J. Org. Chem. 1989, 54, 4203-4205 4203

The product was purified by precipitating it from a chloroform solution by addition of carbon tetrachloride. This gave 0.216 g (81%) of methyl 1-anthraquinonesulfonate (7): mp 209–210 °C; IR ($CHCl_3$) 1690 (C=O), 1370 and 1170 (SO_2) cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.07 (s, 3 H), 7.65–8.71 (m, 7 H). Anal. Calcd for $C_{15}H_{10}O_5S$: C, 59.60; H, 3.33. Found: C, 58.98; H, 3.28.

Kinetics. The procedure was the same as previously outlined for the reaction of 3 with *n*-BuSH, except that a solution of MCPBA in methanol, rather than a solution of the thiol, was used. The reaction was followed at 450 nm.

Oxidation of 2 by MCPBA. Products. 1-Anthraquinonesulfenic acid (0.26 g, 1 mmol) was dissolved in 10 mL of acetone, 2 mmol of MCPBA was added, and the mixture was allowed to stand at room temperature for 48 h. The solvent was removed under reduced pressure, and the residue was dissolved in hot 5% sodium bicarbonate. The pH of the resulting solution was then adjusted to 3.5 by careful addition of 6 N HCl from a buret. This led to the precipitation of *m*-chlorobenzoic acid, which was filtered off. The pH of the filtrate was then decreased to 0.0 by the addition of more 6 N HCl. At that point sodium 1-anthraquinonesulfonate (0.25 g, 81%) precipitated and was filtered off, mp >300 °C. Comparison of its infrared spectrum, IR (KBr) 2480, 1680, 1570, 1415, 1310, 1280, 1210, 1050, 950, 805, 700, and 610 cm^{-1}, with that of an authentic sample of this salt (Kodak) showed the two to be identical.

Kinetics. A solution of 2 (10^{-4} M) in 15% CH_3CN–85% H_2O was prepared immediately prior to use. After a measured aliquot had been placed in the thermostated spectrophotometer cell the reaction was initiated by the addition from a microsyringe of a measured amount of a solution of MCPBA. When used, trifluoromethanesulfonic acid was also added in the same manner. The reaction was monitored by observing the decrease in the absorbance of the solution at 462 nm.

Determination of the pK_a of 2. To 3.5 mL of 15% acetonitrile–85% water, contained in a 1-cm spectrophotometer cell, was added 60 μL of a 0.007 M solution of 2 in acetonitrile. The UV–visible absorption spectrum of this solution was recorded. Sufficient 1.0 N sodium hydroxide was then added by microsyringe to give a solution containing 0.02 N OH^-, and the spectrum for the anion of 2 (4) was recorded. In 15% acetonitrile 2 has its long-wavelength maximum at 462 nm; its anion shows its λ_{max} at 676 nm.

To determine the pK_a of 2 0.350 mL of one of a series of tris buffers of pH 7.5–8.5, prepared as outlined by Bates and Bower,[9] was added to 3.5 mL of a 10^{-4} M solution of 2 in 15% acetonitrile, and the optical density of the solution was immediately determined at the wavelengths corresponding to the long-wavelength absorption maxima of both the sulfenic acid (462 nm) and its anion (676 nm). The concentration ratio $[ArSO^-]/[ArSOH]$ was estimated for that particular buffer from the absorbance of the solution at the two wavelengths and the extinction coefficients for $ArSO^-$ and ArSOH at these two wavelengths.

Photocyclization of Terthiophenes

Nimal Jayasuriya and Jacques Kagan*

Department of Chemistry, University of Illinois at Chicago, P.O. Box 4348, Chicago, Illinois 60680

John E. Owens, Eugene P. Kornak, and Daniel M. Perrine*

Department of Chemistry, Loyola College in Maryland, 4501 N. Charles St., Baltimore, Maryland 21210

