Photochemical and Thermal Transformations of Thiophene o-Distyrylbenzene Analogues in Acidic Media†

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Abstract. Intramolecular photochemical reactions of thiophene analogues of o-distyrylbenzene, 2,2’-(o-phenylenedivinylene)dithiophenes (1a,b), 3,3’-(o-phenylenedivinylene)dithiophene (2a) and 3,3’-(o-phenylenedivinylene) dibenzothiophene (2b), were studied in acidic media at low concentrations. A 1,6- and 1,5-ring closure of hexatriene system leading to dihydronaphthalene or indene derivatives, respectively, was observed. (doi: 10.5562/cca2120)

Keywords: electrocyclization, photochemistry, protonation, thiophenes, o-divinylbenzenes

INTRODUCTION

Our recent research on the intramolecular photochemical reactions of conjugated thiophene derivatives1,2 continues the work on furan3–10 and pyrrole11–16 derivatives of o-divinylbenzenes. Dithiophene derivatives 1, 2 react differently2 in comparison to previously studied difuran3–8 and dipyrrole4–12 derivatives (Figure 1). While difuran substituted o-divinylbenzenes 3, upon irradiation in anaerobic condition at low concentrations give, via initial intramolecular 1,5-ring closure benzobicyclo[3.2.1]octadiene derivatives 5,8 dipyrrole derivatives 4 afford the dimeric product 6 as the result of initial intramolecular 1,5-ring closure followed by intermolecular addition12 (Figure 1).

In contrast, the hexatriene systems with terminal thiophene rings (1 and 2)7 undergo photochemical 6π electrocyclization reactions affording 2,3-dihydronaphthalene intermediates. In the case of 2-thienyl derivatives 1, the 1,2-dihydronaphthalenes 7 are formed by 1,5-H shift whereas the 3-thienyl derivatives 2 undergo [4+2] intramolecular reaction with thiophene or di-π-methane rearrangement giving polycyclic compound 8. This type of ring closure, and the existence of the 2.3-dihydronaphthalene intermediates, has not been detected before in o-distyryl benzenes17–23 or their diheteroaryl substituted o-divinylbenzenes.8,12

Stimulated by the Tong-Ing Ho’s work24–29 on photochemical behavior of styryl-furans and -thiophenes, who found that their photoreactivity could be entirely changed in acidic media. We report herein the photochemical and thermal behavior of dithiophene substituted o-divinylbenzenes 1 and 2 in acidic media.

EXPERIMENTAL

The 1H and 13C NMR spectra were recorded on a Bruker AV-600 Spectrometer at 300 and 600 MHz. All NMR spectra were measured in CDCl3 using tetramethylsilane as reference. The assignment of the signals is based on 2D-CH correlation and 2D-HH-COSY and NOESY experiments. UV spectra were measured on a Varian

Figure 1. Chemical diagrams of the compounds studied.
† This article belongs to the Special Issue devoted to the 85th anniversary of Croatica Chemica Acta.
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Yield 5 %; colourless oil; UV (EtOH)

General Procedure.

2922, 1589, 1223, 1078, 748, 694; 1H NMR (CDCl 3)

acid (w

were isolated and characterized. High-molecular-weight

and thyn layer chromatography the photoproducts

rechromatographed and after the repeated column

eluent. The obtained mixtures of the products were

removed in vacuo and the oily residue chromatographed

products remained on the column.

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were performed in a quartz or Pyrex vessel in acetoni-

treter/tion reflector mode. Elemental analyses were carried out

for chromatographic purifications. Thin-layer chroma-

tion. Melting points were obtained using an Original

Kofler Mikroheiztisch apparatus (Reichert, Wien) and

are uncorrected. HRMS analysis were carried out on a

et al.

125 (d), 124 (d), 123 (d), 120 (d), 119 (s), 116 (s), 116 (d), 48 (d), 47 (d, C3); Anal. Calcd. mass fraction of elements, w/% for

C18H14S2 (M= 294.43) are: C 73.43, H 4.79, S 21.78; found C 73.32, H 4.96.

