Electron-Transfer in the Light-Promoted 1,6-Cyclodimerization of 1,1-Di-2-thienylethylene. A Thermal and Photochemical Study

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1,1-Di-2-thienylethanol (**1**) undergoes light-induced (λ >400 nm) dehydration to afford 1,1-di-2-thienylethylene (**2**). Compound **2** is selectively converted into 1,6-cyclodimers under thermal or photochemical conditions. In these latter case the non-aromatic Diels-Alder adduct **3** can be characterized. An ET mechanism involving a methyldithienylcarbenium ion (**9**) as electron acceptor and a chain mechanism is proposed to account for the products.

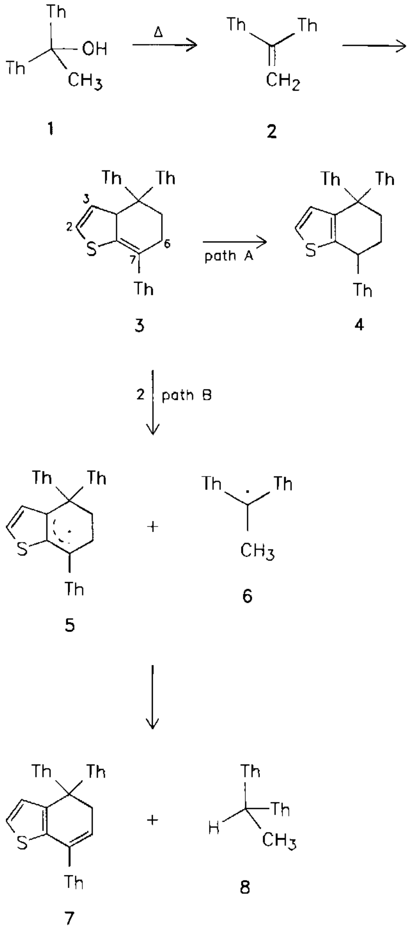
Arylethylenes are known to undergo several types of dimerization processes under thermal or photochemical conditions to afford 1,4- and 1,6-cycloadducts as well as open-chain dimers. The relative amount obtained of each class of products depends both on the nature of the subtituents attached to the aryl groups and the reaction conditions. Photochemical dimerizations are usually promoted by sensitizers and proceed via intermediate radical cations[1]. The light-promoted dimerization of olefins substituted by strong electron donors involves a chain mechanism[2]. An alternative thermal methodology to promote cycloadditions via cation radicals by chain reactions is based on the use of ammoniumyl salts as electron acceptors[3]. However, in spite of the extensive studies performed on the reactivity of diarylethylenes, the behavior of their heteroaromatic counterparts towards the dimerization remains unknown.

We report now on our study on the dimerization of 1,1-di-2-thienylethylene (**2**) under thermal and photochemical conditions. Ethylene **2** is an unstable compound which polymerizes[4] very easily and is therefore difficult to characterize and to handle. However, the precursor alcohol **1** is stable and can be purified in the dark. Compound **2** is obtained by thermal dehydration of **1**, but dimers and polymerization products are formed simultaneously. Surprisingly, irradiation (λ >400 nm) of **1** in non-nucleophilic solvents for a short time gives rise to quantitative formation of **2**.

Heat-Promoted Cyclodimerization of 2

1,1-Di-2-thienylethanol (**1**) is heated in the dark at 150°C for 60 minutes in a sealed tube to afford the aromatic cycloadduct **4** in more than 70% yield besides about 15% of its dehydro derivative **7** and 1,1-di-2-thienylethane (**8**). The formation of these products can be easily rationalized by assuming the initial formation of the Diels-Alder adduct **3** which is converted into the products by two alternative pathways (see Scheme 1). In the main way (path A), the bridgehead hydrogen migrates to C-7 leading to the aromatic dimer **4**. In the secondary reaction (path B) the behavior of **3** resembles that of other aryl-substituted olefins with respect to their polymerization processes[5]. Thus, the hydrogen is abstracted by a molecule of unreacted olefin **2** to afford a pair of radicals **5** and **6**, which are the immediate precursors of compounds **7** and **8** due to simple hydrogen

