J. Am. Chem. Soc. **2000,** *122,* 8575−8576

Novel Acid-Catalyzed Hydrolysis of an Intermediate from a Photorearrangement of Stilbenes

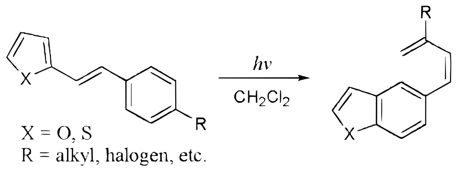
Tong-Ing Ho,* Jinn-Hsuan Ho, and Jin-Yi Wu

Department of Chemistry
National Taiwan University
Taipei, Taiwan (R.O.C.)

Received April 3, 2000
Revised Manuscript Received July 14, 2000

Stilbene and its derivatives represent one of the most reactive systems in photochemistry. The various reactions of stilbenes include *cis*−*trans* photoisomerization, oxidative photocyclization, eliminative photocyclization, photocycloaddition with various alkenes, photoaddition with amines and which have been described in a vast literature.[1−8]

We have recently reported[9] a novel photochemical rearrangement reaction of styrylfurans and styrylthiophenes (eq 1) that consist of photocyclization, the [1,9] hydrogen shift and ring opening.

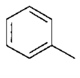
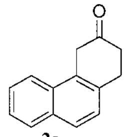
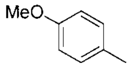
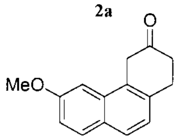
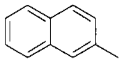
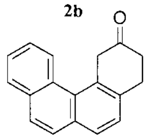
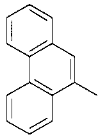
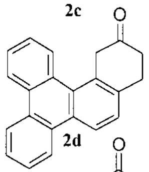
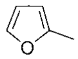
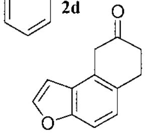
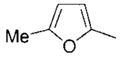
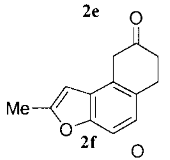
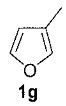
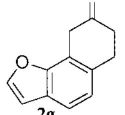
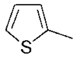
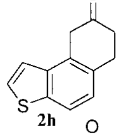
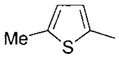
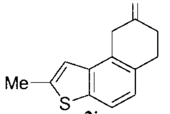
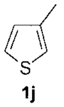
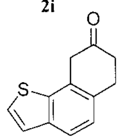
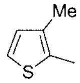


(1)

The [1,9] hydrogen shift is the key step for this photorearrangement reaction. It is believed that the presence of a heteroatom in the system might cause the greater acidity of the hydrogen atom needed for the [1,9] hydrogen shift. Thus it is not unexpected that the corresponding stilbene derivatives were not able to show similar photorearrangement. However we have prepared *p*-methoxy-*trans*-stilbene **1a** and styrylarenes **1b**−**1k** (Scheme 1), and would like to report a novel rearrangement reaction, which is catalyzed by a protic acid.

A degassed acetonitrile solution containing 5 × 10^{-3} M *p*-methoxy-*trans*-stilbene **1a** and 0.5 M hydrochloric acid is irradiated with a Rayonet apparatus at 350 nm for 43 h, and then the solvent is evaporated and the acid is removed to obtain 1,2,4-trihydrophenanthren-3-one **2a** as the sole isolated product. The compound **2a**[10] shows ^{1}H NMR at δ 3.94 (singlet; Ar−CH$_2$−CO), 3.26 (triplet, J = 6.9 Hz; CO−CH$_2$−C$\underline{H}_2$−Ar) and 2.73 (triplet, J = 6.9 Hz; CO−C$\underline{H}_2$−CH$_2$−Ar), and shows ^{13}C NMR at δ 210.1 (C═O) corresponding to the data reported in the literature.[11] Similarly there is one product isolated by irradiating *p*-methoxy-styrylaromatics **1b**−**1d** and *p*-methoxy-styryl-heterocycles **1e**−**1j** in the presence of hydrochloric acid (Scheme 1). Most of the reactions are with complete conversion. The isolated yields are very good (Table 1). Compounds **2c**, **2g,** and **2j** are regioselective products.