Starting compounds 1a, b and 2a, b were prepared by Wittig reaction from o-xylenebis(triphenylphos-

phonium bromide) and the corresponding thiophene

aldehydes as described previously in the literature. 3

Irradiation Experiments of 1a, b and 2a, b in the Presence of Hydrochloric acid

General Procedure. A mixture of cis, cis-, cis, trans- and

trans, trans-isomers of 1a, 1b, 2a and 2b in acetonitrile

(c = 4 × 10–3 mol dm–3), with addition of hydrochloric acid (w = 36 %, 1 ml, 35 eq), was purged with argon for

30 min and irradiated at λ = 300 nm in a Rayonet reactor

(16 lamps) in a quartz vessel. After irradiation (1a: 2.5

h; 1b: 4 h; 2a: 8 h; 2b: 2 h) the reaction mixture was

neutralized with solution of sodium hydroxide (w = 10 %)

and extracted with ethylacetate (4 × 5 ml). After
drying over magnesium sulphate the solvents were

removed in vacuo and the oily residue chromatographed

on a silica gel column using petroleum ether as theights. The obtained mixtures of the products were

rechromatographed and after the repeated column and thyn layer chromatography the photoproducts

were isolated and characterized. High-molecular-weight products remained on the column.

All analytical data for 7a, b, 12a and 14 were identical
to those described in our previous paper. 2 The data of

the new compounds are given below.

2-{(E)-(2-(2-thienyl)-2,3-dihydro-1H-inden-1-ylidene)-

methyl}thiophene (cis-9a)

Yield 2 %; colourless crystals; m.p. 78 °C; UV (EtOH)

λmax/nm: 346, 331, 317 and 237 (log ε/dm3mol–1cm–1:

4.28, 4.37, 4.22, sh and 4.09); IR νmax/cm–1: 2922,

1421, 1223, 903, 748, 694; 1H NMR (CDCl 3) δ/ppm:

7.64 (d, 1H, J = 6.9 Hz, H-ar), 7.17–7.40 (m, 5H), 7.01–

7.09 (m, 2H), 6.97 (dd, 1H, J = 4.8, 3.7 Hz), 6.78–6.86

(m, 2H), 4.48 (d, 1H, JH, JBC = 8.0 Hz; H-B), 3.63 (dd, 1H,

JBC = 16.4 Hz, H-D); 13C NMR (CDCl 3) δ/ppm: 148

(s), 144 (s), 140 (s), 138 (s), 129 (d), 127 (d), 127 (d), 126 (d), 126 (d), 125 (d), 125 (d), 125 (d), 124 (d), 116 (d), 48 (d), 47 (d, C3); Anal. Calcd. mass fraction of elements, w/% for

C18H14S2 (M= 294.43) are: C 73.43, H 4.79, S 21.78; found C 73.32, H 4.96.

5-(2-thienyl)-4,5-dihydroacenaphtho[4,5-b]thiophene

(10a)

Yield 5 %; colourless oil; UV (EtOH) λmax/nm: 335,

314, 303, 292, 260, 246 and 218 (log ε/dm3mol–1cm–1:

3.10, 3.87, 3.95, 3.80, 4.30, 4.50 and 4.17); IR νmax/cm–1:

2918, 1599, 1396, 1085, 692; 1H NMR (CDCl 3) δ/ppm:

