行政院國家科學委員會專題研究計畫成果報告

雜環化合物光化學之研究
Studies on the Photochemistry of Heterocyclic Compounds

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† 八十六年度及以前的一般國科會專題計畫(不含產學合作研究計畫)亦可選擇適用，惟較特殊的計畫如國科會規劃案等，請先洽得國科會各學術處同意。

中文摘要

研究苯乙烯雜環化合物例如苯乙烯呋喃及苯乙烯噻吩之光化學反應，發現一種新的轉位反應，當苯乙烯呋喃之苯的 4 位置上具有烷基、氟基及氯基時，產物為在 5 位置上具有 1,3-二丁烯官能基的苯呋喃化合物，此種新的轉位反應包括了六電子的光環化反應，[1,9]氫移動反應及六個電子的光開環反應，此種新的轉位反應產量高，產物單一，具有合成上之應用價值。

關鍵詞：光轉位反應，苯乙烯雜環化合物，光開環反應，光閉環反應，[1,9]**氫移動。**

Abstract

A novel photochemical rearrangement reaction is reported with styrylthiophenes and styrylfurans with substituent at the 4-position of the phenyl ring. The product isolated is the 5-(3-substitutent-buta- 1,3-dienyl)benzo[b]furan or thiophene. The yields are very high for the alkyl substituents and for the fluoro and chloro substituents yields are less. For strong electron donation or withdrawing substituents the yields are close to zero. The mechanism of novel photochemical rearrangements include six-electron photocyclization of *cis*-stilbene type compound, [1,9] hydrogen shift and six-electron ring opening reaction.

Keywords: photorearrangement reaction, styrylheterocycles, photocyclization, ring opening, [1,9] hydrogen shift

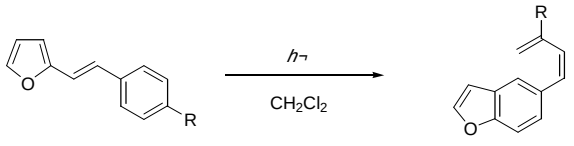
Introduction

The Stiblene and its derivatives are photochemical active[1],[2]. The major reactions include *cis-trans* isomerization, exciplex reactions, additions and oxidative cyclization to phenanthrene. The mechanism for the oxidative cyclization involves a six-electron conrotatory process to form a *trans*-dihydrophenanthrene intermediates[3] Styrylfuran is also known to undergo photochemical isomerization, and in the presence of oxygen of iodine it affords cyclized product.

Results

We have prepared several styrylfurans **1**–**11** with substituents at the *para* position of the benzene ring and would like to report a novel skeletal rearrangement for the styrylfurans (Scheme 1). The starting materials were prepared from 2-furaldehyde and the corresponding benzyl chloride using Wittig reaction, when N_2 degassed *p*-methylstyrylfuran **1** (1×10^{-2} M, in CH_2Cl_2) was irradiated (350 nm) with a Rayonet reactor for 4 hr, the only product isolated is the 5-(3-methylbuta-1,3-dienyl)-benzo[b]furan **12** (96 % isolated yield).[6] The presence of 3-substituted-1,3-buta-dienyl group can be obviously identified by the chemical shift of the compound **12** at 6.53 (doublet, J = 12.2 Hz, –CH=), 6.17 (doublet, J = 12.2 Hz, =CH–) and 5.00 (multiplet, $=CH_2$). The yields for this new type of photochemical rearrangement are summarized in Table 1[7] for the series of styrylfurans. The isolated

yields are pretty good. For most cases, only the *Z* isomer is obtained. Since prolonged photolysis of the *Z* isomer will produce a mixture of *Z* and *E* isomer in which *Z* isomer is still the major product. The *Z* form is the primary photoproduct. The reaction cannot be quenched by *trans*-1,3-pentadiene, a triplet quencher.[8] For both strong electron withdrawing substituents (**9**, **10**) and strong electron donating substituent (**11**), the reaction can not occur in dichloromethane for prolonged photolysis (64 hours). The reaction yield for the fluoro derivative (**18**) is moderate and for the chloro derivative (**19**) is only 52 %.



