

NOTE

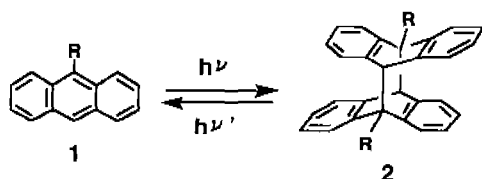
PHOTOCHEMICAL FORMATION OF ANTHRACENE, 9-ANTHRALDEHYDE AND [4+4]-DIMER FROM 9-(METHYLAMINOMETHYL)ANTHRACENE

SUNG SIK KIM*, YOON JUNG MAH AND MI HYUN SO

Department of Chemistry, Chonbuk National University, Chonju 561-756, Korea

(Received 17 March 1999; accepted 13 April 1999)

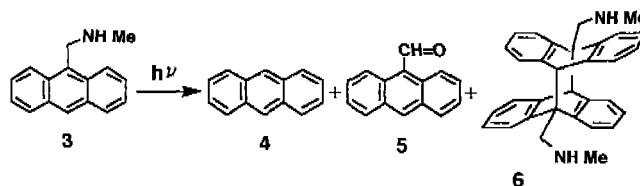
During the course of his studies on solid hydrocarbons that were obtainable from coal tar by distillation, J. Fritzsche discovered in 1866 that solutions of anthracene upon exposure to sunlight gave a colorless crystalline precipitate which regenerated anthracene upon melting.¹ Nowadays, there is nothing remarkable about anthracenes which dimerize photochemically to give dianthracenes, *i.e.*, [4 π + 4 π]-dimers.¹⁻⁶ The basic reactions involve the formation of [4 π + 4 π]-photocycloadducts across the 9,10-positions of anthracenes, and the reactions can be reversed if shorter-wavelength radiation is used. With olefins anthracene gives [4+2]-cycloaddition products upon irradiation. Conjugated dienes, on the other hand, give both [4+2]- and [4+4]-adducts, including products that arise by reaction at the terminal rather than the central ring of the anthracene moiety. Photoexcitation of 9-substituted anthracenes **1** are known to form dimers on irradiation with light of wavelength $\lambda > 300$ nm, in which head-to-tail dimers **2** typically predominate, though evidence for the concomitant formation of thermally more labile head-to-head dimers has been obtained in some instances.^{7,8} As a matter of fact, 9-substituted anthracenes have been investigated as luminescent sensors for metal cations, luminescent probes for anions, pH sensitive fluorescent sensors, etc.⁹



Scheme 1.

We now report a photochemical reaction of 9-(methylaminomethyl)anthracene (Mama) **3**, in which anthracene **4** and 9-anthraldehyde **5**, as well as [4+4]-dimer **6**, were produced when irradiated in solution. Irradiation of Mama **3** in benzene with 300 nm UV light yielded only [4+4]-dimer **6**. On the other hand, irradiation (300 nm UV light) of Mama **3** in diethyl ether gave Mama **3** (221 mg, 1.0 mmol) in diethyl ether (40 mL) was irradiated with 300 nm UV light for 18

h, a [4 π +4 π]- homodimer **6** of Mama was isolated in 60% yield simply by filtration followed by crystallization of the photoreaction mixture. ¹H-NMR spectrum (CDCl₃) of **6** showed three singlets at δ 3.74 (s, CH₂), 3.71 (s, CH), and 2.60 (s, CH₃). ¹³C-¹H correlation spectrum of **6** was also observed, in which carbon signals at δ 61.7, 56.5 and 36.5 correlated with proton signals at 3.71, 3.74 and 2.60, respectively. The residue was chromatographed over silica gel (230-400 mesh) with *n*-hexane and ethyl acetate as the eluent (9:1, v/v). The other products obtained by flash column chromatography was found to be anthracene **4** (2%) and trace amount of 9-anthraldehyde **5**, in which *ca.* 20% of **3** was recovered. Interestingly, irradiation of Mama **3** in the similar condition with visible light gave anthracene **4** (22%) and 9-anthraldehyde **5** (1%), in which [4 π +4 π]-dimer **6** was not found. Irradiation of Mama **3** in diethyl ether, in the pres-



