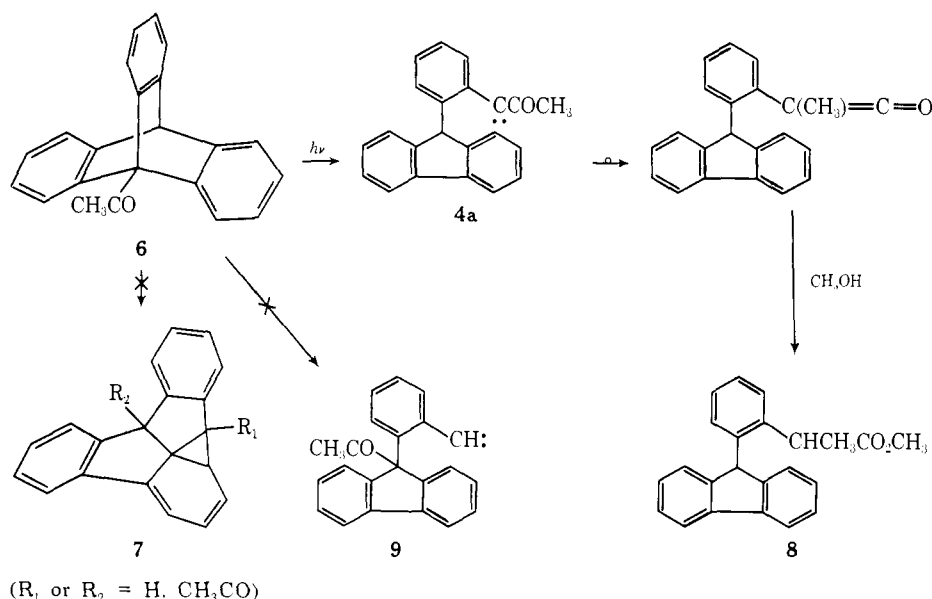
(10) N. Campbell and A. Marks, *J. Chem. Soc.*, 2941 (1951).

(11) Small amount of intractable oil containing the methoxyl group as revealed by its nmr is also obtained.

**Scheme I**

1     *hν*     path a     3

path b

CH₂OCH₃

5    CH₃OH    4    inert solvents    2

**Scheme II**

CH₃CO

6    *hν*    CCOCH₃    4a    C(CH₃)=C=O

CH₃OH

R₂   R₁

7     CH₃CO CH:    9    CHCH₃CO₂CH₃   8

(R₁ or R₂ = H, CH₃CO)

hydrogens at 7.0–7.9. The minor conformer has the corresponding signals at 0.66 (d, $J = 7.1$ Hz), 3.17 (s), 2.45 (q), 5.00 (s), and 7.0–8.0 with high-field aromatic signals missing.[12,13]

(12) The corresponding signals within each group start to coalesce at temperatures 60–100°. At temperatures higher than 150°, the spectrum is composed of sharp lines at averaged chemical shifts (in hexachloro-1,3-butadiene from hexamethyldisiloxane): 1.28 (d, $J = 7.3$ Hz, CH₃), 3.42 (s, OCH₃), 3.70 (q, $J = 7.3$ Hz, H), 5.18 (s, H), 6.8–7.7 (m, aromatic, 12 H). The data are fully in accord with those of a series of 9-(ortho-substituted phenyl)fluorenes in which rotation around the aryl–C₉ bond is frozen at room temperature with respect to the time scale of nmr frequency.[8,13] The high-field shift of the corresponding signals in the minor component is ascribed to the ring current effect of the fluorene rings and enables the conformational assignment as shown below.

H H CHCH₃CO₂CH₃     H CHCH₃CO₂CH₃

major conformer     minor conformer
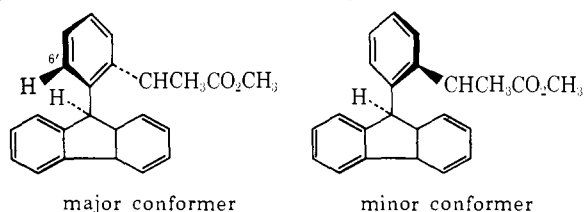
(13) E. A. Chandross and C. F. Sheley, Jr., *J. Amer. Chem. Soc.*, **90**, 4345 (1968); T. H. Siddall, III, and W. E. Stewart, *Tetrahedron Lett.*, 5011 (1968); A. Rieker and H. Kessler, *ibid.*, 1227 (1969); W. V. McKinley, P. A. Grieco, A. E. Young, and H. H. Freedman, *J. Amer. Chem. Soc.*, **92**, 5900 (1970).