1 – **11** **12** – **19**

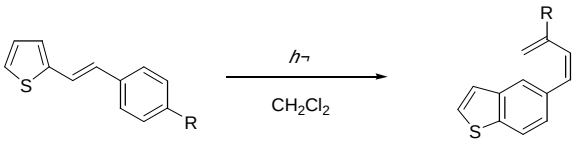
1, **12**, R = CH_3
2, **13**, R = CH_2CH_3
3, **14**, R = $CH(CH_3)_2$
4, **15**, R = $CH_2CH_2CH_3$
5, **16**, R = $C(CH_3)_3$
6, **17**, R = CH_2Ph
7, **18**, R = F
8, **19**, R = Cl
9, R = CN
10, R = NO_2
11, R = $N(CH_3)_2$

Scheme 1. Photochemical rearrangements of styrylfuran derivatives **1–11.**

Table 1: The chemical yields for the photochemical reactions of **1**–**8** at 350 nm in dichloromethane solvent.

Reactants	Times [hr]	Products	Conversions [%]	Yields [%]
1	4	**12**	84	96[b]
2	3	**13**	81	81[a]
3	4	**14**	94	85[a]
4	3	**15**	90	82[a]
5	4	**16**	89	88[c]
6	3	**17**	81	95[d]
7	4	**18**	63	67[a]
8	64	**19**	62	52[e]

[a] Only *Z* form isomer
[b] With *Z*: *E* ratio of 89 : 11
[c] With *Z*: *E* ratio of 84 : 16
[d] With *Z*: *E* ratio of 95 : 5
[e] With *Z*: *E* ratio of 86 : 14



21 – **25** **31** – **35**

21, **31**, R = CH_3
22, **32**, R = CH_2CH_3
23, **33**, R = $CH(CH_3)_2$
24, **34**, R = CH_2Ph
25, **35**, R = F

Scheme 2. Photochemical rearrangements of styrylthiophene derivatives **21–25.**

Table 2: The chemical yields for the photochemical reactions of **21**–**25** at 350 nm in dichloromethane solvent.

Reactants	Times [hr]	Products	Conversions [%]	Yields [%]
21	60	**31**	49	63[a]
22	60	**32**	65	45[b]
23	48	**33**	59	40[a]
24	48	**34**	60	52[c]
25	60	**35**	16	64[a]

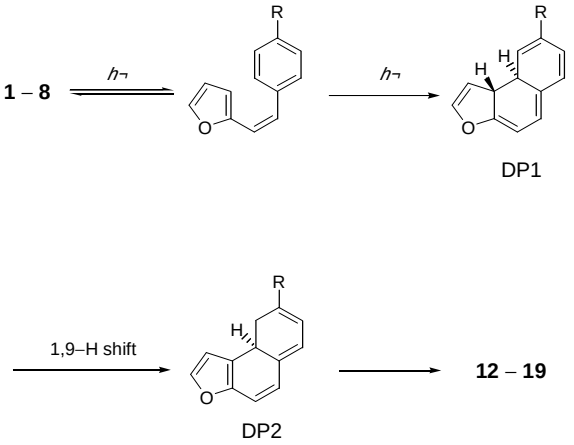
[a] Only *Z* form isomer
[b] With *Z*: *E* ratio of 96 : 4
[c] With *Z*: *E* ratio of 95 : 5

Discussion

A reasonable explanation for this photoreaction is provided in Scheme 3. The reaction starts from the most stable helical conformers of the *cis*-**1**–**8** that absorb the light to cause a conrotatory six–electron phenanthrene type photocyclization reaction to yield the trans fused dihydrophenanthrene type[4] intermediate (DP1). Then it was followed by a 1,9–hydrogen shift to get the dihydrophenanthrene type (DP2) intermediate. Then followed a six–electron electrocyclic ring opening[5], which is initiated by the rearomatization of the benzofuran from DP2 to get the final product **12**–**19**.

In conclusion, this novel and efficient photochemical rearrangement is both mechanistically and synthetically[9] interesting. The mechanism consists of a conrotory photocyclization, a novel 1,9–hydrogen shift and a lateral ring opening. Compare to

the stilbene system, presence of the furan oxygen atom might cause the higher acidity of the hydrogen to initiate the 1,9–hydrogen shift. We believe that this novel rearrangement is initiated by the presence of a hetero atom and there must be other similar reaction we are investigating this possibilities and also hoping to carry out higher level theoretical calculations to obtain deeper insights into this novel reaction.



Scheme 3. Mechanisms for the photochemical rearrangements of styrylfuran **1–8**.