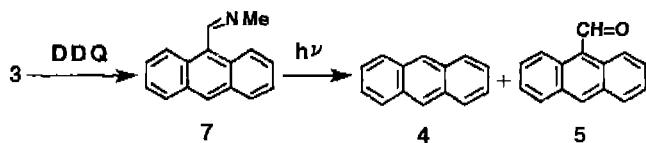
Scheme 2.

ence of molecular oxygen, with 300 nm UV light gave 40% of anthracene **4** and 5% of 9-anthraldehyde **5**, in which [4+4]-dimer **6** was not found. This implies that the [4+4]-dimer **6** is formed by way of the triplet state of Mama **3**.

At this point we are just able to speculate on the mechanism for the formation of the anthracenes. It may be rationalized that anthracene **4** and 9-anthraldehyde **5** are produced *via* an unstable intermediate initially formed by intramolecular energy-transfer followed by C-C or C-N bond cleavage, respectively. Addition of water molecule to the excited **3**, whether it was radical ion or not, would form 9-anthraldehyde **5**. In comparison with UV light, visible light cleaves only the weaker bond, *i.e.*, C-N bond, instead of C-C bond. Bond energy values of C-N and C-C bond are 69-75 kcal/mol and 83-85 kcal/mol, respectively, in which 75 kcal/mol is equal to 381.3 nm, and 85 kcal/mol is equal to 336.5 nm. Irradiation of **3** with visible light actually yielded only 9-anthraldehyde **5**, but not anthracene **4**.

*To whom correspondence should be addressed.

Oxidation of Mama **3** with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) to give **7** followed by irradiation with 300 nm UV light also gave rise to anthracene **4** and 9-anthraldehyde **5**. A phenyl analog of 9-substituted anthracene **7** was also synthesized from 9-anthraldehyde and aniline, and irradiated in the similar condition to yield anthracene **4** and



Scheme 3.

9-anthraldehyde **5**.

Many spectroscopic studies of intramolecular electron transfer involving photoexcited anthracenes have been devoted to the formation of exciplexes with aromatic amines.¹⁰ The fluorescence intensity of Mama **3** in methanol increased with increasing the concentration of HCl. Addition of NaOH to methanolic solution of Mama **3** containing HCl led to the dramatic decrease in the fluorescence intensity of **3**. It is conceivable that the formation of anthracene **4** and 9-anthraldehyde **5** involves photoinduced intramolecular electron transfer processes. Intramolecular electron transfer from nitrogen atom of methylamino group to anthracene moiety can lead to a radical ion, in which the formation of imine followed by hydrolysis may yield aldehyde **5**. The formation of anthracene **4** seems to be produced by carbon-carbon bond cleavage of the initially formed radical ion leading to anthracene radical, which finally yield anthracene **4** via hydrogen atom abstraction process.

In conclusion, irradiation of Mama **3** in diethyl ether with 300 nm UV light gave 9-anthraldehyde **5** as the major product and anthracene **4**, as well as $[4\pi + 4\pi]$ -homodimer of Mama **3**. In contrast, irradiation of Mama **3** with visible light yielded only 9-anthraldehyde **5**. Further work is in progress to study the mechanistic aspects of the photoreactions in more detail.

EXPERIMENTAL SECTION

9-(Methylaminomethyl)anthracene was purchased from Aldrich Chemical Company and used as received. Diethyl ether, *n*-hexane, and ethyl acetate were purchased from Dong Yang Chemical Company and fractionally distilled before use. ¹H and ¹³C NMR spectra were recorded on a Jeol-JMN EX (400 MHz) spectrometer in CDCl₃ with TMS as the internal standard. IR spectra were observed on a Nicolet 5-DX1 FT-IR spectrophotometer in KBr pellets or NaCl cells. UV spectra were determined on a Beckman DU 7500 spectrophotometer. Mass spectra were observed on a Hewlett-Packard 5985A GC/MS spectrometer. Silica gel used for column chromatography was from Merck company as 230-400 mesh particles. Analytical TLC plates were purchased from

Merck company as 200x200 mm aluminum sheets precoated with 0.25 mm Silica Gel together with fluorescent indicator.