8.05 (d, 1H, J = 8.1 Hz, H-ar), 7.93 (d, 1H, J = 4.8 Hz),

7.66 (s, 1H, H-A), 7.62 (dd, 1H, J = 7.2, J2α3 = 8.1 Hz,

H-ar), 7.54 (d, 1H, J = 4.8 Hz), 7.38 (d, 1H, J = 7.2 Hz,

H-ar), 7.19 (dd, 1H, J = 4.8; 2.0 Hz), 6.95–6.99 (m, 2H),
Yield 7%; colourless oil; UV (EtOH) λmax/nm: 321 and 236 (log ε/ dm³mol⁻¹ cm⁻¹: 4.30 and 4.20); IR νmax/cm⁻¹: 3067, 1433, 1225, 1030, 687; ¹H NMR (CDCl₃) δ/ppm: 7.43 (d, 1H, J = 7.5 Hz, H-αr), 7.31 (d, 1H, J = 7.5 Hz, H-αr), 7.28 (dd, 1H, J₂,₃ = 5.0; J₂,₄ = 0.8 Hz, H-2), 7.25 (t, 1H, J = 7.5 Hz, H-αr), 7.20 (dd, 1H, J₃,₄ = 3.6; J₃,₄ = 0.8 Hz, H-4), 7.18 (dt, 1H, J = 7.5; 0.8 Hz, H-αr), 7.09 (dd, 1H, J₂,₃ = 4.9; J₂,₄ = 1.0 Hz, H-2'), 7.05 (dd, 1H, J₂,₃ = 5.0; J₂,₄ = 3.6 Hz, H-3'), 6.84-6.88 (m, 2H), 4.39 (s, 2H, -CH₂), 3.87 (s, 2H, -CH₂); ¹³C NMR (CDCl₃) δ/ppm: 146 (s), 141 (s), 141 (s), 139 (s), 135 (s), 135 (s), 127 (d), 126 (d), 125 (d), 124 (d), 123 (d), 119 (d), 41 (t, CH₃), 27 (t, CH₃); MS m/z: 294 (M⁺, 100%); Anal. Calc'd. mass fraction of elements, w/%M for C₁₉H₁₄S₂ (Mₛ = 294.43) are: C 73.43, H 4.79, S 21.78; found C 73.32, H 4.96.

2-methyl-5-[(Z)-2-(5-methyl-2-thienyl)-2,3-dihydro-1H-inden-1-ylidene)methyl]thiophene (cis-9b)

Yield 5%; colourless oil; UV (EtOH) λmax/nm: 334 and 244 (log ε/ dm³mol⁻¹ cm⁻¹: 3.94 and 4.28); IR νmax/cm⁻¹: 2922, 1599, 1412, 1231, 689; ¹H NMR (CDCl₃) δ/ppm: 7.78 (d, 1H, J = 7.4 Hz, H-αr), 7.27 (d, 1H, J = 7.4 Hz, H-αr), 7.22 (dt, 1H, J = 7.4; 0.6 Hz, H-αr), 7.11 (dt, 1H, J = 7.4; = 0.6 Hz, H-αr), 6.88 (d, 1H, J₃,₄ = 3.4 Hz, H-4'), 6.72 (d, 1H, J₃,₄ = 3.4 Hz, H-4'), 6.64 (dd, 1H, J₃,₄ = 3.4; J₃,₄ = 1.0 Hz, H-3), 6.57 (dd, 1H, J₃,₄ = 3.4; J₃,₄ = 1.1 Hz, H-3'), 6.32 (s, 1H, H-A), 4.35-4.39 (m, 1H, H-B), 3.43 (dd, 1H, J₃,₄ = 15.8; J₃,₄ = 8.3 Hz, H-C), 3.12 (dd, 1H, J₃,₄ = 15.8; J₃,₄ = 6.1 Hz, H-D), 2.47 (d, 3H, J₁,₃ = 1.0 Hz, -CH₃), 2.42 (d, 3H, J₁,₃ = 1.0 Hz, -CH₃); ¹³C NMR (CDCl₃) δ/ppm: 146 (s), 146 (s), 145 (s), 143 (s), 139 (s), 138 (s), 129 (s), 129 (d), 126 (d), 126 (d), 125 (d), 125 (d), 124 (d), 124 (d), 123 (d), 120 (d), 120 (d), 120 (d), 120 (d); Anal. Calc'd. mass fraction of elements, w/%M for C₂₂H₁₈S₂ (Mₛ = 322.49) are: C 74.49, H 5.63, S 19.89; found C 74.49, H 5.88.