Scheme 1



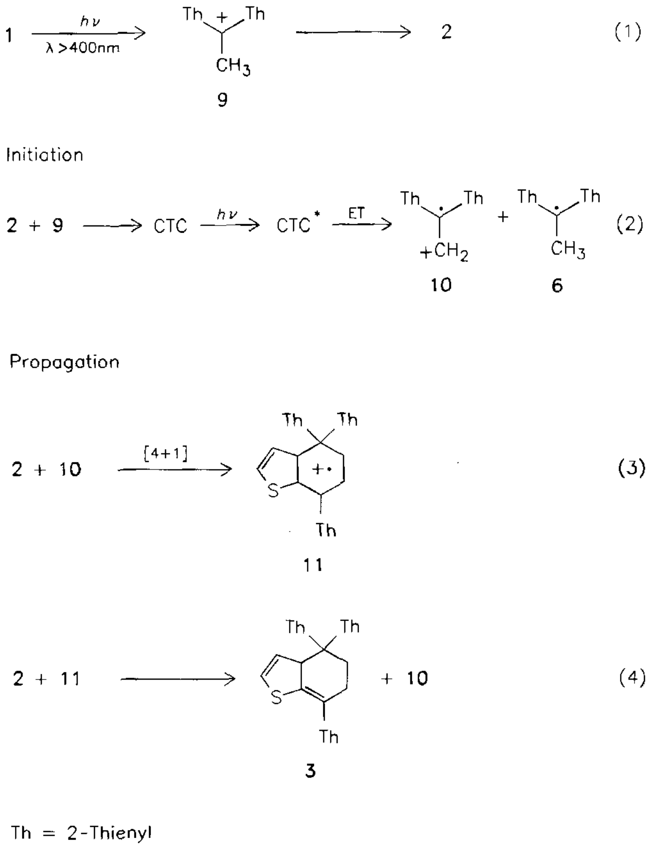
Th = 2-Thienyl

transfer. To ascertain the formation of **3** as intermediate, we studied by NMR spectroscopy the cyclodimerization of **2** in the temperature range of 60 to 150°C. The alcohol **1** is stable below 90°C. At this temperature it undergoes dehydration to the olefin **2**. This olefin is readily converted into the cycloadduct **3** and small amounts of its aromatic derivative **4**. Above 110°C compound **3** cannot be detected. Path B is nearly inhibited at the lower temperatures.

Light-Promoted Cyclodimerization of 2

When the alcohol **1** or the olefin **2** is exposed to sun light they decompose totally within a few days. This has prompted us to examine the photochemical behavior of **2** in the absence of sensitizers using the alcohol **1** as an in situ precursor. The course of the phototransformation is followed by NMR spectrometry. Irradiation of **1** ($\lambda > 400$ nm) in deuteriochloroform readily furnishes the alkene **2** which is subsequently transformed into the cycloadduct **3**. The [4+2] nature of this photoadduct suggests that it arises by a stepwise reaction most likely via radical cations. However, the photodimerization of arylethylenes by radical cations usually needs the presence of a sensitizer to act as an electron acceptor[1]. Since **2** dimerizes without any added sensitizer it appears that the solution subjected to irradiation itself contains an electron acceptor. This might be the methyldi-2-thienylcarbenium ion (**9**) resulting from the light-induced ionization of the precursor alcohol **1**[6]. It has been shown that diarylcarbenium ions are suitable electron acceptors in photoinduced electron-transfer reactions[7]. To ascertain this possibility we have submitted the alcohol **1** to protonation and recorded the UV spectrum under different conditions. Alcohol **1** and ethylene **2**[4] do not show any absorption maximum above 300 nm. The addition of trace amounts of trifluoroacetic acid to a dichloromethylene solution of **1** results in the appearance of new absorption bands at 305, 367, 507, and 668 nm. On the other hand, compound **1** dissolved in neat 96% sulfuric acid shows a strong absorption band at 509 nm which must be assigned to cation **9**. Thus, the band at 668 nm, which does not appear in the presence of an excess of acid, is tentatively assigned to the existence of a charge-transfer complex (CTC) between olefin **2** and cation **9**.