Preparative photochemical reactions were conducted in a photoreactor composed of a water-cooled system and a Pyrex reaction vessel with 300 nm UV lamps (The Southern New England Ultraviolet Company, Rayonet Photochemical Reactor, Model RPR-208), after purging with nitrogen gas (purity; 99.9%) for 30 min. Visible lamps used in this study were 250 W incandescent lamps. Irradiation of a solution of 9-(methylaminomethyl)anthracene **3** (221 mg, 1.0 mmol) in diethyl ether (100 mL) with 300 nm UV light for 18 h afforded $[4\pi+4\pi]$ -homodimer **6** in 60% yield, 9-anthraldehyde **5** (2%) and anthracene **4** (trace amount), in which ca. 20% of 9-(methylaminomethyl)anthracene **3** was recovered. Irradiation with visible light in the similar condition gave only anthracene **4** (22%) and 9-anthraldehyde **5** (1%). The $[4+4]$ -dimer **6** was not formed when irradiated **3** in the presence of molecular oxygen.

6: IR(KBr), 3311, 3065, 2871, 2841, 1475, 1449, 1132, 737 cm⁻¹; ¹H-NMR(CDCl₃), δ 7.03-6.79 (16H, aromatic), 3.74 (s, 2H), 3.71 (s, 1H), 2.60 (s, 3H); ¹³C-NMR(CDCl₃), δ 127.5, 125.6, 125.5, 125.4, 61.7 (2CH₃'s), 56.5 (2CH₂'s), 36.5 (2CH₃'s); Mass(EI), *m/e* 442(M), 221(100%).

The structures of anthracene **4** and 9-anthraldehyde **5** were confirmed by comparing with spectral data of the authentic samples purchased from Aldrich Chemical Company.

Acknowledgement—We appreciate the financial support of this work by the Korea Research Foundation (Project No. 1997-001-D00279).

REFERENCES

1. Becker, H-D. (1993) Unimolecular Photochemistry of Anthracenes, *Chem. Rev.* **93**(1), 145-172.
2. Yang, N. C., M-J. Chen, P. Chen and K. T. Mak (1982) Chemistry of Exciplexes. 12. Chemistry of Heterodimers of Benzene and Anthracene, *J. Am. Chem. Soc.* **104**, 853-855.
3. Wolff, T. (1985) Temperature Dependence of Regioselectivity and Excimer Equilibrium in the Photodimerization of 9-Methylanthracene, *Z. Naturforsch.* **40a**, 1105-1107.
4. Yang, N. C., J. Masnovi, W-L. Chiang, T. Wang, H. Shou and D. H. Yang (1981) Chemistry of Exciplexes. 11. Photocycloaddition of 1,3-Cyclohexadiene to Polynuclear Aromatic Hydrocarbons, *Tetrahedron*, **37**(19), 3285-3300.
5. Yang, N. C., M-J. Chen and P. Chen (1984) Chemistry of Benzene-Anthracene Cyclodimers, *J. Am. Chem. Soc.*, **106**, 7310-7315.
6. Yang, N. C., H. Gan, S. S. Kim, J. M. Masnovi, P. W. Rafalko, E. F. Ezell and G. R. Lenz (1990) *Tetrahedron Lett.*, **31**(27), 3825-3828.
7. Wolff, T. (1981) Micelle-directed Regioselective Photodimerization of 9-Hydroxymethylanthracene, *J. Photochem.*

- 16, 343-346.
8. Becker, H-D., V. Langer, and H-C. Becker (1993) Photochemistry of 9-Benzoylanthracene, *J. Org. Chem.* **58**, 6394-6396.
9. Pietraszkiewicz, M. (1996) In *Comprehensive Supramolecular Chemistry*, ed. by Reinhoudt, D. N., Elsevier Science Inc., New York, Vol. 10, pp. 225-266.
10. Turro, N. J. (1978) In *Modern Molecular Photochemistry*, The Benjamin/Cummings Publishing Co., Inc., pp. 143.