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Solvent-Dependent Photochemical Rearrangements of Ethers of Styrylheterocycles

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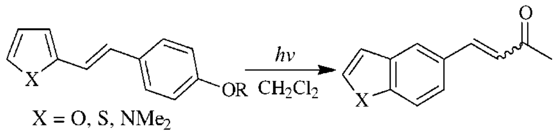
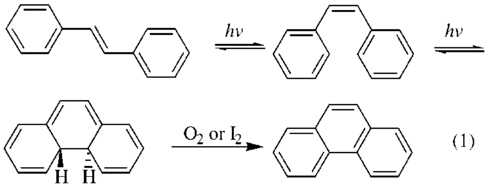
ABSTRACT



Direct photolysis of *p*-RO(R = alkyl or aryl)-2-styrylfurans (1a–f), 2-styrylthiophenes (2a–f), and 2-styryl-*N*-methylpyrrole (3) in hydrated dichloromethane gives 5-(3-oxo-1-butenyl)benzo[*b*]furan (4), -thiophene (5), and *N*-methylpyrrole (6), respectively, in good isolated yields. However, photolysis of 1a,b,e and 2a,b,e in dehydrated benzene gives 5-(3-RO-1,3-butadienyl)benzo[*b*]furans (7a,b,e) and -thiophenes (8a,b,e) in good yields. Photolysis of 7 and 8 in hydrated dichloromethane produces 4 and 5, respectively.

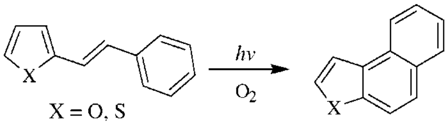
Rearrangement is one of the most important topics in photochemical reactions. It is especially important for reactions involving a complicated skeletal change that can provide abundant information for mechanistic considerations.[1] Solvent-dependent photochemical reactions have recently become a topic of interest.[2−4]

Stilbene and its derivatives are photochemically active.[5,6] Under oxidative conditions, phenanthrene can be a major product through isomerization and oxidative photocyclization (eq 1).[7]



(1)

Styrylthiophene[8] and styrylfuran[9] can also be transformed photochemically into the corresponding heterocycles through oxidative cyclization (eq 2). Using the Wittig reaction,[10] we



(2)

have prepared *p*-RO(R = alkyl or aryl)-2-styrylfurans (**1a−f**),[11] 2-styrylthiophenes (**2a−f**),[12] and 2-styryl-*N*-methylpyrrole (**3**)[13] (Scheme 1) and report here novel solvent-

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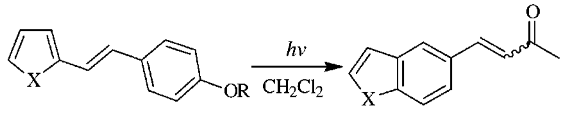
10.1021/ol990828u CCC: $18.00

Scheme 1. Photochemical Rearrangements in CH_2Cl_2



1 - 3 **4 - 6**

1a (X = O, R = Me), **2a** (X = S, R = Me), **3** (X = NMe, R = Me),
1b (X = O, R = Et), **2b** (X =S, R = Et), **4** (X = O),
1c (X = O, R = ^{n}Bu), **2c** (X = S, R= ^{n}Bu), **5** (X = S),
1d (X = O, R = Ph), **2d** (X = S, R = Ph), **6** (X = NMe),
1e (X = O, R = PhMe), **2e** (X = S, R = PhMe),
1f (X = O, R = Me (5-Me)), **2f** (X = S, R = 1-naphthyl).

dependent photochemical rearrangements for this series of styrylheterocycles.

Irradiation of a 1 × 10^{-2} M undehydrated solution (CH_2Cl_2) of *p*-methoxystyrylfuran (**1a**) with a Rayonet reactor (350 nm) for 3 h gave 5-(3-oxo-1-butenyl)benzo[*b*]furan (**4**)[14] as the sole isolated product in 94% yield. The infrared spectrum indicated strong absorption at 1662 and 1635 cm^{-1} for the conjugated carbonyl functional group (^{1}H NMR ($CDCl_3$) δ 7.59 (d, $J = 16.1$ Hz, 1H), 6.69 (d, $J = 16.1$ Hz, 1H), 2.36 (s, 3H); ^{13}C NMR δ 198.1) are consistent with this structure. The products consist of two isomers. The major *E* isomer can be isolated in large quantity. Similarly, irradiation of other ether derivatives (**1b**−**f**) in dichloromethane solution gave the corresponding benzo[*b*]furan (**4**) in high yields, and again the major products were the *E* isomers (Table 1). Irradiation of the starting material (**1a**−**f**) in dehydrated dichloromethane resulted in decreased yields of **4**.