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[6] The photochemical reaction is carried out in the degassed dichloromethane solution in a Pyrex tube using a Rayonet reactor (350 nm) at room temperature. The product **12** was isolated using silica gel column chromatography, no other byproduct was observed in the crude ^{1}H NMR spectra. For **12**: ^{1}H NMR (200MHz, $CDCl_3$, 25 °C, TMS): δ = 7.59 (d, *J* = 2.2 Hz, 1H), 7.52 (d, *J* = 0.8 Hz, 1H), 7.40 (d, *J* = 8.5 Hz, 1H), 7.27 (dd, *J* = 1.7, 8.5 Hz, 1H), 6.72 (dd, *J* = 0.8, 2.2 Hz, 1H), 6.53 (d, *J* = 12.2 Hz, 1H), 6.17 (d, *J* = 12.2 Hz, 1H), 5.02–4.97 (m, 2H), 1.70 (s, 3H); ^{13}C NMR (50MHz, $CDCl_3$): δ = 154.0, 145.2, 142.1, 132.7, 132.1, 129.5, 127.1, 125.4, 121.3, 116.9, 110.6, 106.6, 22.1; MS (70 eV, EI): *m/z* (%): 184 (67) [M^+], 169 (100) [M^+–CH_3], 155 (59), 141 (89), 115 (39), 105 (41), 91 (26), 77 (26); HR-MS: calcd. for $C_{13}H_{12}O$: 184.0888, found: 184.0882.

[7] Spectral data for compound **13**: ^{1}H NMR (200 MHz, $CDCl_3$, 25°C, TMS): δ = 7.58–7.57 (m, 2H), 7.39 (d, *J* = 8.5 Hz, 1H), 7.32 (dd, *J* = 1.6, 8.5 Hz, 1H), 6.71 (d, *J* = 2.2 Hz, 1H), 6.50 (d, *J* = 12.3 Hz, 1H), 6.10 (d, *J* = 12.3 Hz, 1H), 4.98 (s, 2H), 2.10 (q, *J* = 7.4 Hz, 2H), 1.01 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 154.0, 147.7, 145.1, 132.6, 131.2, 129.7, 127.2, 125.4, 121.3, 113.5, 110.8, 106.6, 28.8, 12.8. **14**: ^{1}H NMR (200MHz, $CDCl_3$, 25°C, TMS): δ = 7.63 (s, 1H), 7.58 (d, *J* = 2.2 Hz, 1H), 7.38 (s, 2H), 6.71 (d, *J* = 2.2, Hz, 1H), 6.50 (d, *J* =