Scheme 2



Based on the above results it may be suggested that irradiation of the CTC promotes the electron transfer to give the radical cation **10** from which compound **3** is generated by a chain reaction (see Scheme 2).

The following observations support the proposed mechanism. To ascertain the role of cation **9** in the initiation step suggested by the CTC band in the UV spectrum we have carried out the irradiation of **2** in the presence of sodium azide. The dimerization is inhibited as expected under these conditions due to quenching of **9** by the azide anion. Radical **6** is generated only in the initiation step, and for this reason the formation of 1,1-dithienylethane **8** or open-chain dimers by collapse of two radicals cannot be detected by NMR in the crude reaction mixture. The absence of open-chain dimers or 1,4-cycloadducts is in good agreement with a [4+1] concerted cycloaddition[8] between the "diene" **2** and the radical cation **10** in the propagation step. The reaction rate strongly depends on the polarity of the solvent as expected for reactions involving radical cations (see Table 1). In apolar solvents such as tetrachloromethane the irradiation of **1** leads to the alkene **2** uncontaminated by dimerization products unless long reaction periods are used. However, the irradiation of **1** in chloroform leads to mixtures of compounds **2** and **3** even with a short reaction time. The addition of methanol to the irradiation medium or the use of acetonitrile as solvent accelerates the formation of **3**. Unfortunately, compound **3** is unsoluble in polar solvents precluding any accurate kinetic measurement.

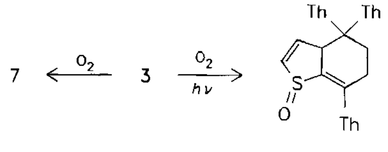
Table 1. Influence of the solvent on the light-induced dehydration of 1 and further dimerization

Solvent	Reaction time (min)	Molar ratio (%)[a] 1	2	3
CCl_4	<120	–	100	–
$CDCl_3$	120	11.7	70.5	17.6
CD_3CN[b]	120	–	28.6	71.4
$CDCl_3/CD_3OD$ (4:1)	120	–	20	80

[a] Based on ^{1}H-NMR spectra. – [b] Spectrum recorded in $CDCl_3$ solution.

Compound **3** has been found to be stable to light when stored in a sealed tube but it undergoes aromatization upon heating at ca. 100°C to afford compound **4**. In contrast, **3** is converted into two different oxidation products when exposed to air (see Scheme 3). Oxidation in the dark leads to the unsaturated aromatic dimer **7**. The same dehydrogenation process also occurs quantitatively when **3** is treated with an equimolar amount of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ). The oxidation of **3** by air in the presence of sun light leads to a mixture of **7** and the sulfoxide **12**. Due to the ease with which these oxidation reactions take place, compound **3** must be carefully handled in the absence of air.

Scheme 3



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Th = 2-Thienyl

In summary it can be concluded that the course of the light-induced dimerization of di-2-thienylethylene **2** is determined by the ready formation of the methyldi-2-thienyl cation **9** by light-induced ionization of the starting alcohol **1**. The increased tendency of the 2-thienyl group to stabilize cationic or radical cationic centers as compared to that of the aryl substituents present in the diarylethylenes previously studied[9] accounts for the high degree of selectivity found in the dimerization of **2**. On the other hand, the great tendency of radical cation **11** to abstract an electron from the starting olefin **2** allows the chain reaction to proceed thus leading to high yields of the cyclodimer **3**.