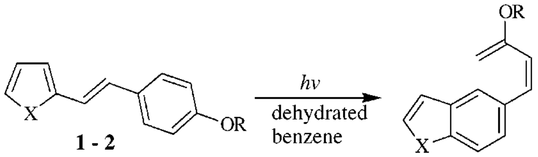
Table 1. Chemical Yields for the Photochemical Reactions of **1a**−**f**, **2a**−**f**, and **3** at 350 nm in Undehydrated Dichloromethane Solvent

reactions	irrad times (h)	products	conversions (%)	yields (%)	*E*/*Z* ratio
1a	3	**4**	97	94	93/7
1b	3	**4**	97	96	100/0
1c	3	**4**	95	95	94/6
1d	3	**4**	80	93	100/0
1e	3	**4**	75	89	100/0
1f	4	**4**	97	90	93/7
2a	10	**5**	98	88	93/7
2b	10	**5**	91	90	88/12
2c	10	**5**	89	93	94/6
2d	10	**5**	98	98	97/3
2e	10	**5**	93	90	87/13
2f	10	**5**	97	96	96/4
3	20	**6**	51	75	100/0

This novel photochemical rearrangement can also be applied to styrylthiophenes (**2a**−**f**)[15] and styryl-*N*-methylpyrrole (**3**)[16] (Scheme 1). The yields are also good for the styrylthiophenes; however, more time is needed for photolysis (10 and 20 h for styrylthiophenes and styrylpyrrole, respectively).

In dehydrated benzene (or toluene), however, upon irradiation of a 1 × 10^{-2} M *p*-ethoxystyrylthiophene (**2b**), the isolated compound shows ^{1}H NMR peaks at δ 7.39 (d, $J = 15.8$ Hz, 1H), 6.62 (d, $J = 15.8$ Hz, 1H), 4.28 (d, $J = 1.3$ Hz, 1H), and 4.18 (d, $J = 1.3$ Hz, 1H). On the basis of these results, the isolated product is considered to be 5-(3-ethoxy-1,3-butadienyl)benzo[*b*]thiophene (**8b**) (Scheme 2). Similarly, upon irradiation of **1a**,**b**,**e**,**f** and **2a**,**e** in dehydrated benzene, the photochemical products are the corresponding *Z*- and *E*-dienol ethers.[17] The yields are also good, and a mixture of *E*- and *Z*-isomers is usually obtained. It is difficult to

Scheme 2. Photochemical Rearrangements in Dehydrated Benzene



1 - 2 **7 - 8**

1a (X = O, R = Me),
1b (X = O, R = Et),
1e (X = O, R = PhMe),
1f (X = O, R = Me (5-Me)),
2a (X = S, R = Me),
2b (X = S, R = Et),
2e (X = S, R = PhMe).

7a (X = O, R = Me),
7b (X = O, R = Et),
7e (X = O, R = PhMe),
7f (X = O, R = Me (2-Me)),
8a (X = S, R = Me),
8b (X = S, R = Et),
8e (X = S, R = PhMe).

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(11) Spectral data for compound **1a**: mp 73.5−74 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.36−7.41 (m, 3H), 6.99 (d, $J = 16.3$ Hz, 1H), 6.86 (d, $J = 8.8$ Hz, 2H), 6.75 (d, $J = 16.3$ Hz, 1H), 6.39 (dd, $J = 1.9$, 3.3 Hz, 1H), 6.28 (d, $J = 3.3$ Hz, 1H), 3.79 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) 159.3, 153.5, 141.7, 129.8, 127.5, 126.8, 114.6, 114.1, 111.5, 107.6, 55.3; MS (70 eV, EI) 186 (M^+, 69), 185 (42), 171 (100), 143 (43), 115 (45).

(12) **2a**: mp 134−135 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.40 (d, $J = 8.8$ Hz, 2H), 7.15 (d, $J = 5.4$ Hz, 1H), 7.10 (d, $J = 16.1$ Hz, 1H), 6.96−7.06 (m, 2H), 6.90 (d, $J = 8.8$ Hz, 2H), 6.88 (d, $J = 16.1$ Hz, 1H), 3.81 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 159.2, 143.2, 129.7, 128.0, 127.5, 127.4, 125.3, 123.7, 119.7, 114.1, 55.2; MS (70 eV, EI) 216 (M^+, 100), 201 (36), 171 (22), 129 (32), 115 (42).

(13) **3a**: ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.38 (d, $J = 8.7$ Hz, 2H), 6.87 (d, $J = 8.7$ Hz, 2H), 6.82 (s, 2H), 6.61 (dd, $J = 1.9$, 4.3 Hz, 1H), 6.43 (dd, $J = 1.7$, 3.7 Hz, 1H), 6.13 (dd, $J = 2.7$, 3.7 Hz, 1H), 3.81 (s, 3H), 3.67 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 130.1, 127.1, 126.9, 125.8, 123.1, 115.2, 114.1, 113.4, 108.1, 106.0, 55.3, 34.1; MS (70 eV, EI) 213 (M^+, 9), 185 (38), 126 (100), 95 (48), 83 (72).

