Nonclassical Condensed Thiophenes. II. Tetraphenylthieno[3,4-*c*]thiophene

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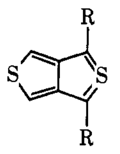
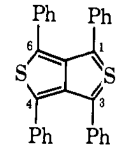
Abstract: Tetraphenylthieno[3,4-*c*]thiophene-2-S^{IV} (**4**) has been synthesized in several steps starting from *sym*-tetrabenzoylethane (**5**). Compound **4** is a remarkably stable, nonpolar, purple material giving no esr signal in solution; it appears to contain sulfur atoms having considerable tetracovalent character. Some simple reactions of **4** are discussed, including catalytic reduction, oxidation, addition of dienophiles, and acid-catalyzed addition of methanol.

In the preceding paper in this series, we described the generation of two disubstituted derivatives (**1** and **2**) of the nonclassical heterocycle thieno[3,4-*c*]thiophene-2-S^{IV} (**3**).[2] The existence of **1** and **2** was shown by trapping experiments, since neither compound was sufficiently stable to permit isolation.[3a]

Several years ago in a preliminary communication, we reported the synthesis of tetraphenylthieno[3,4-*c*]thiophene-2-S^{IV} (**4**), a stable derivative of **3**.[3b] We now report details of this work, as well as considerable new chemistry concerning this unusual compound.



1, R = CH_3
2, R = $COOCH_3$
3, R = H



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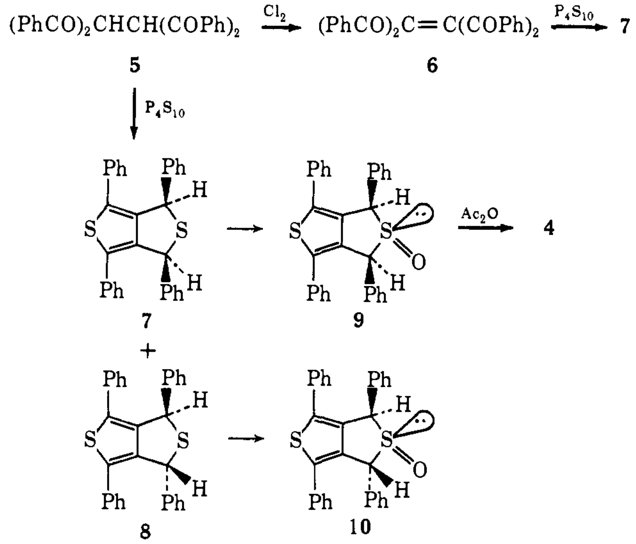
Synthesis of Tetraphenylthieno[3,4-*c*]thiophene-2-S^{IV}. The reaction of phosphorus pentasulfide with either *sym*-tetrabenzoylethane (**5**) or tetrabenzoylethylene (**6**) appeared to offer the most direct approach to the synthesis of tetraphenylthieno[3,4-*c*]thiophene-2-S^{IV} (**4**). The literature synthesis of ketone **5**[4] proved, in our hands, to be quite unsatisfactory. It was found, however, that good syntheses of both **5** and **6** exist in an older unpublished dissertation.[5] In view of the relative inaccessibility of this work, we have included reliable preparations of **5** and **6** in the Experimental Section of this paper.

The reaction of ketone **5** with phosphorus pentasulfide in refluxing xylene afforded, in 40–50% yield, an 85:15 mixture of the two isomeric 1,3-dihydrotetraphenylthieno[3,4-*c*]thiophenes. The readily isolable major isomer (mp 195–196°) and the difficultly isolable minor isomer (mp 160–161°) were assigned the cis and trans configurations (structures **7** and **8**, respectively) on the basis of the nmr spectra of their sulfoxides. Thus, the cis sulfide **7** is oxidized rapidly by periodate[6] to give the single less hindered sulfoxide **9**. The two benzylic hydrogens of **9** are equivalent and appear as a singlet at δ 5.36. The trans sulfide **8** is oxidized by periodate only slowly, both sides of the sulfur being blocked by a phenyl substituent. The resulting single sulfoxide **10** has two benzylic hydrogens which are nonequivalent and which appear as singlets at δ 5.60 and 5.18.[7]



Brief examination of the reaction of tetrabenzoylethylene (**6**) with phosphorus pentasulfide led to the isolation of the cis sulfide **7** in 18–30% yields. Since this reaction offered no synthetic advantage over that of ketone **5**, it was not investigated further.