Received February 21, 1989

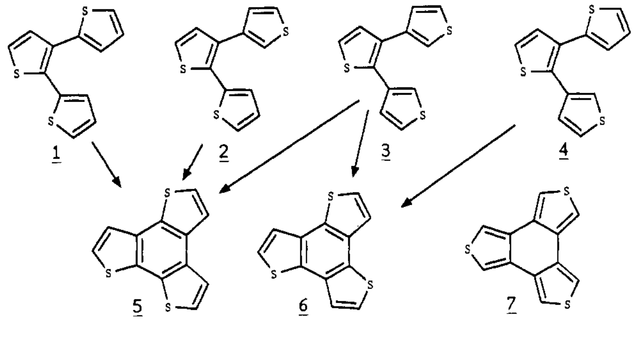
The terthiophenes in which thienyl groups are attached to the 2- and 3-positions of a central thiophene ring undergo oxidative photocyclization to benzotrithiophenes. A single product, unsymmetrical benzotrithiophene 5, was obtained from 2,2′:3′,2″- and 2,2′:3′,3″-terthiophenes, and its symmetrical isomer 6 from 2,3′:2′,3″-terthiophene. However, a mixture of these two products was produced by irradiation of 3,2′:3′,3″-terthiophene, indicating that a rearrangement of a β- into an α-substituted thiophene had occurred. This is a very rarely encountered photochemical rearrangement.

Introduction

Two of the seven possible benzotrithiophenes, 6 and 7 (Scheme I), have been reported. Through sequential treatment of hexakis(bromomethyl)benzene with Na_2S and DDQ, Hart and Sasaoka synthesized benzo[1,2-*c*:3,4-*c*′:5,6-*c*″]trithiophene, 7, an "exocyclic benzene" with D_{3h} symmetry which contains only 3,4-disubstituted (*c*-fused) thiophene rings.[1] Three other benzotrithiophene isomers containing one or two *c*-fused thiophene rings are possible; none has been reported to date.

The remaining two isomers contain only *b*-fused thiophene rings. Benzo[1,2-*b*:3,4-*b*′:5,6-*b*″]trithiophene 6, with C_{3h} symmetry, has been described.[2] However, it is not very conveniently available, particularly on a large scale, since it was produced from γ-thiobutyrolactone at 170–200 °C under 15–20 kbar pressure.

Scheme I



Since its isolation from marigold (*Tagetes erecta*) blossoms by Zechmeister in 1943, there has been much interest in α-terthienyl, 2,2′:5′,2″-terthiophene, one of the most highly phototoxic substances known. In a related study, two of us (N.J., J.K.) recently reported the first synthesis of α-terthienyl isomers 1 to 4,[3] which may be

---

[1] Hart, H.; Sasaoka, M. *J. Am. Chem. Soc.* **1978**, *100*, 4326–4327.

[2] Proetzsch, R.; Bieniek, D.; Korte, F. *Tetrahedron Lett.* **1972**, 543–544.

0022-3263/89/1954-4203$01.50/0

viewed as substituted 1,2-diarylethylenes. Since the oxidative photocyclization of stilbenes and *o*-terphenyls is a reliable method for making phenanthrene and triphenylene derivatives,[4] the irradiation of compounds **1** to **4** seemed to offer a promising entry into the benzotrithiophene ring systems **5** and **6**.

Discussion

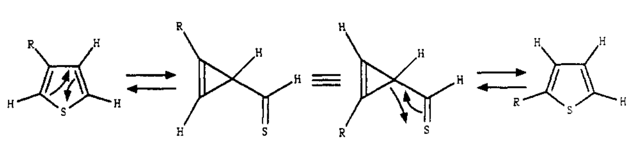
In this work, the irradiations were performed aerobically at 320–400 nm in a Rayonet apparatus, in dilute toluene containing a catalytic amount of iodine. The irradiation of either **1** or **2**, monitored by HPLC, produced a single product. The same product was obtained in both reactions, the isolated yields being 72% and 23%, respectively. Its structural assignment to the previously unknown benzotrithiophene **5** rests primarily on the mass spectral data ($m/e = 246$) and on the ^{1}H NMR analysis at 400 MHz in acetone-d_6, where each of the 12 lines corresponding to the six nonequivalent protons was visible (partial overlap occurred in $CDCl_3$).

The irradiation of **4** was expected to yield the benzotrithiophene **6**. When the progress in the photolysis of **4** was monitored by HPLC, a single product was detected. It was isolated in 34% yield, and its analytical data were in accord with **6**. In particular, the 3-fold symmetry was apparent both from the ^{1}H NMR data, which showed only two doublets with the coupling constant of 5.3 Hz characteristic of 2,3-disubstituted thiophenes,[5] and from the ^{13}C NMR data, which showed only four signals, two representing quaternary carbons.