(14) 4-Oxainden-5-yl-but-3-en-2-one (**4**): mp 74−75 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.76 (s, 1H), 7.65 (d, $J = 2.2$ Hz, 1H), 7.62 (d, $J = 16.1$ Hz, 1H), 7.50 (d, $J = 0.8$ Hz, 2H), 6.78 (d, $J = 2.2$ Hz, 1H), 6.72 (d, $J = 16.1$ Hz, 1H), 2.36 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.1, 156.1, 146.0, 143.8, 129.4, 128.0, 126.0, 124.3, 121.8, 111.9, 106.7, 27.4; MS (70 eV, EI) 186 (M^+, 87), 171 (100), 143 (44), 115 (64); HR-MS calcd for $C_{12}H_{10}O_2$ 186.0681, found 186.0683.

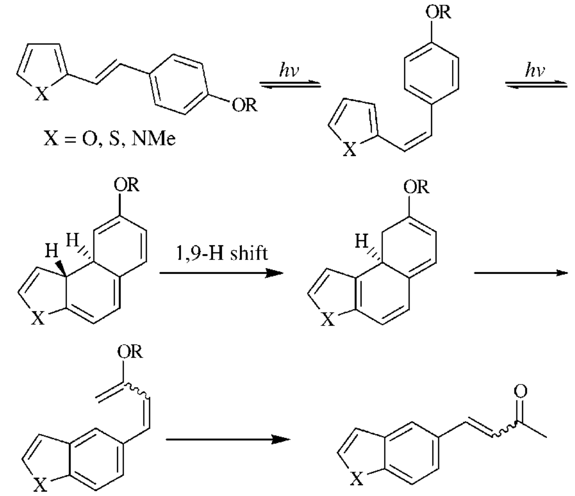
Table 2. Chemical Yields for Photochemical Reactions of **1a**,**b**,**e** and **2a**,**b**,**e** at 350 nm in Dehydrated Benzene

reactions	irrad times (h)	products	conversions (%)	yields (%)	*E*/*Z* ratio
1a	16	**7a**	90	87	54/46
1b	20	**7b**	68	82	80/20
1e	20	**7e**	58	74	68/32
2a	36	**8a**	68	72	68/32
2b	36	**8b**	78	77	92/8
2e	48	**8e**	58	64	61/39

isolate the pure isomers. In some cases, we did isolate the pure *Z*-form (Table 2). Further irradiation of the isolated pure *Z*-isomer or a *Z*,*E*-mixture of **7** or **8** in hydrated dichloromethane leads to the isolation of **4** or **5,** respectively. Thus, it is clear that the dienol ether compounds (**7**, **8**) are precursors of the 3-oxo-1-butenyl compounds (**4**, **5**). The decreased yields for **4** and **5** when **7** and **8** are photolyzed in hydrated benzene solution indicates that photochemical hydration is less efficient in hydrated benzene. No dienol ethers (**7**, **8**) are obtained upon photolysis of a dehydrated dichloromethane solution containing the starting material (**1**, **2**).

The mechanism for this novel photochemical rearrangement involves a photochemical conrotatory cyclization, a novel 1,9-hydrogen shift, lateral ring opening,[18] and finally photochemical conversion of the dienol ether to the conjugated ketone (Scheme 3).

Scheme 3. Mechanism of Photochemical Rearrangements



In conclusion, a novel solvent-dependent photochemical rearrangement reaction is reported for the alkoxy or aryloxy ethers of styrylfuran, styrylthiophene, and styrylpyrrole. The reaction yields are high, and the product is clean. These constitute novel synthetic routes for the transformation of styrylheterocycles to benzo[*b*]heterocycles with a substituent that contains a dienyl ether or conjugated ketone functionality, which can be controlled by choosing a suitable solvent. The reaction mechanism of this novel rearrangement includes photochemical cyclization, 1,9-hydrogen shift, ring opening, and photochemical transformation of dienol ether to conjugated ketone. The final step is very sensitive to the solvent and can occur efficiently in hydrated dichloromethane medium; if the solvent is less-polar dehydrated benzene, the hydration reaction dose not occur.

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(15) 4-Benzo[*b*]thiophen-5-ylbut-3-en-2-one (**5**): mp 101−102 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.94 (d, $J = 1.6$ Hz, 1H), 7.86 (d, $J = 8.4$ Hz, 1H), 7.62 (d, $J = 16.2$ Hz, 1H), 7.52 (dd, $J = 1.6, 8.4$ Hz, 1H), 7.47 (d, $J = 5.5$ Hz, 1H), 7.34 (dd, $J = 0.6, 5.5$ Hz, 1H), 6.77 (d, $J = 16.2$ Hz, 1H), 2.39 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 198.1, 143.6, 141.7, 139.9, 130.7, 127.6, 126.6, 124.3, 124.0, 123.1, 122.9, 27.5; MS (70 eV, EI) 202 (M^+, 100), 187 (88), 159 (27), 115 (51); HR-MS calcd for $C_{12}H_{10}OS$ 202.0452, found 202.0451.