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Experimental

Melting points: Reichert apparatus, uncorrected. – UV: Perkin-Elmer Lambda-15 spectrophotometer. – NMR: Bruker WP 80 SY, Varian Gemini-200, and Varian XL-500 spectrometers, resp. – Irradiations: The solutions were placed into NMR tubes surrounding a centrally positioned quartz cooling jacket (external diameter 55 mm) containing a 125-W medium pressure mercury lamp. The temperature was kept below 30°C by means of a water bath. An Indo® Sulvi lens was used as filter (λ >400 nm).

All solvents used were purified by usual methods and were treated with KOH pellets to remove traces of acid. 1,1-Di-2-thienylethanol (**1**) was obtained from 2-acetylthiophene[10] and 2-thienyllithium in anhydrous ether according to literature methods[11]; it was purified by distillation under reduced pressure.

Thermal Cyclodimerization of 1,1-Di-2-thienylethylene (**2**): 1,1-Di-2-thienylethanol (**1**) (1.0 mmol, 0.21 g) was heated in a sealed NMR tube at 150°C for 60 min. The resulting mixture was allowed to reach room temp. and then dissolved in $CDCl_3$. ^{1}H-NMR analysis showed the presence of compounds **4**, **7**, and **8** in a molar ratio of 7:1:1. The mixture was separated by column chromatography (silica gel, hexane), and the products were eluted in the order **8**, **7**, and **4**. Contamination of compound **4** by less than 5% of compound **7** could not be avoided even after HPLC purification. Runs at different temperatures in the range 60 to 110°C were performed as described above.

1,1-Di-2-thienylethane (**8**): ^{1}H NMR ($CDCl_3$, TMS): δ = 1.7 (d, 3H), 4.5 (q, 1H), 6.7–7.0 (m, 6H). – ^{13}C NMR ($DCCl_3$, TMS): δ = 24.6 (q), 36.1 (d), 123.6 (d), 123.7 (d), 126.5 (d), 150.0 (s).

4,5,6,7-Tetrahydro-4,4,7-tri-2-thienylbenzo[b]thiophene (**4**): ^{1}H NMR ($DCCl_3$, TMS): δ = 2.0–2.4 (m, 2H), 2.7–2.8 (m, 2H), 4.5 (t, 1H), 6.7–7.1 (m, 11H). – ^{13}C NMR ($DCCl_3$, TMS): δ = 30.9 (t), 37.0 (d), 40.3 (t), 47.0 (s), 123.0 (d), 123.8 (d), 124.1 (d), 124.2 (d), 124.6 (d), 125.8 (d), 126.0 (d), 126.1 (d), 126.4 (d), 127.8 (d), 139.8 (s), 141.2 (s), 149.2 (s), 152.9 (s).

Photochemical Dimerization of 1,1-Di-2-thienylethylene (**2**). *General Procedure:* A solution of **1** (0.5 mmol, 0.105 g) in $CDCl_3$/CD_3OD (4:1) (0.5 ml) was irradiated (λ >400 nm) in a tightly closed NMR tube and the degree of transformation monitored by NMR at selected reaction times. After 4 h 90% of compound **3** was obtained leaving a 10% of **2** unreacted.

3a,4,5,6-Tetrahydro-4,4,7-tri-2-thienylbenzo[b]thiophene (**3**): ^{1}H NMR ($CDCl_3$, TMS): δ = 2.5–2.7 (m, 4H), 4.3–4.5 (m, 1H), 5.8 (dd, 1H), 6.2 (dd, 1H), 6.1–7.3 (m, 9H). – Attempts to purify compound **3** by column chromatography were unsuccessful but the corresponding oxidation products **7** and **13** were isolated.