3,3'-(1,2-dihydropthalene-2,3-diyl)di(benzothiophene) (13a)

Yield 16%; colourless crystals; m.p. 95–97 °C; UV (EtOH) λmax/nm: 327, 311, 301 and 234 (log ε/ dm³mol⁻¹ cm⁻¹: 3.94, sh, 4.12, 4.09, sh and 4.17); IR νmax/cm⁻¹: 2918, 1460, 1225, 689; ¹H NMR (CDCl₃) δ/ppm: 7.37 (dd, 1H, J = 5.1; 1.3 Hz), 7.27-7.30 (m, 2H), 7.23 (dd, 1H, J = 2.9; 1.3 Hz), 7.17-7.18 (m, 2H), 7.11 (dd, 1H, J = 4.9; 2.9 Hz), 7.03 (d, 1H, J = 7.4 Hz), 7.01 (s, 1H, H-A), 6.87-6.88 (m, 1H), 6.84 (dd, 1H, J = 5.0; 1.3 Hz), 4.18 (dd, 1H, J₁,₃ = 7.3; J₃,₄ = 1.6 Hz, H-B), 3.44 (dd, 1H, J₃,₄ = 15.6; J₁,₃ = 7.3; J₃,₄ = 1.1 Hz, H-C), 3.02 (dd, 1H, J₃,₄ = 15.6; J₁,₃ = 1.6 Hz, H-D); ¹³C NMR (CDCl₃) δ/ppm: 142 (s), 135 (s), 134 (2s), 132 (s), 128 (d), 127 (d), 126 (d), 126 (d), 125 (d), 125 (d), 124 (d), 124 (d), 123 (d), 123 (d), 120 (d), 120 (d, C₆), 38 (d, C₆), 36 (t, C₆); HRMS: M⁺ calc'd. 294.0531; M⁺ exp'd. 294.0537.

A mixture of cis,cis-, cis,trans- and trans,trans-isomers of 1a and 1b in acetonitrile (c = 4 × 10⁻³ mol dm⁻³), with addition of sulphuric acid (w = 36 %, V = 1 ml, 50 eq), was purged with argon for 30 min and irradiated at 300 nm in a Rayonet reactor (16 lamps) in a quartz vessel for 4 h. After irradiation the reaction mixture was neutralized with solution of sodium hydroxide (w = 10 %) and extracted with ethylacetate (4 × 5 ml). After drying over magnesium sulphate the solvents were removed in vacuo and the oily residue chromatographed on a silica gel column using petroleum ether as the eluent. The compounds 7a (20 %), 7b (10 %), 10b (3 %) and 15 (15 %) were isolated followed by a mixture of several unidentified products (< 2 %). High-molecular-weight products remained on the column.

Irradiation Experiments of 1a,b in the Presence of Sulphuric Acid

A mixture of cis,cis-, cis,trans- and trans,trans-isomers of 1a and 1b was dissolved in acetonitrile (c = 4 × 10⁻³ mol dm⁻³) with addition of sulphuric acid (w = 36 %, V = 1 ml, 50 eq), and was purged with argon for 30 min and irradiated at 300 nm in a Rayonet reactor (16 lamps) in a quartz vessel for 4 h. After irradiation the reaction mixture was neutralized with solution of sodium hydroxide (w = 10 %) and extracted with ethylacetate (4 × 5 ml). After drying over magnesium sulphate the solvents were removed in vacuo and the oily residue chromatographed on a silica gel column using petroleum ether as the eluent. The following compounds were isolated from 1a or 1b, respectively: trans,trans-1a (24 %), trans,9a (46 %), 11a (21 %) and trans,9b (42 %), 11b (14 %).