Table 1. The Yields of the Reactions for Compounds **1a**−**1k**

entry	**1** Ar	time/hr	**2**	Conv./%	Yield/%
1	 **1a**	43	 **2a**	52	96
2	 **1b**	48	 **2b**	81	91
3	 **1c**	50	 **2c**	100	90
4	 **1d**	45	 **2d**	100	90
5	 **1e**	3.5	 **2e**	100	98
6	 **1f**	3.5	 **2f**	100	85
7	 **1g**	16	 **2g**	75	78
8	 **1h**	17	 **2h**	100	95
9	 **1i**	17	 **2i**	100	93
10	 **1j**	17	 **2j**	100	85
11	 **1k**	17	*cis/trans*-**1k**	0	--

---

(1) (a) Stephenson, L. M.; Hammond, G. S. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 261−270. (b) Hammond, G. S.; Saltiel, J. *J. Am. Chem. Soc.* **1962**, *84*, 4983−4984. (c) Hammond, G. S.; Turro, N. J. *Science* **1962**, *142*, 1541−1553.

(2) Zimmerman, H. E. In *Rearrangement in Ground and Excited States*; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 3, pp 131−166.

(3) Somers, J. B. M.; Couture, A.; Lablache-Combier, A.; Laarhoven, W. H. *J. Am. Chem. Soc.* **1985**, *107*, 1387−1394.

(4) Kaupp, G. *Angew. Chem.* **1980**, *92*, 245−277; *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 243−275.

(5) Lewis, F. D. *Acc. Chem. Res.* **1979**, *12*, 152−158.

(6) Gusten, H.; Schulte-Frohlinde, D. *Chem. Ber.* **1971**, *104*, 402−406.

(7) Mallory, F. B.; Mallory, C. W. *Org. React.* **1980**, *30*, 1.

(8) Waldeck, D. H. *Chem. Rev.* **1991**, *91*, 415−436.

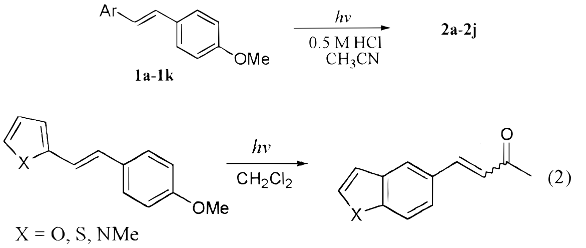
(9) Ho, T.-I.; Wu, J.-Y.; Wang, S.-L. *Angew. Chem., Int. Ed.* **1999**, *38*, 2558−2560.

(10) Spectral data for compound **2a**: ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.86−7.81 (m, 2H), 7.73 (d, J = 8.4 Hz, 1H), 7.56−7.45 (m, 2H), 7.33 (d, J = 8.4 Hz, 1H), 3.94 (s, 2H), 3.26 (t, J = 6.9 Hz, 2H), 2.73 (t, J = 6.9 Hz, 2H). ^{13}C NMR (75 MHz, CDCl$_3$) δ 210.1, 133.2, 132.4, 131.4, 128.7, 128.2, 127.1, 126.5, 126.5, 125.4, 122.3, 40.4, 38.8, 29.6.

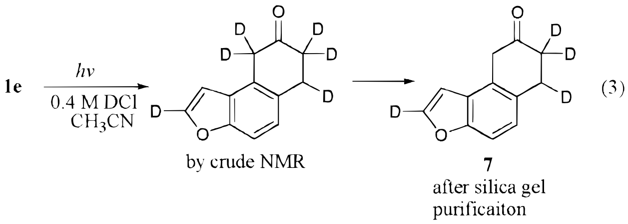
(11) Manitto, P.; Monti, D.; Speranza, G. *J. Org. Chem.* **1995**, *60*, 484−485.

10.1021/ja0011562 CCC: $19.00 © 2000 American Chemical Society
Published on Web 08/18/2000

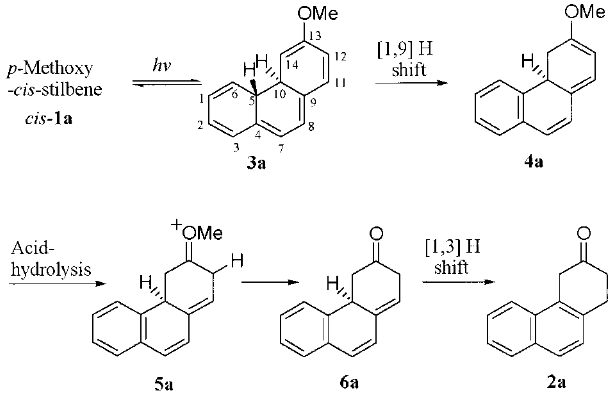
Scheme 1. Photochemical Rearrangement of *p*-Methoxy-*trans*-Stilbene and Its Dreivatives **1a**−**1k**



