行政院國家科學委員會專題研究計畫成果報告

二苯乙烯光酸催化反應研究
Acid-Catalyzed Photochemistry of Stilbene Compounds

計畫編號：NSC 89－2113－M－002－049－
執行期限：89 年 08 月 01 日至 90 年 07 月 31 日
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中文摘要

研究二苯乙烯衍生物及類似物在酸催化下之光化學反應。當此類化合物以含有過量氯化氫之乙腈為溶劑進行光化學反應時，分別可得 1,3,4-**三氫菲**-3-**酮之產物及其各種類似物，此種與酸有關之光化學反應之反應機構包含了順反異構化作用，酸催化**[1,9]**氫位移，酸催化水解及酸催化**[1,3]**氫位移。當溶劑中所含之氯化氫分子為一當量時，此類化合物則反應產生 4-芳香基丁-3-烯-2-酮及其類似物，此時反應機構為順反異構化作用，**[1,9]**氫位移，開環反應及丁二烯醚之水解作用。此種反應不但產率高且產物單純，而且利用酸濃度的變化能控制光化學反應的路徑，極具實用價值。**

關鍵詞：二苯乙烯類化合物，水解反應，光轉位反應。

Abstract

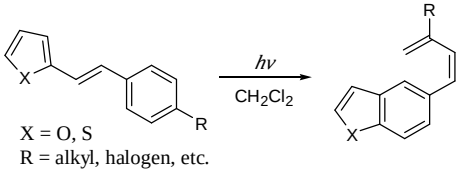
Photolysis of 4-methoxystilbene derivatives and analogues in acetonitrile with exceeded hydrochloric acid affords 1,3,4-trihydrophenthren-3-one and its analogues in good yields. Photolysis of 4-methoxystilbene derivatives and analogues in acetonitrile with one equate hydrochloric acid gives 4-arylbut-3-en-2-one and derivatives in good isolated yields. Changing the concertration of hydrochloric acid can control these two reaction pathways

Keywords:
Stilbenes, Photorearrangement, Hydrolysis.

Introduction

The final course of a photochemical reaction is sometimes sensitive to its environments. The factors include irradiation wavelengths[1], physical restraint to motion[2], solvents[3], temperature[4] and magnetic field[5]. Recently, the research on the external effects of an acid on the pathways of a photochemical reaction has become increasingly important.[6,7,8] The presence of an external acid can even switch the eventual product of mesityl cyclohexanecarboxylate from that of decarboxylation to transesterification completely.[7]

We have recently shown an interesting photo-rearrangement reaction of styrylthiophene and styrylfuran.[3f] This novel reaction occurs through a series of processes *trans-cis* isomerization, conrotatory photocyclization, an apparent [1,9]H shift and cycloreversion. The sulfur and oxygen atoms of the heterocyclic rings have played a vital role of such reaction. Their electron-donating characteristics through resonance interactions increased its basicity of the remote carbon to initiate an apparent [1,9]H shift.



(1)

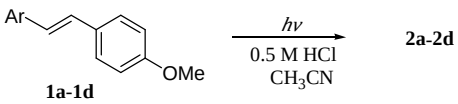
For the inactive stilbene systems without an electron donating group, it is possible to activate this photochemical reaction by the aid of an external protic acid. We now wish to report a perfect control of the nature of the final product in such photochemical

reactions by adjusting the concentration of the protic acid.

Results

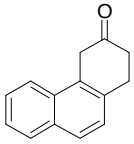
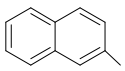
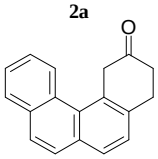
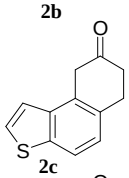
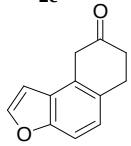
Irradiation of a degassed acetonitrile solution containing 5×10^{-3} M *p*-methoxy-*trans*-stilbene **1a** and 0.5 M hydrochloric acid with a Rayonet apparatus at 350 nm for 43 hours, then the solvent is evaporated and the acid is removed to obtain 1,2,4-trihydrophenanthren-3-one **2a** as the sole isolated product. The compound **2a**[9] 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.[10] Similarly there is one product isolated by irradiating *p*-methoxy-styrylaromatics **1b**–**1d** in the presence of hydrochloric acid (Scheme 1). Most of the reactions are with complete conversion. The isolated yields are very good (Table 1).

Scheme 1. Photorearrangement of Compounds **1a-1d**.