The readily available cis sulfoxide **9** was dehydrated smoothly in refluxing acetic anhydride to give the crystalline tetraphenylthieno[3,4-*c*]thiophene-2-S^{IV} (**4**) in 87% yield.

Physical and Spectral Properties of Tetraphenylthieno[3,4-*c*]thiophene-2-S^{IV}. Tetraphenylthieno[3,4-*c*]thiophene-2-S^{IV} (**4**) crystallizes from acetic anhydride as glistening reddish-purple needles, mp 257–258°, which appear to be stable indefinitely at room tempera-

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[2] The numbering of the thienothiophene ring system in this paper differs from that in the preceding paper.[3a] According to the numbering used earlier, **4** would be 1,3,4,6-tetraphenylthieno[3,4-*c*]thiophene-5-S^{IV}. The reader should bear in mind that the designation -2-S^{IV} in this paper is that of -5-S^{IV} in *The Ring Index*.

(3) (a) M. P. Cava, N. M. Pollack, and G. A. Dieterle, *J. Amer. Chem. Soc.*, **95**, 2558 (1973); (b) M. P. Cava and G. E. M. Husbands, *ibid.*, **91**, 3952 (1969).

(4) R. D. Abell, *J. Chem. Soc., London, Trans.*, **101**, 997 (1912).

(5) A. Andres, Dissertation, Strassburg, 1911.

(6) N. J. Leonard and C. R. Johnson, *J. Org. Chem.*, **27**, 282 (1962).

(7) This type of argument has been proposed as a general method for the assignment of configuration to *dl* and *meso* sulfides, sulfoxides, and sulfones: C. Y. Meyers and A. M. Malte, *J. Amer. Chem. Soc.*, **91** 2123 (1969).

ture. It has quite nonpolar properties, *i.e.*, it can be crystallized from hexane and is readily eluted from a basic alumina column by hydrocarbon solvents. Its solution in benzene gives no esr signal, showing it to have a singlet ground state. The intense permanganate-like color of solutions of **4** is due to a broad but intense visible band, which has a maximum of 553 nm (log ϵ 4.04) in 1,2-dichloroethane solution.

The mass spectrum of **4** shows it to be a very stable molecule toward fragmentation. The base peak is the molecular ion at 444, the next strongest peak above 130 being the doubly charged molecular ion at 222.

The nmr spectrum of **4** is unusual in that it consists only of a single sharp peak at δ 7.12. This result is inconsistent with either a coplanar or perpendicular arrangement of the phenyl substituents in relation to the heterocyclic nucleus.[8] An intermediate arrangement of the phenyls of **4** has, in fact, been shown to exist in the solid state. Thus, a recent X-ray crystallographic analysis of **4**[9] has shown that the phenyls at C-1 and C-4 are rotated out of the plane of the bicyclic nucleus by 39.6°, while those at C-3 and C-6 are even further (58.4°) out of the bicyclic plane. The X-ray analysis has also revealed some interesting features concerning the heterocyclic nucleus; among these are the relatively short C–S bond length (1.706 Å) and the relatively long C_α–C_β bond length (1.407 Å) and C_β–C_β bond length (1.452 Å), compared with the corresponding values for thiophene[10] (1.714, 1.370, and 1.423 Å, respectively).

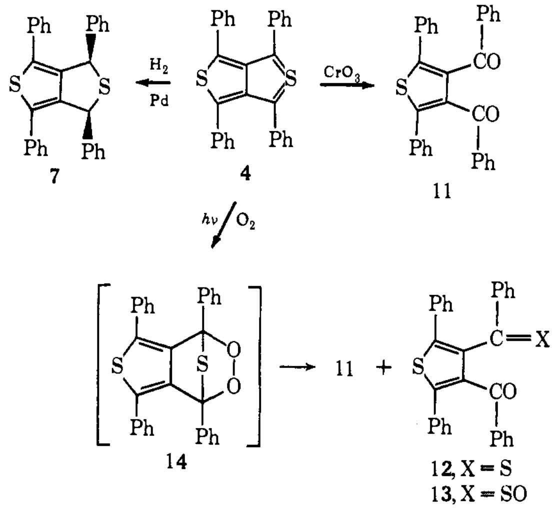
Some Chemical Reactions of Tetraphenylthieno[3,4-*c*]thiophene-2-S^{IV}. As indicated below, we have succeeded in carrying out reactions of **4** with hydrogen, oxygen, chromic acid, methanol, and dienophiles. The common factor in all of these reactions is an addition of reagent to C-1 and C-3 of the thienothiophene system.