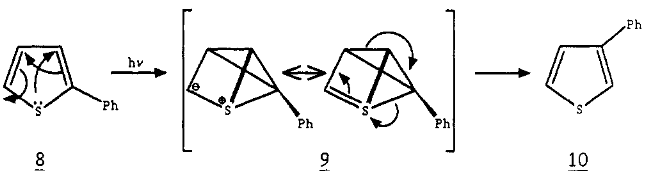
The most surprising observation in this work was in the irradiation of **3**, which had been expected to yield unsymmetrical product **5**. Monitoring of the irradiated solution by HPLC disclosed that a mixture of *both* products **5** and **6** encountered earlier had been formed. The formation of this mixture was also confirmed spectroscopically when the starting material was irradiated in ethanol. The yield of **5** and **6** from the photolysis of **3** (estimated by HPLC) was quite small in contrast to that from **1** and **4** and was accompanied by formation of numerous uncharacterized decomposition products—a pattern of photoreactivity analogous to that observed by Wynberg and others for di-3-thienylethylene.[6] However, repeated HPLC treatment of the mixture led to the isolation of **5** and **6** in sufficient quantity to provide their characteristic UV spectra.

Since neither product **5** nor **6** rearranged into the other under the experimental conditions, the photochemical formation of **6** from **3** required a molecular rearrangement *before* the cyclization step leading to **3**. The cyclization of the starting material and of the rearranged intermediate have very similar rates, since the two observed products were formed simultaneously.

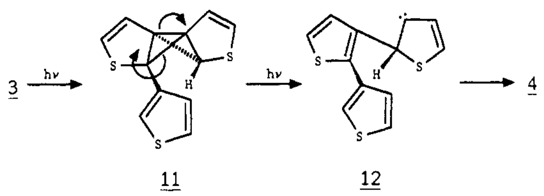
Scheme II



Scheme III



Scheme IV



The simplest explanation for the observed reaction leading to **3** requires a rearrangement whereby the thiophene ring attached to the 3-position of the central thiophene changes its mode of attachment from β to α. It must be pointed out that a similar rearrangement occurring in the β-substituted ring of **2** (leading to **1**) would not have been noticed in the absence of further labeling, since the same product of photocyclization, **5**, would have been formed.

The photochemical rearrangement of thiophenes has been extensively studied.[7] Thanks to the pioneering work of Wynberg and his collaborators with chemically and isotopically labeled molecules, the conversion of an α-substituted thiophene into its β-substituted isomer is particularly well known. One accepted mechanism involves the reversible formation of a cyclopropenyl thioketone intermediate, a mechanism which should also apply to the isomerization of a β- into an α-substituted thiophene (Scheme II). Wynberg has proposed another mechanism[8] based on the participation of sulfur 3d electrons, giving intermediate **9**, leading to **10** (Scheme III). Still other mechanisms have been suggested.[9]

Although the photolysis of α-substituted thiophenes generally produces the β-isomers, the reverse process, in which a simple β-substituted thiophene is converted into its α-substituted isomer, is very unusual. Wynberg's group has reported two examples of the photorearrangement of a β- to α-substituted thiophene. The first is that of 3,4-diphenylthiophene, which led to its 2,4-isomer in very small yield, the major product being phenanthro[9,10-*b*]thiophene, presumably formed from the photocyclization of the intermediate 2,3-isomer.[10] The second example is

---

[3] The last four of the terthiophene isomers to be synthesized were reported in (a) Jayasuriya, N.; Kagan, J. *Heterocycles* **1986**, *24*, 2901–2904. Leading references to the other syntheses can be found in (b) Jayasuriya, N.; Kagan, J. *Heterocycles* **1986**, *24*, 2261–2264. (c) Carpita, A.; Rossi, R. *Gazz. Chim. Ital.* **1985**, *115*, 575–583. For studies of α-terthienyl, see Bohlmann, F.; Zdero, C. In *Thiophene and Its Derivatives*; Gronowitz, S., Ed. [Vol. 44 of *The Chemistry of Heterocyclic Compounds*; Weissberger, A., Taylor, E. C., Eds.]; John Wiley: New York, 1985; Part 1, pp 261–323 and references cited therein.

[4] (a) Mallory, F. B.; Mallory, C. W. *Org. React.* **1984**, *30*, 1–456. (b) Sato, T.; Shimada, S.; Hata, K. *Bull. Chem. Soc. Jpn.* **1967**, *40*, 2484–2490.

[5] Kellogg, R. M. *Comprehensive Heterocyclic Chemistry*; Katritzky, A. R., Rees, C. W., Eds.; Pergamon: Oxford, 1985; Vol. 4, Part 4, p 730.