Heating of 2a and 2b in Acetonitrile/Hydrochloric Acid Solutions

A mixture of cis,cis-, cis,trans- and trans,trans-isomers of 2a or 2b (2a: c = 4 × 10⁻³ mol dm⁻³; 2b: c = 3 × 10⁻³ mol dm⁻³) was dissolved in acetonitrile with addition of hydrochloric acid (w = 36 %, V = 1 ml, 35 eq) and refluxed for 17 hours. After cooling to room temperature the reaction mixture was neutralized with solution of sodium hydroxide (w = 10 %) and extracted with ethylacetate (4 × 5 ml). After drying over magnesium sulphate the solvents were removed in vacuo and the oily residue chromatographed on a silica gel column using petroleum ether as the eluent. Only the mixture of 2a and 2b isomers, respectively, was recovered.

Irradiation of cis,-9a,b and 10a,b Mixtures in the Presence of Iodine

An acetonitrile solution (c = 4 × 10⁻³ mol dm⁻³) of compounds cis-9 and 10 is irradiated in the presence of iodine at 350 nm for 4 hours. After irradiation the solvent was removed in vacuo and the oily residue chromatographed on a silica gel column using petroleum ether as the eluent. The compounds 10a and 10b, respectively, were isolated.

Heating of cis-9a,b or trans-9a,b in the Presence of Iodine

A toluene solution (c = 8 × 10⁻³ mol dm⁻³) of compounds cis-9 or trans-9 or a mixture was refluxed in the presence of iodine for 1.5 hours. After cooling to the room temperature the solvent was removed in vacuo and the oily residue chromatographed on a silica gel column using petroleum ether as the eluent. The compounds 11a (60 %) and 11b (80 %), respectively, were isolated.

RESULTS AND DISCUSSION

Compounds 1 and 2, prepared by Wittig reaction from o-xylylenebis(triphenylphosphonium bromide) and the corresponding thiophene aldehydes as described, were irradiated in argon purged acetonitrile solutions.

(c ~ 4 × 10⁻³ mol dm⁻³) with the addition of hydrochloric acid. After irradiation, the reaction mixture was neutralized with sodium hydroxide solution, extracted with ethyl acetate and after the evaporation of the solvents the residue chromatographed on silica gel column using petroleum ether as eluent. The ¹H NMR spectra of 1a and 1b photomixtures showed signals of the dihydronaphthalene products 7a and 7b, respectively, also obtained on irradiation of the starting compounds in neutral media,² along with several additional signals of the products in different ratio, depending on the starting compounds (Scheme 1).

In contrast, photomixtures obtained on irradiation of 3-thienyl derivatives 2a and 2b (Scheme 2) contained no polycyclic structures 8 (Figure 1), like those found on irradiation in neutral media, but instead the dihydronaphthalene derivatives 13a and 13b, respectively, were produced. Dimeric cyclophane products 12a (Scheme 1) and 14 (Scheme 2) have been also isolated. In all irradiation experiments, material remained on the column as unidentified high-molecular-weight products. The isolated photoproducts were characterized by spectroscopic methods. The aliphatic region of the ¹H NMR spectra of intramolecular photoproducts found on irradiation of unsubstituted 2-thienyl derivative 1a is presented in Figure 2. Each shows similar characteristic three-proton pattern of ABX systems, except 11a. Signals shift to lower or higher magnetic field depending on the structure. The different photoproducts behave similarly during column chromatography which greatly complicates their separation and characterization.

It was thus necessary to perform the additional photochemical and thermal experiments (Scheme 3) that, in combination with column and thin layer chromatography, allow us easier separation and identification of the products. Photoproducts 10a and cis-9a are inseparable as are trans-9a and 11a. So a mixture of 10a and cis-9a was irradiated in acetonitrile solution in the presence of iodine whereupon cis-9a underwent electrocyclization reaction to 10a. So pure 10a was isolated and completely characterized. When a mixture of trans-9a and 11a was irradiated, but without iodine, trans-9a isomerizes to cis-9a which was separated more easily from 11a. Compound 11a is formed by thermal reaction in refluxing toluene with catalytic quantity of iodine, either from cis- or trans-9a.

