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Substituent dependent photochemical rearrangements of halostyrylheterocycles in acid media☆

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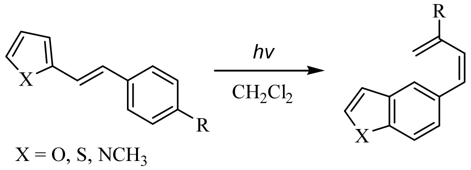
Dedicated to Professor F. D. Lewis on his 60th birthday

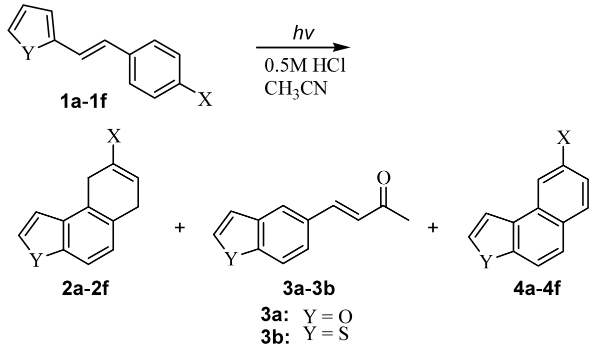
Abstract—New photorearrangement product **2** and hydrolysis product **3** are obtained by irradiating acidic halostyrylheterocycles **1a**–**f**. The competing formal [1,3]hydrogen shift and ring opening of dihydrophenanthrene intermediate is responsible for the product formation. The halogen substituent effect on the product distribution has been studied. Photolysis of **5** can reversibly be converted to **2**. Similar photoreactivity for the styrylfuran and styrylthiophene systems is observed. © 2003 Elsevier Science Ltd. All rights reserved.

Stilbenes are unique in terms of their diverse photoreactivity.[1–7] Their reactions include *cis–trans* photoisomerization,[8,9] oxidative[10–12] and eliminative[13,14] photocyclization, photocycloaddition with various alkenes,[15] photoaddition with amines[16–18] and photorearrangement using primary amines.[8,19,20] Styrylheterocycles are also reactive[21–23] photochemically and a photorearrangement has been reported (Eq. (1)).[24,25] It is known that photochemical reactivity is greatly influenced by environment.[26–33] The photorearrangement of stilbenes can be changed completely by acid-catalyzed hydrolysis of the reactive intermediates.[34,35] The competition between the two reaction pathways can be controlled by adjusting the concentration of hydrochloric acid. In this work, we report the substituent dependent photochemical reaction of 4′-halostyrylfurans **1a**–**c** and 4′-halostyrylthiophenes **1d**–**f**.



(1)

An N_2-deoxygenated acetonitrile solution containing 5×10^{-3} M 4′-fluorostyrylfuran **1a** and 0.5 M hydrochloric acid was irradiated with a Rayonet apparatus at 350 nm for 3.5 h. After the acid was neutralized and the solvent was evaporated, two products, 8-fluoro-6,9-dihydronaphtho[2,1-*b*]furan **2a** (17% yield) and (*E*)-4-(oxainden-5-yl)but-3-en-2-one **3** (83% yield) were isolated. The new compound **2a**[36] shows ^{1}H NMR at δ 3.64–3.57 (m; Ar-C$\underline{H}_2$-CH=CF), 3.73–3.68 (m; Ar-C$\underline{H}_2$-CF) and 5.48 (dm, $J_{H-F} = 16.9$ Hz; Ar-CH$_2$-C$\underline{H}$=CF), and shows ^{13}C NMR at δ 156.4 (d, $J^1_{C-F} = 248.9$ Hz, –F) similar to the spectral data reported for 1,4-dihydrophenanthrenes.[20] The photoreactions of the other 4′-halostyrylheterocycles **1b**–**f** were also studied (Scheme 1), phenanthrene type products **4** being formed



a: Y=O, X=F; **b**: Y=O, X=Cl; **c**: Y=O, X=Br; **d**: Y=S, X=F;
e: Y=S, X=Cl; **f**: Y=S, X=Br

Scheme 1.

