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Proton-Assisted Switching of Reaction Pathways of Stilbene Analogues Brought by Direct Irradiation

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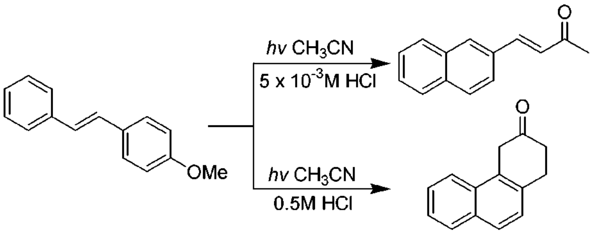
ABSTRACT



Photochemical reaction pathways during direct irradiation of stilbene analogues (1a–1d) can be switched completely by adjusting the concentration of hydrochloric acids. Competitive ring opening and acid-catalyzed hydrolysis processes are responsible for this novel selectivity.

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] The research on the external effects of an acid on the pathways of a photochemical reaction has always been an important topic.[6−9] The presence of an external acid can even switch the eventual product of mesityl cyclohexanecarboxylate from that of decarboxylation to transesterification completely.[8]

We have recently shown an interesting photorearrangement 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 in such a reaction. Their electron-donating characteristics through resonance interactions increased the basicity of the remote carbon to initiate an apparent [1,9]H shift.

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 the perfect control of the nature of the final product

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in such photochemical reactions by adjusting the concentration of the protic acid.

In the absence of external hydrochloric acid, the only photochemical reaction for *p*-methoxy-*trans*-stilbene **1a** is *trans*−*cis* isomerization when a 5 × 10^{-3} M degassed acetonitrile solution of **1a** was irradiated for 43 h using a Rayonet apparatus at 350 nm. When less than 5 × 10^{-3} M hydrochloric acid was added to the photolysis solution, the only isolated product became 4-naphth-2-yl-3-buten-2-one **2a** in 96% yield.[10] As the concentration of hydrochloric acid was increased to 0.5 M, an entirely different photoproduct was obtained: 1,2,4-trihydrophenathren-3-one **3a** was isolated as the sole product in 96% yield. In a separate experiment, it was shown that **2a** was stable upon prolong standing under the high acid concentration.

Thus, **1a** represents a unique class of examples in which the complete course of a photochemical reaction is sensitive to the external acid concentrations in acetonitrile (Scheme 1). Different structural photoproducts are produced simply by adjusting the acid concentration during UV irradiation. The group of acid concentration sensitive compounds includes 2-(4′-methoxystyryl)naphthalene **1b**, 2-(4′-methoxystyryl)thiophene **1c**, and 2-(4′-methoxystyryl)furan **1d** (Table 1).

Scheme 1. Photorearrangement of Stilbenes in Different Acid Concentrations

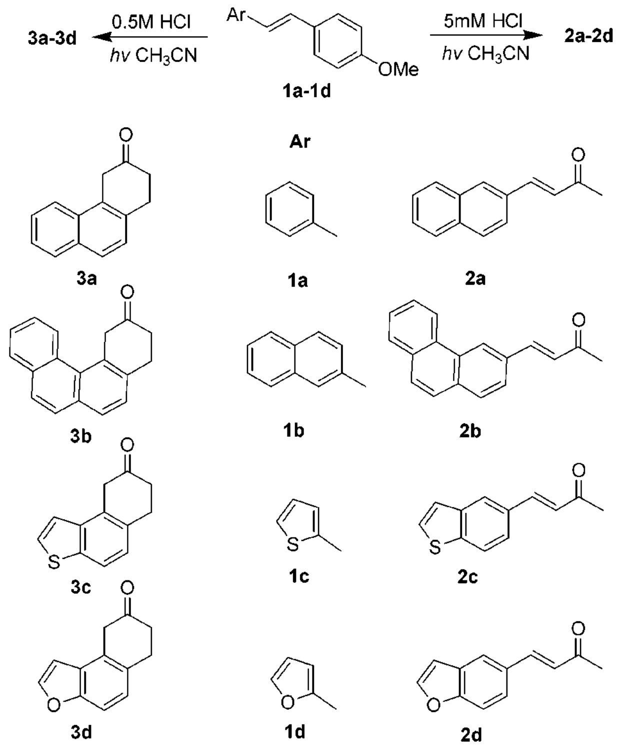

Table 1. Conversions and Yields for Irradiations of 5 × 10^{-3} M *p*-Methoxy-*trans*-stilbene **1a** and Analogues **1b**−**1d** in Acetonitrile in the Presence of Hydrochloric Acid

reactant	HCl (M)	*t* (h)	convn, %	yield, % **2**	yield, % **3**
1a	(0)	43	*e*	0	0
1a	(0.0025)	57	53	96	0
1a	(0.5)	43	52	0	96
1b	(0)	50	*f*	0	0
1b	(0.005)[b]	11	87	95[c]	0
1b	(0.5)	69	100	0	90
1c	(0)	16	*e*	0	0
1c	(0.005)	16	100	92[d]	0
1c	(0.5)	17	100	0	95
1d	(0.0025)	3.5	100	97	0
1d	(0.5)	3.5	100	0	98
1d[a]	(0)	3.5	*e*	0	0
1d[a]	(0.0026)	3.5	100	100	0
1d[a]	(0.0053)	3.5	100	96	4
1d[a]	(0.011)	3.5	100	87	13
1d[a]	(0.026)	3.5	100	49	51
1d[a]	(0.053)	3.5	100	21	79
1d[a]	(0.11)	3.5	100	0	100