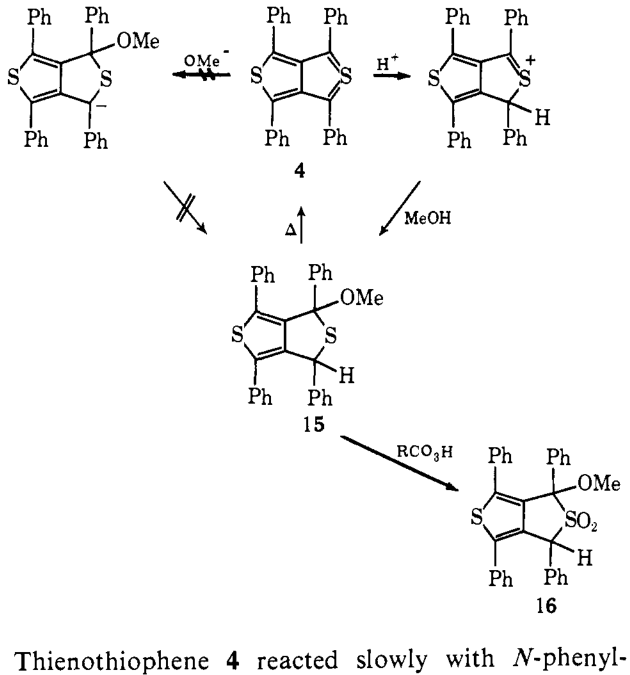
Catalytic reduction of **4** in benzene solution could be achieved in the presence of a large amount of palladium–charcoal catalyst. The cis sulfide **7** was obtained in good yield.

Oxidation of **4** by chromic acid in hot acetic acid proceeded readily to give, in 60% yield, 2,5-diphenyl-3,4-dibenzoylthiophene (**11**), mp 142–143°.

Solutions of **4** in benzene were extremely stable to ultraviolet irradiation in an inert atmosphere. In the presence of oxygen, however, photooxidation took place rapidly, the solution becoming at first green and, eventually, yellow. Isolation of the green product showed it to have the exact composition $C_{30}H_{20}OS_2$; it was assigned the monothioketone structure **12**. The two major yellow photooxidation products could not be separated satisfactorily. One of these was the diketone **11**, and the other (molecular weight = 476) was assumed to have the monosulfine structure **13**; a longer reaction time gave only diketone **11**. Compounds **11**, **12**, and **13** can all arise by way of an initial 1,3 addition of oxygen to **4** to give the intermediate peroxide **14**; ample analogy for this type of photooxidation exists.[11]

In theory, the thieno[3,4-*c*]thiophene system might undergo both acid-catalyzed and base-catalyzed addition reactions. We have been able to add the elements of methanol to **4**, but only under acid-catalyzed conditions. Thus, methanol containing sodium methoxide did not add to **4**. On the other hand, methanol containing sulfuric acid reacted with **4** to give the colorless methoxy sulfide **15**. Compound **15** could not be satisfactorily purified, since it reverted partially to **4** even on attempted recrystallization. Confirmation of **15** as the methanol addition product was obtained by direct peracid oxidation of crude **15** to give the corresponding stable methoxy sulfone **16**.





Thienothiophene **4** reacted slowly with *N*-phenylmaleimide (NPM) in refluxing xylene to give, in high yield, a mixture of two isomeric 1:1 adducts. The major isomer, mp 311–312°, is assigned the endo structure **17** and the minor isomer, mp 274–275°, is assigned the exo structure **18** on the basis of nmr data. Thus, the protons α to the imide carbonyls of **17** appear at lower field (δ 5.16) than the corresponding protons of **18** (δ 4.27), because of the deshielding effect of the sulfur bridge. Analogous effects have been noted for other

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[8] An analogous system occurs in 1,8-diphenylnaphthalene; see H. O. House, R. W. Magin, and H. W. Thompson, *J. Org. Chem.*, 28, 2403 (1963).