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in addition to products of type **2** and **3**. The conversions and yields of the photoreactions are listed in Table 1.

When the irradiation time is shortened, the intermediates **5a**–**c** could be isolated and were stable in neutral solution (Scheme 2). Some intermediates (*cis*-**5a** and *trans*-**5b**) have been reported[24] as stable products in neutral conditions (Eq. (1)). The product distribution and yields for shorter irradiation time are listed in Table 2. The product distribution for the photoreaction of **1a** is similar to that in Table 1. For the photolysis of **1b** at short times (Table 2), the yields of **4b** and **5b** are 0 and 30%, respectively. Product **5b** can be converted into **3a** and **4b** if the irradiation time is increased. For the photoreaction of **1c**, prolonged photolysis converts **5c** exclusively to **2c** and **3a**. Thus, the reaction pathway is dependent upon the halogen substituent. Based on these results, the mechanism shown in Scheme 3 is proposed to explain the formation of products.

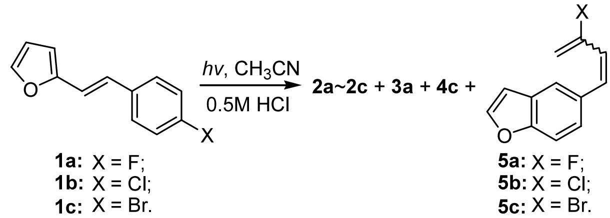
The mechanism involves the irradiation of the *trans*-4′-halostyrylheterocycles to produce *cis*-**1**, then the dihydrophenanthrene intermediate **6** is formed via photocyclization. An acid-catalyzed formal [1,9] hydrogen shift from carbon 9b to 9 of intermediate **6** produces intermediate **7**. In accord with this proposal, PM3 calculations indicate that carbon 9 of **6** possess a partial negative charge. For the intermediate **7**, there are two competing reaction pathways. One is the acid-catalyzed formal [1,3] hydrogen shift that can occur to give compound **2**. The other is the ring-opening reaction to produce **5**. After hydrolysis of haloalkenyl group of **5**, the reaction leads to the formation of product **3**. The acid-catalyzed [1,9] hydrogen shift is a 10 electrons process it is probably a thermal process. The [1,3] hydrogen shift is four electron process and could be a photochemical allowed. Detailed experimental supported is further needed.

Even with the presence of a heavy bromine element in compound **1b**, the reaction is still a singlet state reaction. It is not sensitized by triplet sensitizer and the reaction is not quenched by suitable triplet quencher (e.g. piperylene). The dihydrophenanthrene intermediate **6** of *p*-bromostilbene is reported to come directly from the singlet *cis*-stilbene by Saltiel.[37] This is inconsistent with our system that the reaction is in the singlet manifold.

Irradiation of 8-chloro-6,9-dihydronaphtho[2,1-*b*]furan **2b** in 0.5 M hydrochloric acid/acetonitrile solution shows no photoreaction. Thus, the formation of oxidative photocyclization products **4** may come directly from the redox reaction of the intermediate **6** and hydrochloric acid. This result is similar to the photoreaction of the stilbene and hydrochloride in dichloromethane.[38] Because the formation of cyclized products will compete with the acid-catalyzed formal [1,9] hydrogen shift, the yields of photocyclization products increased as the rate of hydrogen shift decreased. For the fluoro substituent, the carbon 9 of intermediate **6** bears higher partial negative charge (−0.30) than chloro (−0.16) and bromo (0.04) substituents. The reaction rate of [1,9] hydrogen shift for

Table 1. Conversions and yields for photoreactions of **1a**–**f** in the presence of 0.5 M hydrochloric acid