[6] (a) Kellogg, R. M.; Groen, M. B.; Wynberg, H. *J. Org. Chem.* **1967**, *32*, 3093–3100. See also (b) Güsten, H.; Klasing, L.; Volkert, O. *Z. Naturforsch., B: Anorg. Chem., Org. Chem., Biochem., Biophys. Biol.* **1969**, *24B*, 12–15. (c) Timmons, C. J.; Loader, C. E. *J. Chem. Soc. C* **1967**, 1677–1681. (d) Tiecco, M.; Spagnolo, P.; Martelli, G.; De Luca, G. *J. Chem. Soc. C* **1970**, 2504–2508. (e) Perrine, D. M.; Kagan, J.; Huang, D.-B.; Zeng, K.; Teo, B.-K. *J. Org. Chem.* **1987**, *52*, 2213–2216.

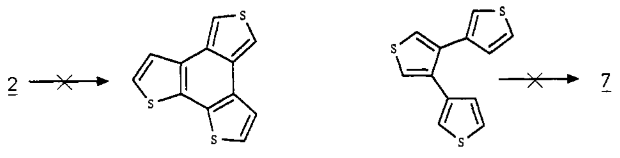
[7] (a) Wynberg, H. *Acc. Chem. Res.* **1971**, *4*, 65–73. (b) Lablanche-Combier, A. In *Thiophene and Its Derivatives*; Gronowitz, S., Ed. [Vol. 44 of *The Chemistry of Heterocyclic Compounds*; Weissberger, A., Taylor, E. C., Eds.]; John Wiley: New York, 1985; Part 1, pp 745–769 and references cited therein.

[8] Wynberg, H.; Kellogg, R. M.; van Driel, H.; Beekhuis, G. E. *J. Am. Chem. Soc.* **1967**, *89*, 3501–3505.

[9] (a) van Tamelen, E. E.; Whitesides, T. H. *J. Am. Chem. Soc.* **1971**, *93*, 6129–6140. (b) Kellogg, R. M. *Tetrahedron Lett.* **1972**, 1429–1432. (c) Mehlhorn, A.; Fratev, F.; Monev, V. *Tetrahedron* **1981**, *37*, 3627–3634.

[10] The 2,4-isomer was not isolated, but the characterization was convincing. Wynberg, H.; van Driel, H.; Kellogg, R. M.; Buter, J. *J. Am. Chem. Soc.* **1967**, *89*, 3487–3494.

Scheme V



13 14

that of the six isomeric methylphenylthiophenes, each isomer of which produced all the others on photolysis.[11] However, the usual absence of β-to-α isomerization reactions does not mean that the starting materials are photochemically inert, since molecular rearrangements of 3-phenylthiophene have been detected,[12] in which the 2-hydrogen of the starting material ended up at the 4- and 5-positions in the photolyzed sample.

This work, therefore, provides a third example of the rearrangement of a β-substituted thiophene into its α-isomer. We note that these examples concern thiophenes bearing aromatic substituents, and another mechanism may also be operative (Scheme IV). Here an initial [2π + 2π]-electrocyclic reaction, analogous to the photorearrangement of 1,3-butadiene to bicyclobutane[13] but involving a π-bond of the central ring and a π-bond of a terminal ring, forms bicyclobutane intermediate **11**. A second step, entirely analogous to the photoextrusion of carbene from 9,10-methanophenanthrene,[14] forms intermediate **12**, the carbene of which then inserts into the adjacent C–H bond to reestablish aromaticity.

Finally, it is worth noting that in principle another mode of oxidative photocyclization for the terthiophenes **2** to **4** could have occurred, as shown for **2** in Scheme V. This would involve utilizing one bond between two β-positions, offering access to benzotrithiophenes such as **13**, which have one or more *c*-fused thiophene rings.[15] No such products were observed, nor could the D_{3h}-symmetric **7** be obtained by irradiation of 3,3′:4′,3″-terthiophene **14**,[3b] its potential precursor.

