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THE EXCITED-STATE REACTIONS OF TRIPTYCENES. II.$^{1)}$ THE CARBENE MECHANISM FOR PHOTOISOMERIZATION OF TRIPTYCENE

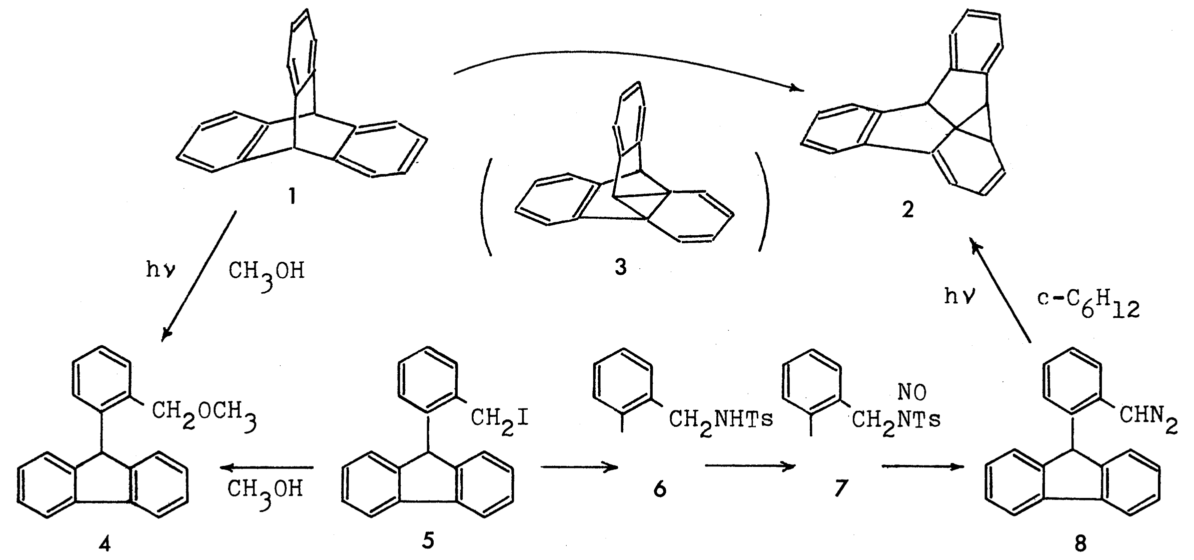
Hiizu IWAMURA

Department of Chemistry, Faculty of Science, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113

Irradiation of triptycene (**1**) in methanol gives 9-(2-methoxymethylphenyl)-fluorene (**4**) in good yield. The reaction is considered to proceed through formation of o-(9-fluorenyl)-phenylcarbene (**9**) followed by attack with the solvent. When the carbene **9** is generated independently by the photolysis of the diazo compound **8** in cyclohexane, the normal photoisomer **2** of **1** is obtained.

The photochemical isomerization of triptycene (**1**)("tribenzobarrelene")$^{2)}$ is unique among barrelene derivatives$^{3,4)}$ in that the single product (**2**) which is neither the expected semibullvalene nor a cyclooctatetraene derivative is formed smoothly in inert as well as in photosensitizing solvents. With the assumption that the pathway for triptycene photoisomerization should not be drastically different from that elucidated for barrelene,$^{3)}$ the photoproduct **2** is postulated to be formed by a 1,5-sigmatropic rearrangement of the semibullvalene (**3**) initially formed by way of the di-π-methane rearrangement.$^{2)}$ However, we have been collecting for a couple of years the circumstantial evidences to suggest the intermediacy of a carbene in the photoisomerization.$^{5)}$ In this communication we wish to report on the trapping experiment and independent generation of the carbene intermediate.