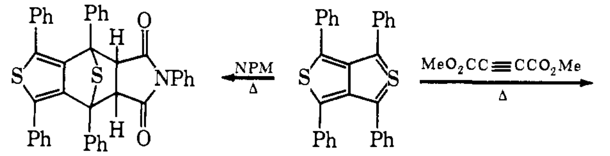
[9] M. D. Glick and R. E. Cook, *Acta Crystallogr., Sect. B*, 28, 1336 (1972).

[10] B. Bak, D. Christensen, L. Hansen-Nygaard, and J. Rastrup-Anderson, *J. Mol. Spectrosc.*, 7, 58 (1961).

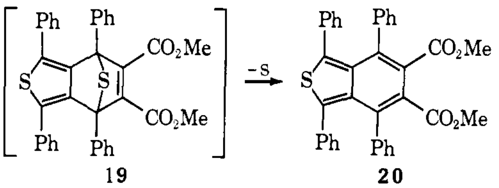
[11] (a) C. N. Skold and R. H. Schlessinger, *Tetrahedron Lett.*, 791 (1970); (b) H. H. Wasserman and W. Strehlow, *ibid.*, 795 (1970); (c) J. M. Hoffman, Jr., and R. H. Schlessinger, *ibid.*, 797 (1970).

related endo–exo adducts pairs containing a sulfur[3a,12] or an oxygen bridge.[13–15]

The reaction of **4** with dimethyl acetylenedicarboxylate in refluxing xylene was much slower than that with NPM, and required over 7 hr. The product, obtained in 80% yield, was not the expected adduct **19**, but rather the isothianaphthene **20**. The spontaneous aromatization of **19** to **20** by the loss of atomic sulfur is analogous to the recently reported formation of phthalonitrile from thiophene and dicyanoacetylene.[16]



17, endo isomer
18, exo isomer
4



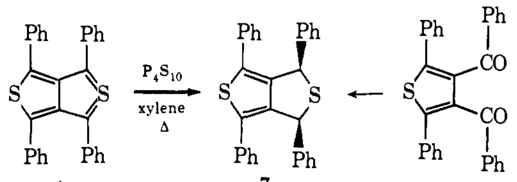
19 **20**

Discussion

The cis sulfide **7** is the key intermediate in the synthesis of thienothiophene **4**. Its synthesis in one operation from tetrabenzoylethane (**5**) or tetrabenzoylethylene (**6**) and phosphorus pentasulfide in xylene poses interesting mechanistic questions. One very likely intermediate in the synthesis should be 2,5-diphenyl-3,4-dibenzoylthiophene (**11**). Although **11** could not be isolated from the reaction products of **5** with phosphorus pentasulfide, it was found that crystalline diketone **11** (prepared from **4**) did indeed afford sulfide **7** on treatment with phosphorus pentasulfide in hot xylene.

Ketones **5**, **6**, and **11** would all be expected to react further with phosphorus pentasulfide to give **4** directly, rather than its dihydro derivative **7**. Small amounts of the intensely purple **4** were visibly present in the reaction mixtures from these ketones; in several runs using ketones **5** and **6**, crystalline **4** was isolated by chromatography in low yield (1–3%). It seemed logical to assume that **4** was initially produced in these reactions and was then being reduced to its dihydro derivatives by the abstraction of benzylic hydrogens from the xylene solvent. In fact, pure **4** was found to be reduced to **7** when refluxed with phosphorus pentasulfide in xylene. Surprisingly, however, no reduction occurred when xylene alone was used. The phosphorus pentasulfide must function in some way to initiate a radical chain reaction between **4** and the xylene.

The observed singlet character of **4** is of interest in view of the predicted triplet ground state of the unsubstituted heterocycle **3**.[17] Ordinarily, this difference would be attributed to conjugative stabilization of the thieno[3,4-*c*]thiophene system by the four phenyl groups. However, if the conformation of the phenyls of dissolved **4** approximates that of the phenyls of crystalline **4**[9] (as suggested by the nmr of **4**) then these substituents must be stabilizing the heterocyclic nucleus more by steric hindrance than by conjugation. We plan to test this hypothesis by attempting the synthesis of a derivative of **3** stabilized only by bulky alkyl groups.