Attempt to Photodimerize **2** *in the Presence of Sodium Azide:* A solution of **1** (0.5 mmol, 0.105 g) in CCl_4 (0.5 ml) was irradiated (λ >400 nm) for 90 min to yield quantitatively, after evaporation of the solvent, alkene **2**. This alkene was dissolved in $CDCl_3$/CD_3OD (1:2) (1.5 ml), and then sodium azide (0.6 mmol, 0.04 g) was added. The mixture was irradiated (λ >400 nm) with stirring for 5 h remaining, however, unchanged. A parallel experiment without sodium azide gave nearly complete cyclodimerization of the alkene **2**.

4,5-Dihydro-4,4,7-tri-2-thienylbenzo[b]thiophene (**7**): A solution of **1** (0.5 mmol, 0.105 g) in $CHCl_3$/CH_3OH (4:1) (0.5 ml) was irradiated for 4 h and then treated with a solution of DDQ (0.5 mmol, 0.110 g) in CH_2Cl_2 (3 ml). The orange solution became dark blue, and a solid precipitated. After filtration it was identified as a hydroquinone by conversion into the corresponding diacetate[12], m.p. 180°C. The filtrate was evaporated to dryness under reduced pressure and the solid residue purified by column chromatography (silica gel, hexane) to afford **7**; yield 0.081 g (85%), m.p. 105°C (hexane). – ^{1}H NMR ($DCCl_3$, TMS): δ = 3.2 (d, 2H), 5.9 (t, 1H), 6.5–7.2 (m, 11H). – ^{13}C NMR (CCl_4, TMS): δ = 42.7 (t), 46.3 (s), 121.8 (d), 123.2 (d), 124.6 (d), 125.2 (d), 125.9 (d), 126.1 (d), 126.5 (d), 127.6 (d), 128.1 (d), 129.0 (s), 143.2 (s), 151.4 (s).

$C_{20}H_{14}S_4$ (382.6) Calcd. C 62.63 H 3.91 S 33.43
Found C 62.49 H 4.02 S 33.41

3a,4,5,6-Tetrahydro-4,4,7-tri-2-thienylbenzo[b]thiophene 1-Oxide (**12**): 1,1-Di-2-thienylethanol (**1**) (1.0 mmol, 0.210 g) was irradiated for 7 h as described above. Then stream of air was bubbled through the solution for additional 8 h adding $CHCl_3$/CH_3OH (4:1) as needed to keep the volume of the solution constant (ca. 10 ml). Solvents were evaporated in vacuo and an ^{1}H-NMR analysis of the crude residue revealed the presence of a 2:1 mixture of compounds **7** and **12**. Column chromatography of the mixture (silica, hexane) gave compound **7**, yield 0.111 g (58%). The polarity of the eluent was enhanced by adding increasing amounts of ethyl acetate and finally methanol to give compound **12** in 23% yield (0.046 g), m.p. 82–85°C. IR ($CHCl_3$): $\tilde{\nu}$ = 1015 cm^{-1} (S=O). – ^1H NMR ($DCCl_3$, TMS): δ = 2.6 (m, 2H); 2.8 (m, 2H); 4.7 (br. s, 1H); 6.8–7.2 (m, 9H); 7.4 (d, 1H), 7.7 (d, 1H). – ^{13}C NMR ($DCCl_3$, TMS): δ = 30.8 (t), 38.9 (t), 45.7 (s), 59.0 (d), 124.3 (d), 124.4 (d), 124.8 (d), 125.7 (d), 126.0 (d), 126.4 (d), 126.5 (d), 127.6 (d), 129.6 (d), 133.4 (d), 136.0 (s), 140.0 (s), 140.3 (s), 141.3 (d), 144.1 (s), 152.5 (s).

$C_{20}H_{16}OS_4$ (400.6) Calcd. C 59.98 H 4.02 S 32.02
Found C 59.67 H 4.17 S 32.08

CAS Registry Numbers

1: 131323-89-2 / **2**: 30782-41-3 / **2** · **9**: 131352-0-40 / **3**: 131323-90-5 / **4**: 131323-91-6 / 7: 131323-92-7 / **8**: 17306-49-9 / **9**: 131323-93-8 / **12**: 131323-94-9

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