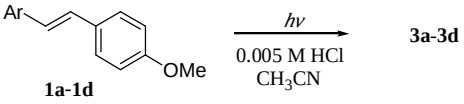
1a-1d

Table 1. The Yields of the Reactions for Compounds.

entry	**1** Ar	time/hr	**2**	Conv./%	Yield/%
1	 **1a**	43	 **2a**	52	96
2	 **1b**	50	 **2b**	100	90
3	 **1c**	17	 **2c**	100	95
4	 **1d**	3.5	 **2d**	100	98
5	 **1e**	17	*cis/trans*-**1e**	0	--

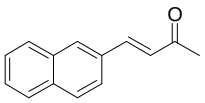
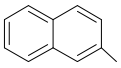
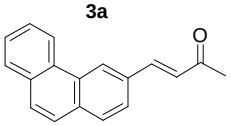
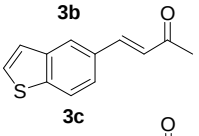
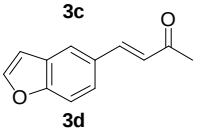
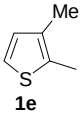
Irradiation of a degassed acetonitrile solution containing 5×10^{-3} M *p*-methoxy-*trans*-stilbene **1a** and 5×10^{-3} M hydrochloric acid with a Rayonet apparatus at 350 nm for 57 hours, then the solvent is evaporated and the acid is removed to obtain 4-(nathphen-2-yl)-*trans*-but-3-en-2-one **3a** as the sole isolated product. The compound **3a**[11] shows ^{1}H NMR at δ 7.59(d, J = 16.1 Hz, 1H), 6.69(d, J = 16.1 Hz, 1H), 2.36(s, 3H), and shows ^{13}C NMR at δ 198.1 ppm corresponding to the data reported in the literature.[12] Similarly there is one product isolated by irradiating *p*-methoxy-styrylaromatics **1b**–**1d** in the presence of hydrochloric acid (Scheme 2). Most of the reactions are with complete conversion. The isolated yields are very good (Table 2).

Scheme 2. Photorearrangement of Compounds **1a-1d**.



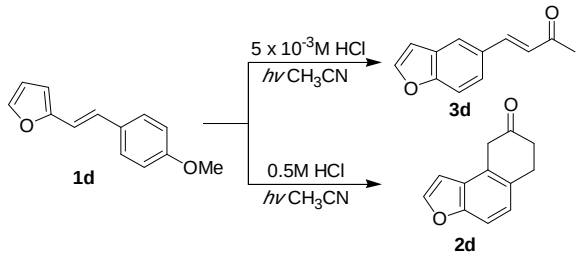
1a-1d

Table 2. The Yields of the Reactions for Compounds.

entry	**1** Ar	time/hr	**3**	Conv./%	Yield/%
1	 **1a**	57	 **3a**	53	96
2	 **1b**	11	 **3b**	87	95
3	 **1c**	17	 **3c**	100	92
4	 **1d**	3.5	 **3d**	100	97
5	 **1e**	17	*cis/trans*-**1e**	0	--

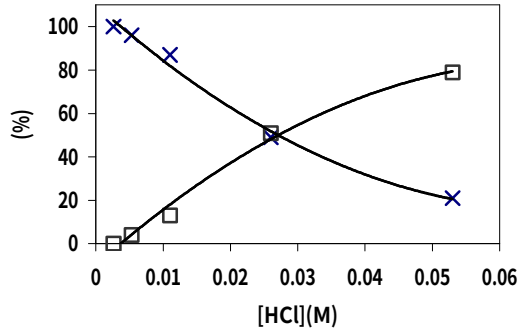
Since compound **1d** is the most sensitive to changes in concentration of hydrochloric acid, the photolysis was carried out in six different acid concentrations (Table 3). In intermediate acid concentration, both products **2d** and **3d** were observed. At low acid concentration, **3d** was the major product. As the acid concentration was increased to 0.026 M, **2d** and **3d** were of equal yields. At 0.11 M the only product observed became **2d**. A plot of product yields of **2d** and **3d** against the changing hydrochloric acid concentrations in acetonitrile was obtained (Figure 1).