These results clearly demonstrate that carbenes are involved in the photolysis of triptycenes. Formation of **5** under irradiation in methanol can be interpreted in terms of the efficient trapping of **4** by the reactive solvent.[14] In inert solvents the intramolecular addition of the arylcarbene **4** to the fluorene ring takes place to give the normal photoisomer **2**. The transformation of 1-acetyltriptycene to **8** can most probably be brought about by the Wolff rearrangement of the initially formed acetylcarbene (**4a**) (Scheme II).

It is interesting to note that the formation of **2** cannot be quenched by 1,3-pentadiene and that conversion of **1** to **2** also occurs smoothly in benzene. Molecular models indicate that the divalent carbon atom is very favorably situated for addition to the C₈–C₈ₐ and C₉–C₉ₐ bonds of the fluorene ring in **4**. Therefore it is not unreasonable that **4** cannot be trapped externally by olefins and aromatic solvents which have the reactivity toward carbenes comparable to the fluorene ring. Par-

(14) For an efficient trapping of the photochemically generated carbenes with methanol, see, for example, D. R. Morton and N. J. Turro, *J. Amer. Chem. Soc.*, **95**, 3947 (1973); R. W. Binkley and D. J. Donovan, *ibid.*, **95**, 5827 (1973). The examples given by the latter authors can be regarded as the acyclic analogs of triptycenes.

ticular mention must also be made of the fact that neither the originally expected **7** nor 9-acetylfluorene derivative due to **9** can be found in the photolysis of **6**.[15] In other words, extrusion of the bridgehead carbon atom from **6** is limited to the $C_1$ attached to the acetyl group. It is not clear at this time if the acetyl group favors the bridging of the di-$\pi$-methane moiety in its vicinity or the phenyl-$C_1$ bonds $\beta$ to the carbonyl group are weakened in the excited state. Although it is usually the case that the photochemical Wolff rearrangement dominates the carbene addition,[16] the work of Jones and Ando[17] has shown that the ketocarbene generated by the benzophenone sensitized decomposition of $\alpha$-diazo ketones can be trapped even by external olefins. Our results that only the Wolff rearrangement is operative in **4a** in spite of the favorable orientation of the $\pi$ system of the fluorene ring together with the failure of the quenching experiment with 1,3-pentadiene in the case of **1** suggest that the excited state responsible for formation of the carbene intermediates is singlet. The concerted loss of two geminal aryl residues to give arylcarbenes **4** and **4a** should be a symmetry-allowed process in the excited state.[18,19]

**Acknowledgment.** The authors wish to express their appreciation to Professor M. Ōki for his stimulating discussion of this work.

(15) The uv and nmr spectra of the crude reaction mixtures from photolysis were carefully examined. In cyclohexane and ether the photolysis of **6** is very sluggish and the expected **7** can never be obtained.
(16) W. Kirmse, "Carbene Chemistry," 2nd ed, Academic Press, New York, N. Y., 1971, pp 339, 475.
(17) M. Jones, Jr., and W. Ando, *J. Amer. Chem. Soc.*, **90**, 2200 (1968).
(18) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Verlag Chemie and Academic Press, New York, N. Y., 1970, p 144.
(19) Turning lastly to the reason why the di-$\pi$-methane rearrangement which is operative in barrelene[2] and its benzo and dibenzo derivatives[3] cannot hold true in the tribenzo case, we note that the excited singlet of barrelenes leads to cyclooctatetraene derivatives rather than to semibullvalenes. A path from triptycenes to cyclooctatetraenes may be energetically unfavorable due to loss of aromaticity of two aryl rings in the course of their rearrangement through the quadricyclene type intermediate. Recently a diversion of the di-$\pi$-methane reaction to the carbene mechanism has been reported for 2-methylenebenzonorbornene (F. Scully, J. Grutzner, and H. Morrison, *J. Amer. Chem. Soc.*, **95**, 5100 (1973)). The high strain in the normal di-$\pi$-methane product is considered as the driving force for the observed reaction.

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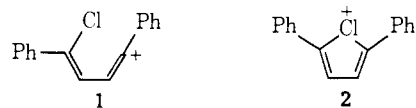## Silver Assisted Solvolysis of Halobutadienes. Evidence for a Chlorolium Ion Intermediate

*Sir:*

Neighboring halogen is known to interact with carbonium ion centers in aliphatic systems[1] and participation of $\beta$-sulfur[2,3] and iodine[4] has been reported in the solvolysis of vinyl derivatives. We here report the results of a study aimed at detecting the capture of a vinyl cation[5] (**1**) by neighboring chlorine. Present in



this system is an additional feature of interest since the intermediate formed is the potentially aromatic chlorolium ion (**2**).

