CHEMISTRY LETTERS, pp. 1205-1208, 1974. Published by the Chemical Society of Japan

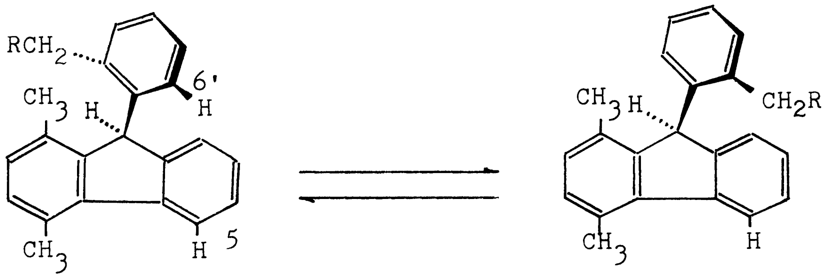
A PHOTOLYTIC ONE-STEP SYNTHESIS AND STEREOCHEMISTRY OF 1,4-DIMETHYL-9-ARYLFLUORENES(1)

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

Photolysis of 2,5-dimethyltriptycene (**3**) in methanol gives 1,4-dimethyl-9-(2-substituted phenyl)fluorenes **1** and **2** in 89 and 5 % yields, respectively. The results are interpreted in terms of the regioselective formation of intermediate carbene **4**. The temperature dependent NMR study gives a rough estimate of $\Delta G_c^{\ddagger}$ value for restricted rotation around the $C_{(9)}$-aryl bond in **2** as 19.4 kcal/mol (104°C).

9-Arylfluorenes have been the subject of recent interest in view of their high barrier to the restricted rotation around the $C_{(9)}$-aryl bond.(2) Our recent findings that triptycenes produce 2-(9-fluorenyl)phenyl carbenes on photolysis[1] have developed a convenient way to 9-(2-substituted phenyl)fluorenes which are otherwise amenable to tedious synthetic routes. We report here regioselective formation of 1,4-dimethyl-9-(2-methoxymethylphenyl)fluorene (**1**) and 1,4-dimethyl-9-(2-methylphenyl)fluorene (**2**) by photolysis of 2,5-dimethyltriptycene (**3**) and a conformational study of the photoproducts **1** and **2**.

Irradiation of a 4 mM solution of **3** in methanol under nitrogen for 2 hr with a Vycor filtered Ushio UM-452 500 W mercury source in an immersion apparatus resulted in 98 % consumption of the starting material. The photoproducts were separated by chromatography on alumina and have been identified on the basis of spectral analysis as **1**: mp 99 ~ 100°C; 89 % yield based on the unrecovered **3**, and **2**: mp 147.5 ~ 148°C; 5 % yield.(3) The nmr spectrum of **1** is essentially first order and, in accord with 9-(2-substituted phenyl)fluorenes in which rotation around the $C_{(9)}$-aryl bond is frozen with respect to the time scale of nmr frequency, shows the presence of two conformers in a ratio of 4.6 to 1. The major conformer shows in CCl_4 a CH_3O singlet at δ 3.49, a CH_2 singlet at 4.81, a $C_{(9)}$-H singlet at 5.30, and a characteristic double doublet due to $C_{(6')}$-H[2] at 6.30, in addition to two aromatic CH_3 singlets at 1.91 and 2.72, a double doublet due to $C_{(5)}$-H[2,4] at 7.79, and the remaining eight aromatic hydrogens at 6.7 ~ 7.4. The minor conformer has the singlets at 2.54 (CH_3O), 3.06 (CH_2), and 4.82 (CH) with the high-field aromatic signals at 6.3 missing. 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 follows.



major conformer

1a (R = OCH_3)

2a (R = H)

minor conformer

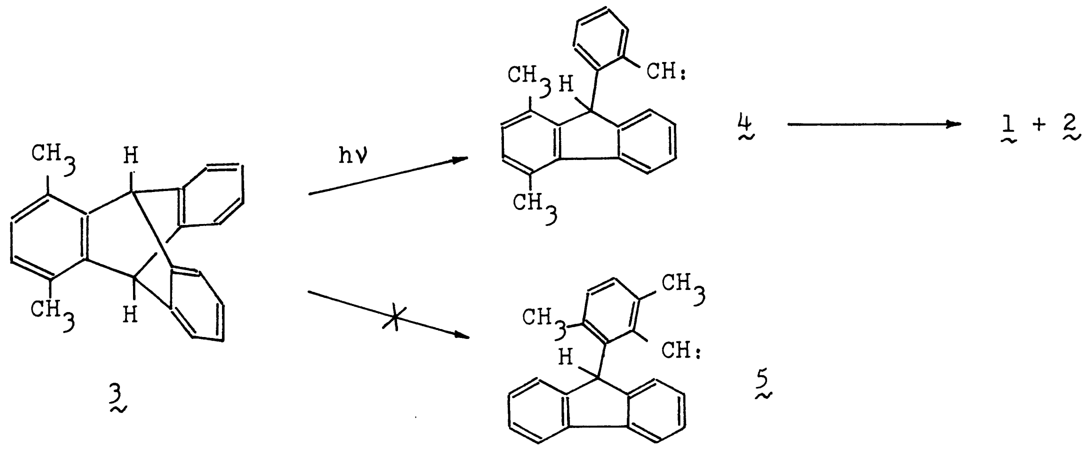
1b (R = OCH_3)

2b (R = H)

2 shows nmr (CCl_4) signals at δ 1.11(s, 0.32 CH_3), 1.90(s, 1 CH_3), 2.70(s, 1 CH_3), 2.75(s, 0.68 CH_3), 4.87(s, 0.32 H), 5.18(s, 0.68 H), 6.21(dd, 0.68 H), 6.7 ~ 7.5(m, 8.32 H), and 7.80(dd, 1 H). The 1,4-dimethylfluorene structure is again supported by the presence of a characteristically high-field $C_{(6')}$-H in the major conformer and only one low-field aromatic proton due to $C_{(5)}$-H. Population of two conformers in **2** is 2.1 to 1.