Table 3. The Yields of Competing Pathways for **1d**.



react	HCl (M)	*t* (hr)	Convn %	Yield, % **2d**	**3d**
1d[a]	(0)	3.5	--[e]	0	0
1d[a]	(0.0026)	3.5	100	0	100
1d[a]	(0.0053)	3.5	100	4	96
1d[a]	(0.011)	3.5	100	13	87
1d[a]	(0.026)	3.5	100	51	49
1d[a]	(0.053)	3.5	100	79	21
1d[a]	(0.11)	3.5	100	100	0

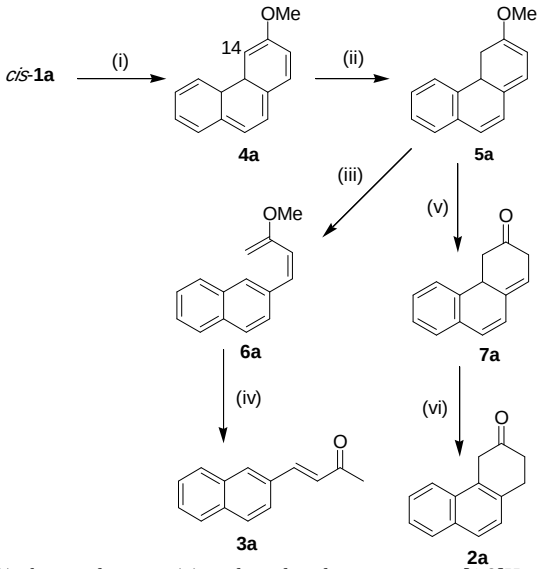
Figure 1. The Yields of Competing Pathways for **1d**.



Discussion

In order to explain the product dependence on, and a remarkable tuning process by acid concentration, a reasonable reaction mechanism is proposed with competing processes (Scheme 3). The reaction starts

Scheme 3. Mechanism of Photorearrangements.



(i) photocyclization; (ii) acid-catalyzed rearrangement [1,9]H shift; (iii) ring-opening; (iv) hydrolysis; (v) hydrolysis; (vi) acid-catalyzed rearrangement [1,3]H shift.

from irradiating *p*-methoxy-*trans*-stilbene **1a** to isomerize to *cis*-**1a**. The ensuring well-known 6e-conrotatory electrocyclization reaction yields the dihydrophenanthrene intermediate **4a**. This is followed by an acid-catalyzed reaction that is equivalent to [1,9] hydrogen shift to intermediate **5a**, possibly by protonation at the carbon 14 of **4a** since PM3 calculation indicated that carbon 14 of **4a** bears a partial negative charge of c.a. –0.42[8]. For the intermediate **5a**, two competing reaction paths are possible. One is a six-electron ring-opening reaction to form product **3a**; the other is an acid-catalyzed hydrolysis of methyl cyclohexadienyl ether to produce product **2a**. Because the rate of hydrolysis increases as the concentration of acid is increased, it is reasonable that the rates of these two reactions become competitive when the acid is in the range from 0.0025 M to 0.5 M. Approximately, the rate constant of hydrolysis (k_h) is forty times larger than that of

ring-opening (k_o) at the acid concentration of 0.026M. Because the k_h value would increase with increasing acid concentration, the smaller k_h in the low acid concentration and the higher k_h in the high acid concentration will result in the high selectivity between product **2a** and **3a**. The acid catalyzed [1,9] hydrogen shift step is an essential process which is shown by the fact that compound **1e** with a methyl substituent at the 3-position of the thiophene ring prevent the [1,9] hydrogen shift thus stop the photoreaction completely and the only photoreaction is *trans-cis* isomerization of **1e**.

In conclusion, we have demonstrated an interesting photochemical system that is sensitive to the acid concentration. Different reaction products can be obtained quantitatively by simply adjusting the acid concentration. Competiting ring opening and hydrolysis processes are believed to be the reason for the highly selective process. Since the hydrolysis process is sensitive to the acid concentration, compounds **1a**-**1d** become unique examples of photochemical sensors sensitive torward acid concentrations. It also should be mentioned that the results described here is equivalent to trapping of an reaction intermediate (**5a**) by acid, a situation analogues to the recent interesting report on a hindered ester.[7]

References

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(9) 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). 13C NMR (75 MHz, CDCl3) 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.

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(11) Spectral data for compound **3a**: ^{1}H NMR (300MHz, CDCl3): δ 7.94 (s, 1H), 7.87-7.82 (m, 3H), 7.67 (d, J = 16.2 Hz, 1H), 7.67 (dd, J = 8.8,1.5 Hz, 1H), 7.54-7.48 (m, 2H), 6.83 (d, J = 16.2Hz, 1H), 2.42 (s, 3H). ^{13}C NMR (75MHz, CDCl3): δ 198.31, 143.45, 134.29, 133.24, 131.88, 130.27, 128.74, 128.51, 127.76, 127.33, 127.21, 126.74, 123.45, 27.55.

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