Experimental Section

Benzo[1,2-*b*:3,4-*b*′:6,5-*b*″]trithiophene (5) from 2,2′:3′,2″-Terthiophene (1). A solution of 1.50 g (0.006 mol) of **1**[3b] and 15 mg of iodine in 500 mL of toluene was irradiated in a quartz vessel placed in a Rayonet apparatus equipped with 15 tubes RPR-3500, emitting between 320 and 400 nm, with a maximum at 350 nm. During the irradiation, a slow stream of air was allowed to bubble through the solution, which was stirred magnetically. The progress of the reaction was monitored by HPLC, and after 25 h of photolysis, the solution was concentrated, the residue was extracted twice with 200 mL of boiling hexanes, and the extracts were filtered under pressure through a 2-cm column of silica gel. The filtrate was concentrated and cooled to yield 1.10 g (74%) of product >98% pure by HPLC. Recrystallization (hexanes) yielded 1.03 g (69%) of **5** as pale yellow crystals: mp 161–166 °C; ^{1}H NMR (acetone-d_6) δ 7.74 (d, 1 H, J = 5.3 Hz), 7.76 (d, 1 H, J = 5.4 Hz), 7.77 (d, 1 H, J = 5.3 Hz), 7.80 (d, 1 H, J = 5.4 Hz), 7.97 (d, 1 H, J = 5.3 Hz), 7.98 (d, 1 H, J = 5.3 Hz); ^{13}C NMR ($CDCl_3$) δ 122.49, 122.67, 122.82, 124.36, 124.40, 124.98, 130.69, 130.99, 131.52, 132.19, 132.68, 132.73; MS *m/e* (relative intensity) 246 (M^+, 100), 201 (26), 170 (13), 169 (12), 93 (27), 69 (23), 45 (31); UV (MeOH) λ_{max} nm (ε) 218 (21 200), 263 (41 100), 272 (47 300), 298 (13 500), 309 (13 000), 320 (sh, 4700), 335 (3000).

Benzo[1,2-*b*:3,4-*b*′:6,5-*b*″]trithiophene (5) from 2,2′:3′,3″-Terthiophene (2). The same procedure, applied to 1.0 g of **2**,[2b] afforded 0.229 g (23%) of recrystallized **5**, mp 162–166 °C, after 16 h of irradiation.

Benzo[1,2-*b*:3,4-*b*′:5,6-*b*″]trithiophene (6) from 2,3′:2′,3″-Terthiophene (4). The same procedure, applied to 1.0 g of **4**,[3a] afforded 0.335 g (34%) of recrystallized **6** after 11 h of irradiation: mp 157–161 °C (lit.[2] mp 161 °C); ^{1}H NMR ($CDCl_3$) δ 7.53 (d, 1 H, J = 5.4 Hz), 7.63 (d, 1 H, J = 5.3 Hz); ^{13}C NMR ($CDCl_3$) δ 122.32, 124.98, 131.44, 131.82; MS *m/e* (relative intensity) 246 (M^+, 100), 214 (9), 201 (23), 123 (16), 93 (14), 69 (16), 45 (15); UV (MeOH) λ_{max} nm (ε) 263 (70 600), 285 (15 000).

Photolysis of 3,2′:3′,3″-Terthiophene (3). Photolysis of **3** until it was consumed resulted in the formation of much material insoluble in MeOH; preparative reverse-phase HPLC (MeOH eluant) of the photolysate fraction which was soluble in MeOH showed at least 10 overlapping peaks. The two overlapping peaks having the same retention times as **5** and **6** were collected, and the fractions were rechromatographed until single peaks were obtained; the UV spectra of these solutions were identical with those of pure **5** and **6**.

Acknowledgment. We are grateful for financial support from the National Institute of Environmental Health Sciences (J.K.) and from a Bristol-Myers Company grant of Research Corporation (D.P.).

---

[11] Wynberg, H.; Beekhuis, G. E.; van Driel, H.; Kellogg, R. M. *J. Am. Chem. Soc.* **1967**, *89*, 3498–3500.

[12] Kellogg, R. M.; Wynberg, H. *J. Am. Chem. Soc.* **1967**, *89*, 3495–3498.

[13] (a) Srinivasan, R. *J. Am. Chem. Soc.* **1963**, *85*, 4045–4046. (b) Srinivasan, R.; Levi, A. A.; Haller, I. *J. Phys. Chem.* **1965**, *69*, 1775–1777. (c) Dauben, W. G.; Wipke, W. T. *Pure Appl. Chem.* **1964**, *9*, 539–553. (d) Woodward, R. B.; Hoffmann, R. *The Conservation of Orbital Symmetry*; Verlag Chemie: Weinheim, 1970; pp 75–78.

[14] Richardson, D. B.; Durrett, L. R.; Martin, J. M., Jr.; Putnam, W. E.; Slaymaker, S. C.; Dvoretzky, I. *J. Am. Chem. Soc.* **1965**, *87*, 2763–2765.

[15] No oxidative photocyclization around a *c*-thiophene bond has ever been observed; see ref 10 for Wynberg's study of 3,4-diphenylthiophene. However, some MO calculations suggest it is possible: Muszkat, K. A.; Seger, G.; Sharafi-Ozeri, S. *J. Chem. Soc., Faraday Trans. 2* **1975**, 1529–1544.