The isolated photoproducts were characterized by spectroscopic methods. The aliphatic region of the ¹H NMR spectra of intramolecular photoproducts found on irradiation of unsubstituted 2-thienyl derivative 1a is

**Scheme 1.**

**Scheme 2.**

Analogous experiments were performed with the products of methyl derivative 1b which shows similar photoreactivity to the unsubstituted 10a providing further proof of the product structures.
All of the experiments described were conducted in the presence of hydrochloric acid (w ~ 36 %). Compounds 1a and 1b were also irradiated under the same conditions but in the presence of sulfuric acid (diluted, w ~ 36 %).

Unsubstituted thienyl derivative 1a (Scheme 4) gave dihydronaphthalene 7a in the same yield as in hydrochloric acid, but no other products of 1,5-ring closure were detected. Methyl derivative 1b reacts by 1,6- and 1,5-ring closure giving expected products 7b and 10b, respectively, along with a new product 15, the structure of which is determined by spectroscopic methods. 1H NMR spectrum (Figure 3) shows in the aliphatic region five hydrogen signals on cyclopentalenic structure. Proton H₈ is coupled only with H₇ (J = 6.9 Hz) which is coupled with H₅ (J = 8.5 Hz). H₆ appears as a singlet and the geminal protons H₉ and H₁₀ are in mutual coupling (J = 16.2 Hz). The structure is confirmed by X-Ray analysis (Figure 4).

To determine that all these isolated products are the result of photoinduced reactions we kept the acidic solutions of compounds 1 and 2 in darkened cuvettes while exposing them to the conditions of the Rayonet (t ~ 40 °C). No reaction was detected leading to

\[ \text{Figure 2.} \ 1^H \text{NMR spectra (aliphatic region) in CDCl}_3 \text{ at 300 MHz (7a, 10a and trans-9a) and at 600 MHz (cis-9a and 11a).} \]
conclusion that the products formed on irradiation were formed by photoinduced processes. Acetonitrile solutions of the starting compounds 1 and 2 were also refluxed for 16–22 hours. No reaction was observed without addition of acid. When compounds 1a,b were refluxed in acidic acetonitrile solution two indene derivatives 9 and 11 have been formed (Scheme 5), found also in photoinduced experiments, but in much higher yield. The formation of thermal products trans-9 and 11 can be explained via carbocation intermediates A and B as shown in Scheme 6.

A plausible mechanism for the formation of the photoproducts is presented in Scheme 7. Assuming polarization (A, A') in the excited state this enables an

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Figure 3. 1H NMR spectrum (aliphatic region) of 15 (600 MHz) in CDCl3.
Figure 4. ORTEP drawing of 15. Displacement ellipsoids are drawn for the probability of 50 % and hydrogen atoms are shown as spheres of arbitrary radii.

CONCLUSION

On irradiation in acidic media β,β'-2-thienyl and β,β'-3-thienyl derivatives of o-divinylbenzene (1 and 2) give 1,2-dihydronaphthalene derivatives (7, 13) presumably by protonation of the starting material in the excited state followed by 1,6-ring closure or by protonation of the primarily formed 2,3-dihydronaphthalene intermediate. The 2-thienyl 1 affords the cyclic products of 1,5-ring closure also followed by carbocation rearrangements and photochemical isomerization and electrocyclization. The total yields of the intramolecular cyclic products formed on irradiation in acidic media are much higher with regard to those in neutral media.

Only 2-thienyl derivatives (1a,b) reacted thermally under the described conditions giving the products of 1,5-ring closure of the hexatriene system.
Scheme 7.
Supplementary Materials. — Crystal data and structure refinement of 15 is available free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk). CCDC 891194.

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