The main photoproduct **1** is considered to be formed by insertion of carbene **4** into the O-H bond of methanol, while the minor product **2** derives from hydrogen abstraction by **4**. A precedent for the latter reaction is formation of tetraphenylethane from the photochemical decomposition of diphenyldiazomethane in hydrocarbons. An abstraction of hydrogen by the triplet carbene followed by recombination of the diphenylmethyl radicals is proposed.[5] It is quite conceivable that the second abstraction of hydrogen is preferred in the reaction of **4** owing to the steric hindrance to recombination.

It is noted that no product due to alternative carbene **5** is found.[6)] In other words, benzo-xyleno bridging is a more favorable path than benzo-benzo bridging in the excited state of **3**. Either local excitation of the xyleno ring[7)] in **3** or higher free valency in the xyleno ring is a tentative explanation for the selectivity.



When the nmr measurements are made at higher temperature, the discrete signals due to conformers **a** and **b** start to broaden in the temperature range 60 ~ 90°C and eventually coalesce at 105 ~ 145°C, as expected for increased rates of rotation around the $C_{(9)}$-aryl sp^2-sp^3 bond and rapid equilibration between two conformers **a** and **b** on the nmr time scale.[8)] In the case of **2** in hexachlorobutadiene, the separate signals for the $C_{(2')}$-CH_3 due to **2a** and **2b** have the chemical shift difference of 98.6 Hz and the coalescence temperature of 135°C. The signals for $C_{(9)}$-H with $\Delta\nu$ of 18.3 Hz coalesce at 104°C. The free energy of activation at the coalescene temperature, denoted $\Delta G_c^{\ddagger}$, is roughly estimated at 19.4 (at 104°C) and 19.8 (at 135°C) kcal/mol.[9)] We note a significant increase in the $\Delta G_c^{\ddagger}$ value in **2** as compared with the data ($\Delta G_c^{\ddagger}$ = 16.5 kcal/mole at 60°C) for 9-(2-methylphenyl)fluorene.[2c] So far the studies of the steric influences on the rotational barrier of 9-arylfluorenes have been limited to $C_{(9)}$-X and $C_{(2')}$-substituents.[2] The present results represent the first example in which the $C_{(1)}$-substituent on the fluorene ring has been shown to be effective in raising the transition state energy.

Acknowledgment We are obliged for pertinent suggestions made by Prof. M. Ōki and Dr. M. Nakamura during this work.

REFERENCES AND FOOTNOTES

1) Part IV of "The Excited-State Reactions of Triptycenes." For Part III, see H. Iwamura and K. Yoshimura, J. Amer. Chem. Soc., 96, 2652 (1974).

2) (a) E. A. Chandross and C. F. Sheley, Jr., J. Amer. Chem. Soc., 90, 4345 (1968); (b) T. H. Siddall. III and W. E. Stewart, Tetrahedron Lett., 5011 (1968); (c) T. H. Siddall, III and W. E. Stewart, J. Org. Chem., 34, 233 (1969); (d) A. Rieker and H. Kessler, Tetrahedron Lett., 1227 (1969); (e) W. V. Mckinley, P. A. Grieco, A. E. Young, and H. H. Freedman, J. Amer. Chem. Soc., 92, 5900 (1970).

3) All new compounds have satisfactory analytical data for C and H.

4) D. W. Jones and K. D. Bartle, "Advances in Organic Chemistry. Methods and Results," Vol. 8, E. C. Taylor, Ed., Wiley, New York, N. Y., 1972, p. 317.

5) W. Kirmse, "Carbene Chemistry," 2nd Ed., Academic Press, Inc., New York. N. Y., 1971, p. 213.

6) Products from **5** would have given in the aromatic region of nmr a low-field two proton double doublet for $C_{(4)}$- and $C_{(5)}$-H's and no high-field signal due to $C_{(6')}$-H.

7) Excitation does not delocalize over the entire molecule in triptycenes. The esr study of the triplet triptycene produced photolytically at low temperature reveals that the excited state is essentially that of a benzo ring, although excitation transfer between the aromatic rings are fast (M. S. de Goot and J. H. van der Waals, Mol. Phys., 13, 545 (1963).

8) Nmr measurements were carried out on a Hitachi R-20 B spectrometer (60 MHz). Temperature calibration was obtained using ethylene glycol peak separation.

9) A. Allerhand, H. S. Gutowsky, J. Jonas, and R. A. Meinzer, J. Amer. Chem. Soc., 88, 3185 (1966).

(Received August 27, 1974)