[a] The yields of products **2** and **3** are determined from their ratios in the NMR spectra. [b] Irradiated with a Rayonet apparatus at 300 nm. [c] The ratio of (*trans*-**2b**:*cis*-**2b**) is ca. 9:1. [d] The ratio of (*trans*-**2c**:*cis*-**2c**) is ca. 3:1. [e] Only *cis*−*trans* isomerization occurred. [f] Oxidative photocyclization occurred partly.

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

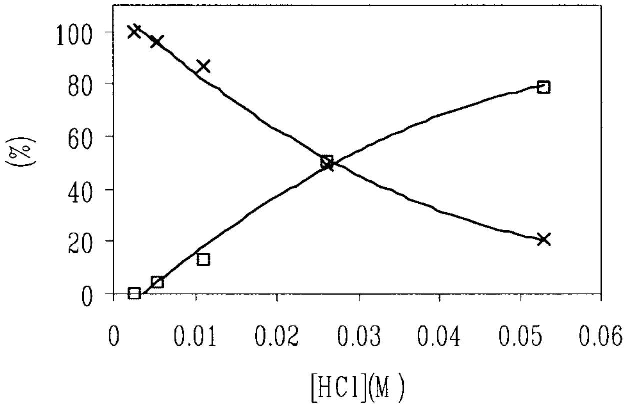

Figure 1. Plot of product yields of **2d** and **3d** with changing hydrochloric acid concentrations in acetonitrile.

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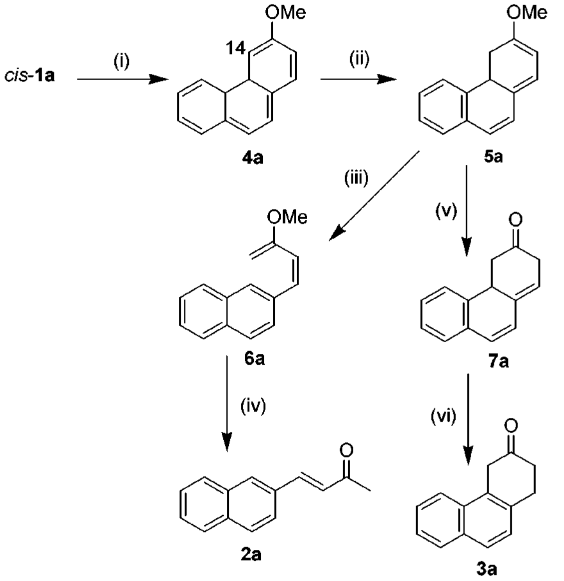
(10) After photolysis, the acid was removed by neutralization and the solvent was evaporated to dryness. The NMR spectrum indicates there is only one product. If necessary, the product can be chromatographed (silica gel and ethyl acetate/*n*-hexane = 1/10 as eluent) to obtain the pure product.

able reaction mechanism is proposed with competing processes (Scheme 2).

Scheme 2. Mechanism of the Acid-Controlled Photorearrangement of Stilbenes[a]



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

The reaction starts with irradiation of *p*-methoxy-*trans*-stilbene **1a** which isomerizes to *cis*-**1a**. The well-known 6e-conrotatory electrocyclization reaction yields the dihydrophenanthrene intermediate **4a**. This is followed by an acid-catalyzed reaction that is equivalent to a [1,9] hydrogen shift to intermediate **5a**, possibly by protonation at carbon 14 of **4a** since PM3 calculation indicated that carbon 14 of **4a** bears a partial negative charge of ca. −0.42.[11] For the intermediate **5a**, two competing reaction paths are possible. One is a six-electron ring-opening reaction to form product **2a**; the other is an acid-catalyzed hydrolysis of methyl cyclohexadienyl ether to produce product **3a**. Because the rate of hydrolysis increases as the concentration of acid is increased, it is inferred from the comparable product yields (**2a**, **3a**) that the rates of these two reactions become competitive when the acid is in the range 0.0025 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 0.026 M. Because the k_h value increases with increasing acid concentration, the smaller k_h in the low acid concentration and the higher k_h in the high acid concentration result in the high selectivity between product **2a** and **3a**.

In conclusion, we have demonstrated an interesting photochemical system that is sensitive to the acid concentration in acetonitrile. Different reaction products can be obtained quantitatively by simply adjusting the acid concentration. Competing 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 to acid concentrations. It also should be mentioned that the results described here are equivalent to trapping of a reaction intermediate (**5a**) by acid, a situation analogous to the recent interesting report on a hindered ester.[8]

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Supporting Information Available: ^{1}H and ^{13}C NMR spectral data of products **2a**−**2d** and **3a**−**3d**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[11] We have since concluded from an isotope labeling experiment of 2-(4′-methylstyryl)furan that the [1,9]-shift in these photoreactions involves a stepwise photoaddition−elimination process.