Reactants	*hν* time (h)	Conversion	Yields (%)		
			2	**3**	**4**
1a	3.5	92	17	83	0
1b	18	100	55	25	19
1c	24	100	49	11	40
1d	21	78	12	75	13
1e	48	87	56	14	24
1f	48	90	36	11	54

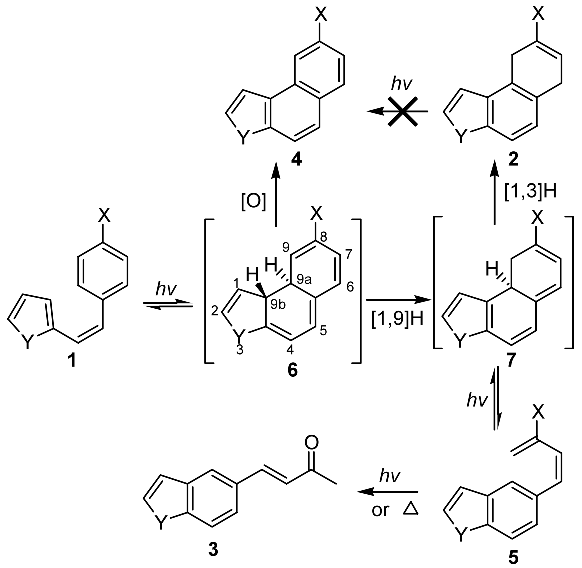


Scheme 2.

Table 2. Conversions and yields for photoreactions of **1a**–**c** in the presence of 0.5 M hydrochloric acid during shorter irradiation time

Reactants	*hν* time (h)	Conv.	Yields (%)			
			2	**3**	**4**	**5**
1a	1	77	14	79	0	<5
1b	3.5	61	53	14	0	30[a]
1c	3.5	92	34	7	42	17

[a] The product is *cis*/*trans* (4/1) mixture.



Scheme 3.

1a might be faster that the oxidative photocyclization reaction can not compete with it, so there is no cyclized product **4** in this case.

The product distributions between products **2** and **3** are also dependent on the substituents. Because the ring-opening step is photoreversible,[39] the formation rate of (*E*)-4-arylbut-3-en-2-one **3** will be effected by the acid-catalyzed hydrolysis of haloalkenyl group of **5**. For further illustration, intermediate *cis*-**5b** was isolated and irradiated in different acid concentrations. Photolysis of *cis*-**5b** with 0.5 M hydrochloric acid give both products **2b** and **3**, but it only gives product **2b** in 0.005 M hydrochloric acid with the same irradiation period. Compared to the reported case of 2-halopropenes,[40] the hydrolysis rate for 2-fluoropropene is 860 times greater than that of 2-bromopropene. Since the hydrolysis rate is accelerated by the fluorine atom, intermediate **5a** must be hydrated rapidly to product **3a**. Thus the yield of product **3a** from irradiation of **1a** is higher than that of the other cases (**1b** and **1c**). The conversion of **5** to **3** can either be photochemical or thermal depending on the halogen substituents.

In summary, we have demonstrated that new rearrangement is possible for the halogen substituted styrylheterocycles when photolysis is carried out in the presence of a protic acid. Due to the competing formal [1,3] hydrogen shift and ring opening of dihydrophenanthrene intermediate **7**, a new product **2** and a new hydrolysis product **3** are observed. The product ratio is dependent on the halogen substituents. It is also shown that photolysis of **5** can reversibly be transferred back to **2**. Halogen substituent effects indicate that yields of products **4** increase while products **3** decrease from fluorine to bromine. The bromine derivative **1c** gives highest yield for product **4**. Finally, it is interesting to note that similar behavior between the styrylthiophenes and styryfurans is observed in terms of their photoresponse both to the acids and to the halogen substituent effects.

Supplementary material

The following supplementary material is available online: ^{1}H and ^{13}C NMR spectral data of products **2a**–**f**, **3a**–**b** and **5a**–**c**.

Acknowledgements

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