In dichloromethane solvent and in the absence of the protic acid, compounds **1e**, **1f**, **1h**, and **1i** have been reported[12] to undergo different reaction pathway (eq 2). Thus, it is clear that the reaction mechanism for our present reaction (Scheme 1) is different from the previous reported reaction. One plausible reaction mechanism for this novel rearrangement in the presence of acid is shown in Scheme 2. The reaction may be derived from the *p*-methoxy-*cis*-stilbene (*cis*-**1a**) to form the dihydrophenanthrene intermediate **3a** through a six-electron conrotatory process. Then an acid-catalyzed [1,9] hydrogen shift has occurred to get intermediate **4a**, possibly by protonation at the carbon 14 of **3a** since PM3 calculations indicated that carbon 14 of **3a** bears a partial negative charge of about −0.42. Hydrolysis of intermediate **4a** to **5a** is simply an acid-catalyzed hydrolysis reaction of enol ether.[13] Intermediate **6a** may undergo a [1,3] hydrogen shift to the product **2a**. This [1,3] hydrogen shift can be also catalyzed by protonation, which is shown a deuterium isotope labeling at the 10 position of **7** (eq 3).[14] Deuterium labeling at 4, 11, 11 positions of **7** are from the result of proton deuterium exchange from the medium.



Scheme 2. Mechanism for the Photochemical Rearrangement of *p*-Methoxy-*trans*-stilbene **1a**



Not all of the intermediates **3a**−**6a** could be isolated or identified by spectroscopic methods. Compounds **1a**−**1d** needs longer photolysis time (Table 1), this can be due to the lack of heteroatoms to render the higher acidity for the [1,9] hydrogen shift, even though this process has been catalyzed by the protonation. Styrylfuran derivatives **1e** and **1f** need the least irradiation period. 3-Styrylfuran **1g** needs longer irradiation times similar to the styrylthiophene systems **1h** and **1i**. The less electron negative sulfur atom is the cause for the lower acidity of the hydrogen atom for [1,9] hydrogen shift; thus, longer irradiation time is needed (for **1h**, **1i**).

The acid-catalyzed [1,9] hydrogen shift step is an essential process which is shown by the fact that compound **1k** with a methyl substituent at the 3-position of the thiophene ring prevents the [1,9] hydrogen shift and thus stops the photoreaction completely, and the only photoreaction is *trans*−*cis* isomerization of **1k**. It is plausible that the [1,3] hydrogen shift might proceed the acid-catalyzed hydrolysis. But the result is the same.

In conclusion, we have shown that by the aid of a protic acid, *p*-methoxy-*trans*-stilbene **1a** and styrylarenes **1b**−**1k** can undergo a clean and efficient photochemical rearrangement reaction to afford the trihydro polyaromatic ketone compounds through a series of six-electron photocyclization, a [1,9] hydrogen shift, hydrolysis, and a [1,3] hydrogen shift. The lateral three steps plausibly are catalyzed by the protonation by the external protic acids. It is also interesting to observe that compounds **1e**−**1j** show different rearrangement reaction pathways with and without the presence of the protic acids. In the absence of the protic acid, the only photochemical reaction for compounds **1a**−**1d** in degassed solution is *trans*−*cis* isomerization.

Acknowledgment. We are grateful to the National Science Council of the Republic of China (Taiwan) for financial support.

Supporting Information Available: ^{1}H and ^{13}C NMR spectral data of products **2a**−**2j** and **7** are available (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA0011562

---

(12) Wu, J.-Y.; Ho, J.-H.; Shih, S.-M.; Hsieh, T.-L.; Ho, T.-I. *Org. Lett.* **1999**, *1*, 1039−1041.

(13) Kresge, A. J.; Chen, H. L.; Chiang, Y.; Murrill, E.; Payne, M. A.; Sagatys, D. S. *J. Am. Chem. Soc.* **1971**, *93*, 413−423.

(14) Spectral data for compound **7**: ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.36 (d, $J = 8.2$ Hz, 1H), 7.16 (d, $J = 8.2$ Hz, 1H), 6.71 (s, 1H), 3.74 (s, 2H), 3.14 (s, 1H). ^{13}C NMR (75 MHz, CDCl$_3$) δ 210.2, 153.7, 145.1 (t, $J_{CD} = 30.5$ Hz), 130.1, 126.4, 125.7, 124.1, 109.6, 104.0, 41.5, 27.8 (t, $J_{CD} = 20.0$ Hz). MS (70 eV, EI) *m/z* (%) 190 (48) [M$^+$], 146 (100), 132 (16), 117 (18); HRMS (EI) Calcd for $C_{12}H_6D_4O_2$: *m/z* 190.0928. Found: *m/z* 190.0938.