12.4 Hz, 1H), 6.07 (d, *J* = 12.4 Hz, 1H), 4.95 (s, 2H), 2.41 (sep, *J* = 6.8 Hz, 1H), 1.12 (d, *J* = 6.8 Hz, 6H); ^{13}C NMR (50MHz, $CDCl_3$): δ = 154.0, 151.6, 145.1, 132.4, 130.4, 130.0, 127.3, 125.4, 121.3, 111.5, 110.8, 106.6, 34.0, 21.7. **15**: ^{1}H NMR (200 MHz, $CDCl_3$, 25℃, TMS): δ = 7.59–7.56 (m, 2H), 7.39 (d, *J* = 8.5 Hz, 1H), 7.33 (dd, *J* = 1.6, 8.5 Hz, 1H), 6.71 (dd, *J* = 0.7, 2.2 Hz, 1H), 6.49 (d *J* = 12.3 Hz, 1H), 6.07 (d, J = 12.3 Hz, 1H), 5.00–4.96 (m, 2H), 2.08 (t, J = 7.6 Hz, 2H), 1.54–1.35 (m, 2H), 0.83 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 154.0, 146.0, 145.1, 132.5, 131.1, 129.7, 129.5, 127.2, 125.4, 121.3, 114.7, 110.7, 106.6, 38.2, 21.5, 13.8. **16**: ^{1}H NMR (200 MHz, $CDCl_3$, 25 ℃, TMS): δ = 7.66 (m, 1H), 7.55 (d, *J* = 2.2 Hz, 1H), 7.45 (dd, *J* = 1.8, 8.6 Hz, 1H), 7.35 (d, *J* = 8.6 Hz, 1H), 6.64 (dd, *J* = 0.8, 2.2 Hz, 1H), 6.50 (d, *J* = 12.4 Hz, 1H), 6.17 (dd, *J* = 1.3, 12.4 Hz, 1H), 4.97–4.93 (m, 2H), 1.18 (s, 9H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 153.9, 153.7, 145.0, 132.3, 129.9, 129.8, 127.2, 125.5, 121.4, 111.3, 110.7, 106.6, 35.9, 29.3. **17**: ^{1}H NMR (300 MHz, $CDCl_3$, 25℃, TMS): δ = 7.57 (d, *J* = 2.2 Hz, 1H), 7.50 (s, 1H), 7.38 (d, *J* = 8.5 Hz, 1H), 7.17–7.29 (m, 4H), 7.09 (d, *J* = 8.3 Hz, 2H), 6.69 (d, *J* = 2.2 Hz, 1H), 6.49 (d, *J* = 12.3 Hz, 1H), 6.07 (d, *J* = 12.3 Hz, 1H), 5.09 (s, 1H), 4.96 (s, 1H), 3.40 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 154.1, 145.2, 145.1, 139.4, 132.4, 130.5, 130.3, 129.0, 128.2, 127.3, 126.1, 125.3, 121.3, 116.6, 110.8, 106.6, 42.5. **18**: ^{1}H NMR (300 MHz, $CDCl_3$, 25℃, TMS): δ = 7.61–7.58 (m, 2H), 7.42 (d, *J* = 8.5 Hz, 1H), 7.28 (td, *J* = 2.1, 8.5 Hz, 1H), 6.73 (dd, *J* = 0.9, 2.1 Hz, 1H), 6.64 (d, *J* = 12.6 Hz, 1H), 5.93 (dd, *J* = 12.6, 26.2 Hz, 1H), 4.75 (ddd, *J* = 1.2, 2.7, 16.4 Hz,1H), 4.56 (dd, *J* = 2.7, 47.4 Hz, 1H). (*E*)-**19**: ^{1}H NMR (300 MHz, $CDCl_3$, 25℃, TMS): δ = 7.66 (s, 1H), 7.61 (d, *J* = 2.1 Hz, 1H), 7.46 (d, *J* = 8.7 Hz, 1H), 7.41 (dd, *J* = 1.5, 8.7 Hz, 1H), 7.09 (d, *J* = 15.3 Hz, 1H), 6.80 (d, *J* = 15.3 Hz, 1H), 6.75 (d, *J* = 2.1 Hz, 1H), 5.46 (s, 1H), 5.42 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 155.1, 145.7, 138.8, 133.7, 131.1, 127.9, 124.5, 123.4, 120.0, 115.2, 111.7, 106.7. **31**: ^{1}H-NMR (300 MHz, $CDCl_3$) : δ 7.74(d, *J* = 8.3 Hz, 1H), 7.72(s, 1H), 7.37(d, *J* = 5.6 Hz, 1H), 7.32(dd, *J* = 1.6, 8.3 Hz, 1H), 7.25(d, *J* = 5.6 Hz, 1H), 6.52(d, *J* = 12.3 Hz, 1H), 6.19(d, *J* = 12.3 Hz, 1H), 5.00(m, 2H), 1.71(s, 3H)；^{13}C-NMR (75 MHz, $CDCl_3$) : δ 142.0, 139.4, 138.2, 134.1, 132.7, 129.3, 126.5, 125.4, 123.8, 123.7, 121.7, 117.0, 22.2. **32**: ^{1}H-NMR (200 MHz, $CDCl_3$)：δ 7.77(s, 1H), 7.73(d, *J* = 8.3 Hz, 1H), 7.37-7.42(m, 2H), 7.28(d, *J* = 5.6 Hz, 1H), 6.52(d, *J* = 12.3 Hz, 1H), 6.14(d, *J* = 12.3 Hz, 1H), 4.99(m, 2H), 2.13(q, *J* = 7.6 Hz, 2H), 1.03(t, *J* = 7.6 Hz, 3H)；^{13}C-NMR (50 MHz, $CDCl_3$)：δ 147.6, 139.6, 138.2, 134.0, 131.8, 129.5, 126.5, 125.2, 124.0, 123.9, 121.8, 113.7, 28.8, 12.8. **33**: ^{1}H-NMR (200 MHz, $CDCL_3$)：δ 7.79(s, 1H), 7.69(d, *J* = 8.4 Hz, 1H), 7.46(dd, *J* = 1.5, 8.4 Hz, 1H), 7.31(d, *J* = 5.5 Hz, 1H), 7.20(d, *J* = 5.5 Hz, 1H), 6.49(d, *J* = 12.3 Hz, 1H), 6.10(d, *J* = 12.3 Hz, 1H), 4.95(s, 2H), 2.41(sep, *J* = 6.8 Hz, 1H), 1.10(d, *J* = 6.8 Hz, 6H)；^{13}C-NMR (50 MHz, CDCl3) : δ 151.5, 139.6, 138.1, 133.7, 131.0, 129.8, 126.4, 125.2, 123.9, 123.7, 121.7, 111.6, 33.9, 21.6. **34**:

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