Dibenzochlorolium, -bromolium, and -iodolium cations form stable salts,[6] and Beringer, *et al.*,[7] have recently reported the synthesis of the benziodolium and tetraphenyliodolium cations. No evidence for the existence of a species such as **2** has been reported, but Shechter[8] has proposed a bromolium ion as the intermediate in the bromination of 1,8-bisphenylethynylnaphthalene.

The required precursor for **1** was synthesized as shown in Scheme I. The *N*-bromosuccinimide bro-

**Scheme I**
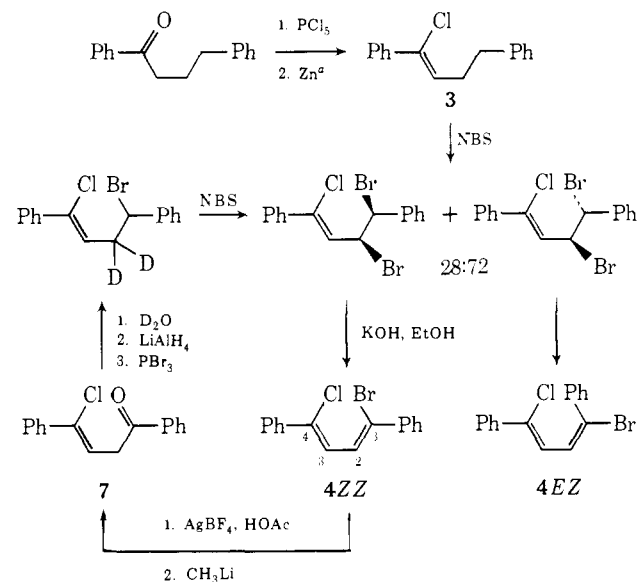


[a] The crude reaction mixture after $PCl_5$ treatment contains 16% 1,1,2-trichloro-1,4-diphenylbutane which can be converted to the desired vinyl chloride with Zn-AcOH.

mination of **3**[9] gave a 72:28 mixture of diastereomers, of which the major isomer could be crystallized to purity, mp 126–127°. Base promoted dehydrohalogenation of this isomer gave **4EZ**[9] (nmr[10] $\delta_{CCl_4}$ 7.32 ($H_2$), 6.64 ($H_3$), ABq, $J = 11$ Hz). Pure **4ZZ**[9] ($\delta_{CCl_4}$ 7.38 ($H_2$), 7.24 ($H_3$), ABq, $J = 11$ Hz) could be isolated by dehydrohalogenation of the crystallization mother liquor.

The vinyl chloride (**3**) was assigned the $Z$ configuration about the double bond since it was the major isomer formed ($Z/E = 4/1$) with the vinyl proton coming at $\delta$ 6.01 ($\delta$ 5.86 for the $E$ isomer). The chemical shift difference is consistent with a number of

(1) P. E. Peterson, *Accounts Chem. Res.*, **4**, 407 (1971).
(2) A. Burighel, G. Modena, and U. Tonellato, *J. Chem. Soc., Perkin Trans. 2*, 2026 (1972).
(3) A. S. Denes, I. G. Csizmadia, and G. Modena, *J. Chem. Soc., Chem. Commun.*, 8 (1972).
(4) P. Bassi and U. Tonellato, *Gazz. Chim. Ital.*, **102**, 387 (1972).
(5) For a review of vinyl cation chemistry, see M. Hanack, *Accounts Chem. Res.*, **3**, 209 (1970); G. Modena and U. Tonellato, *Advan. Phys. Org. Chem.*, **9**, 185 (1971).
(6) R. B. Sandin and A. S. Hay, *J. Amer. Chem. Soc.*, **74**, 274 (1952).
(7) F. M. Beringer, P. Ganis, G. Avitabile, and H. Jaffe, *J. Org. Chem.*, **37**, 879 (1972).
(8) B. Bossenbrock and H. Shechter, *J. Amer. Chem. Soc.*, **89**, 7111 (1967).
(9) Satisfactory elemental analysis by mass spectral peak match was obtained.
(10) The vinyl resonances were unambiguously assigned by comparison with the deuterated compounds, with and without deuterium decoupling.