4 **7** **11**

Experimental Section

General. Melting points are uncorrected. Elemental analyses were reported in the original manuscript and were consistent with the assigned formulas within the limits ±0.3% for compounds **4**, **7–12**, **16–18**, and **20**. Spectra were recorded on a Perkin-Elmer Model 137 ir spectrophotometer, a Perkin-Elmer Model 202 uv-visible spectrophotometer, a Varian A-60A nmr spectrometer, a Perkin-Elmer Model 270B mass spectrometer, and a Perkin-Elmer Model MS-9 mass spectrometer (for exact mass determinations only). Separations by preparative thin-layer chromatography (ptlc) were carried out on silica plates using the indicated solvent as developer.

Dibenzoyliodomethane. Bromine (115 g, 0.72 mol) was added dropwise to a stirred solution of dibenzoylmethane (150 g, 0.67 mol) and sodium acetate (65.0 g, 0.79 mol) in 1000 ml of acetic acid. The reaction mixture was poured into water (5000 ml) and the precipitate was crystallized from 95% ethanol to give dibenzoylbromomethane (169.5 g, 84%), mp 91–91.5°.

A solution of sodium iodide (82.5 g, 0.55 mol) in water (550 ml) was added dropwise to a stirred solution of dibenzoylbromomethane (169 g, 0.55 mol) in a mixture of 95% ethanol (550 ml) and acetone (500 ml). The yellow crystalline precipitate was filtered, washed with water, and dried to give dibenzoyliodomethane (187 g, 95%), mp 100° (lit.[5] 104–105°).

***sym*-Tetrabenzoylethane (5).** Sodium (12 g, 0.54 mol) was dissolved in dry methanol (250 ml), and the resulting solution was added dropwise with stirring to a solution of dibenzoylmethane (112 g, 0.5 mol) in hot dry methanol (750 ml). After refluxing for 30 min, the mixture was cooled and the pale yellow dibenzoylsodiomethane was separated by filtration and dried. Additional material was obtained by concentration of the mother liquor; the total yield was 118 g (96%).

A solution of dibenzoyliodomethane (167 g, 0.477 mol) in acetone (500 ml) was added with cooling to a solution of dibenzoylsodiomethane (120 g, 0.488 mol) in acetone (600 ml). After stirring at room temperature for 22 hr, the precipitate was filtered and recrystallized from acetic acid to give tetrabenzoylethane (**5**, 115 g, 55%), mp 211–213° (lit.[5] 215°).

Tetrabenzoylethylene (6). A suspension of tetrabenzoylethane (**5**, 3.0 g, 6.6 mmol) in acetic acid (60 ml) was heated to reflux for 40 min while a stream of chlorine was passed through the mixture. The clear hot solution was cooled and diluted slowly with cold water to give tetrabenzoylethylene (**6**, 2.3 g, 76%), mp 182–183° (lit.[5] 184°).

Reaction of Tetrabenzoylethane (5) with Phosphorus Pentasulfide. A suspension of tetrabenzoylethane (**5**, 3.0 g, 6.6 mmol) and phosphorus pentasulfide (4.0 g, 14 mmol) in xylene (160 ml) was refluxed with stirring for 3 hr. The supernatant xylene solution was decanted, and the dark residue was extracted with boiling benzene. Evaporation of the xylene and benzene solutions gave residues which were combined, taken up in a small amount of chloroform, and adsorbed on a 40 g silica column. Elution with hexane and benzene gave a green residue which was fractionally crystallized

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[12] M. P. Cava, N. M. Pollack, O. A. Mamer, and M. J. Mitchell, *J. Org. Chem.*, **36**, 3932 (1971).

[13] R. Breslow, G. Ryan, and J. T. Groves, *J. Amer. Chem. Soc.*, **92**, 988 (1970).

[14] M. P. Cava and An-Fei C. Hsu, *ibid.*, **94**, 6441 (1972).

[15] In our preliminary communication, the reversed assignments of configuration were made for adducts **17** and **18** on the belief that the bridgehead phenyls of the exo adduct were greatly deshielding the protons alpha to the carbonyls. Recent nmr data concerning endo–exo adduct pairs derived from 1,3-diphenylisobenzofuran[13,14] indicate that this type of deshielding by a bridgehead phenyl does not in fact occur.

[16] R. Helder and H. Wynberg, *Tetrahedron Lett.*, 605 (1972).

[17] D. T. Clark, *Tetrahedron*, **24**, 2567 (1968).

from cyclohexane. The first fractions afforded the less soluble *cis*-1,3,4,6-tetraphenyl-1*H*,3*H*-thieno[3,4-*c*]thiophene (**7**, 1.0 g): mp 197–198°; nmr ($CDCl_3$) δ 5.80 (s, 2 H); mass spectrum 446 (M^+, 100%), 369 ($M - C_6H_5^+$, 20%); uv spectrum $\lambda_{max}^{dioxane}$ 225 nm ($\log \epsilon$ 4.37), 240 sh (4.21), 317 (4.29).