Irradiation of a 0.003 M solution of **1** in methanol for 2 hr with a Pyrex filtered Ushio UM-452 500 W mercury source in an immersion apparatus results in 80 % consumption of the starting material. The photoproduct is not the reported **2**,$^{2)}$ but is identified as 9-(2-methoxymethylphenyl)-fluorene (**4**): yellow prisms,

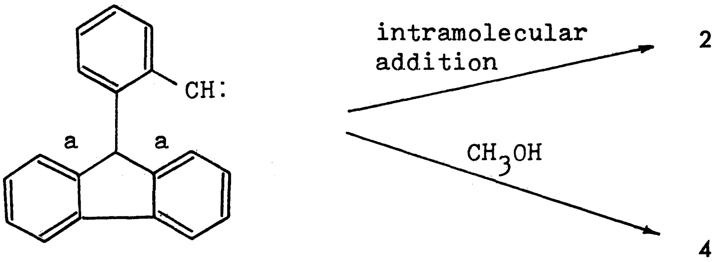


mp 122.5～3°, in 75 % isolated yield based on the unrecovered **1**; NMR ($CDCl_3$), δ 3.51 (s, CH_3O), 4.84 (s, OCH_2), 5.46 (s, $C_{(9)}$-H), 6.39 (dd, J = 8.1, 2.0, $C_{(6)}$-H of the 9-phenyl ring), 7.1～7.5 (m, 9 aromatic H's), and 7.6～7.9 (m, 2 aromatic H's).[6,7] An authentic sample for comparison is prepared by methanolysis of the iodo compound (**5**).[8] A preliminary result on the quantum efficiency (Φ = 0.3) of formation of **4** is not different from that of **2** in cyclohexane.[2]

N-Alkylation of p-toluenesulfonamide with **5** gives a 78 % yield of the primary amide **6** as colorless needles; mp 175°. Treatment of **6** with sodium nitrite in acetic acid at 0° gives a 92 % yield of N-nitroso compound **7**: mp 138°(decomp); NMR ($CDCl_3$), δ 2.42 (s, CH_3), 3.47 (s, N-CH_2), 5.44 (s, $C_{(9)}$-H), 6.40 (dd, $C_{(6)}$-H of the 9-phenyl ring), and 7.1～7.9 (m, 15 aromatic H's). The diazo compound **8** is obtained by the reaction of **7** with sodium methoxide in tetrahydrofuran at 0°. Irradiation of a crude solution of **8** in cyclohexane with a 500 W high pressure mercury vapor lamp fitted with a Pyrex filter at 0° followed by chromatography on silica gel gives the normal photoisomer **2** in 37 % isolated yield based on 7.

These results clearly indicate that the carbene **9** is involved in the photolysis of **1**. Formation of **4** under irradiation in methanol can be interpreted in terms of the efficient trapping of **9** by the reactive solvent.[9] In inert solvents the intramolecular addition of the arylcarbene **9** to the fluorene ring takes place to give the normal photoisomer **2**.

It must be mentioned that the formation of **2** cannot be quenched by 1,3-pentadiene and that conversion of **1** to **2** also occurs smoothly in benzene.[2] Molecular models indicate that the divalent carbon atom is very favorably situated for addition to the a bonds of the fluorene ring in 9. Therefore it is not unreasonable that 9 cannot be trapped intermolecularly by olefins and aromatic solvents of comparable reactivity towards carbenes. Turning now to the reason why the di-π-methane rearrangement which is operative in barrelene3) and its benzo and dibenzo derivatives4) cannot be applied to the tribenzo case, we note that aryl-aryl bonding in 1 may be energetically unfavorable due to loss of aromaticity of two aryl groups. The concerted loss of two geminal aryl groups to give the stable arylcarbene 9 should be a symmetry-allowed process in the excited state.10,11)



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5) The 4th IUPAC Symposium on Photochemistry, Baden-Baden, Germany, July 16 - 22, 1972. Abstracts of Contributed Papers, p 104.

6) All new compounds have satisfactory analytical data.

7) The NMR data are consistent with a series of 9-(o-tolyl)-fluorene derivatives in which one conformer is predominant (T. H. Siddall, III and W. E. Stewart, J. Org. Chem., 34, 233 (1969)).

8) This compound is prepared by treatment of 9-(2-methoxymethylphenyl)-9-

hydroxyfluorene with hydroiodic acid and will be described in full detail elsewhere.

9) For an efficient trapping of the photochemically generated carbene with methanol, see, for example, D. R. Morton and N. J. Turro, J. Amer. Chem. Soc., 95, 3947 (1973).

10) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press Inc., New York, N. Y., 1970, p 144.

11) Recently a diversion of the di-π-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-π-methane product is considered as the driving force of the observed reaction.

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