(16) 4-(1-Methylindol-5-yl)but-3-en-2-one (**6**): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78 (s, 1H), 7.65 (d, $J = 16.2$ Hz, 1H), 7.45 (d, $J = 8.7$ Hz, 1H), 7.29 (d, $J = 8.7$ Hz, 1H), 7.05 (d, $J = 3.0$ Hz, 1H), 6.70 (dd, $J = 16.2$ Hz, 1H), 6.57 (d, $J = 3.0$ Hz, 1H), 3.77 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 198.5, 145.6, 137.9, 130.0, 128.7, 125.8, 124.4, 122.8, 121.1, 109.8, 102.0, 32.9, 27.4; MS (70 eV, EI) 199 (M^+, 86), 184 (100), 156 (26), 141 (19); HR-MS calcd for $C_{13}H_{13}ON$ 199.0997, found 199.1004.

(17) 3-Methoxy-1-oxaiden-5-yl-1,3-butadiene (*Z*-**7a**): ^{1}H NMR (300 MHz, C_6D_6) δ 7.55 (s, 1H), 7.25 (d, $J = 8.6$ Hz, 1H), 7.17 (dd, $J = 1.3, 8.6$ Hz, 1H), 7.11 (d, $J = 2.1$ Hz, 1H), 6.45 (d, $J = 12.5$ Hz, 1H), 6.28 (d, $J = 2.1$ Hz, 1H), 6.00 (d, $J = 12.5$ Hz, 1H), 4.24 (d, $J = 2.0$ Hz, 2H), 3.10 (s, 3H). *E*-**7a**: ^{1}H NMR (300 MHz, C_6D_6) δ 7.41 (s, 1H), 7.34 (d, $J = 15.9$ Hz, 1H), 7.30 (s, 2H), 7.10 (d, $J = 2.1$ Hz, 1H), 6.56 (d, $J = 15.9$ Hz, 1H), 6.32 (d, $J = 2.1$ Hz, 1H), 4.14 (d, $J = 1.7$ Hz, 1H), 4.05 (d, $J = 1.7$ Hz, 1H), 3.34 (s, 3H). 3-Ethoxy-1-oxaiden-5-yl-1,3-butadiene (*Z*-**7b**): ^{1}H NMR (300 MHz, C_6D_6) δ 7.58 (s, 1H), 7.30 (s, 2H), 7.11 (d, $J = 2.2$ Hz, 1H), 6.46 (d, $J = 12.5$ Hz, 1H), 6.32 (d, $J = 2.2$ Hz, 1H), 6.00 (d, $J = 12.5$ Hz, 1H), 4.25 (d, $J = 1.4$ Hz, 1H), 4.08 (d, $J = 1.2$ Hz, 1H), 3.37 (q, $J = 7.1$ Hz, 2H), 0.83 (t, $J = 7.1$ Hz, 3H). 3-Ethoxy-1-benzo[*b*]thiophen-5-yl-1,3-butadiene (*Z*-**8b**): ^{1}H NMR (200 MHz, C_6D_6) δ 7.54 (d, $J = 1.1$ Hz, 1H), 7.45 (d, $J = 8.5$ Hz, 1H), 7.37 (d, $J = 15.8$ Hz, 1H), 7.22 (dd, $J = 1.5, 8.5$ Hz, 1H), 6.90 (s, 2H), 6.62 (d, $J = 15.8$ Hz, 1H), 4.28 (d, $J = 1.3$ Hz, 1H), 4.18 (d, $J = 1.3$ Hz, 1H), 3.59 (q, $J = 6.9$ Hz, 2H), 1.17 (t, $J = 6.9$ Hz, 3H); ^{13}C NMR (50 MHz, C_6D_6) δ 159.1, 140.5, 133.7, 130.5, 129.3, 128.3, 126.8, 125.2, 124.2, 123.1, 122.7, 87.4, 62.9, 14.5; MS (70 eV, EI) 230 (M^+, 100), 209 (93), 201 (74), 194 (64), 185 (57), 173 (38); HR-MS calcd for $C_{14}H_{14}OS$ 230.0766, found 230.0764.

(18) We have studied a similar reaction mechanism for the *p*-alkylstyrylfurans. Ho, T.-I.; Wu, J.-Y.; Wang, S.-L. *Angew. Chem., Int. Ed.* **1999**, submitted.