The later, more soluble fractions from the cyclohexane afforded the crude trans sulfide **8** (0.20 g), mp 153–154°. Expansion of the nmr of this material in the δ 5.8 region showed it to be a 9:1 mixture of trans and cis isomers (**8** and **7**). Further purification was effected by partial periodate oxidation, which converts **7** more rapidly into a sulfoxide, followed by ptlc (chloroform) separation. The pure *trans*-1,3,4,6-tetraphenyl-1*H*,3*H*-thieno[3,4-*c*]thiophene (**8**) melted at 160–161°, nmr ($CDCl_3$) δ 5.82 (s, 2 H), mass spectrum 446 (M^+, 100%).

The total yield of **7** and **8** was 40%, in a ratio of 85:15, respectively.

In another reaction of **5** with phosphorus pentasulfide, the crude reaction product was chromatographed on a dry column of alumina (N–I) to give (hexane elution) a small yield (1.6%) of crystalline thienothiophene **4** in addition to the mixture of **7** and **8**.

Reaction of Tetrabenzoylethylene (6) with Phosphorus Pentasulfide. A suspension of tetrabenzoylethylene (**6**, 1.0 g, 2.2 mmol) and phosphorus pentasulfide (1.0 g) was refluxed in xylene for 1 hr. Evaporation of the xylene phase, followed by chromatography on alumina (basic I, $CHCl_3$, eluent) and crystallization from cyclohexane gave cis sulfide **7** (0.182 g, 18%), mp 188–192°. Chloroform extraction of the reaction residue, followed by alumina chromatography (purple band collected), afforded thienothiophene **4** (0.011 g, 1%), mp 215–220°.

Reaction of Diketone 11 with Phosphorous Pentasulfide. A mixture of 2,5-diphenyl-3,4-dibenzoylthiophene (0.025 g) and phosphorous pentasulfide (0.035 g) was added to xylene (5 ml) and the mixture was refluxed for 3 hr. The reaction mixture was evaporated and the residue was dissolved in a small amount of chloroform. Purification by ptlc (cyclohexane–benzene 9:1 developer) gave 0.012 g (48%) of cis sulfide **7**, mp 188–190°.

***cis*-1,3,4,6-Tetraphenyl-1*H*,3*H*-thieno[3,4-*c*]thiophene 2-Oxide (9).** A solution of sodium periodate (2.45 g, 11 mmol) in water (36 ml) was added to a solution of sulfide **7** (2.79 g, 6 mmol) in 225 ml of benzene and 225 ml of methanol. After refluxing for 2.5 hr, the hot solution was filtered and the filtrate was evaporated to dryness. Water (25 ml) was added, and the suspension was heated (steam bath) for a short while, filtered, and dried to give pure sulfoxide **9** (2.88 g, ~100%): mp 238–239°; ir (KBr) 9.45 μ (S=O); mass spectrum 462 (M^+); uv spectrum $\lambda_{max}^{dioxane}$ 230 nm ($\log \epsilon$ 4.30), 320 4.21); nmr ($CDCl_3$) δ 5.36 (s, 2 H).

***trans*-1,3,4,6-Tetraphenyl-1*H*,3*H*-thieno[3,4-*c*]thiophene 2-Oxide (10).** A solution of sodium periodate (0.15 g, 0.7 mmol) in water (2 ml) was added to a solution of trans sulfide **8** (0.100 g, 0.22 mmol) in 10 ml of benzene and 10 ml of methanol. After refluxing for 3.5 hr, the mixture was worked up as in the preparation of cis sulfoxide (see previous experiment). Separation of the crude product by ptlc ($CHCl_3$ developer) gave 0.018 g of recovered sulfide **8** and 0.028 g of trans sulfoxide **10**: mp 227–228°; ir (KBr) 9.45 μ (S=O); mass spectrum 462 (M^+); nmr ($CDCl_3$) δ 5.60 (s, 1 H), 5.18 (s, 1 H).

Tetraphenylthieno[3,4-*c*]thiophene-*2-S*^{IV} (4). A mixture of sulfoxide **7** (2.0 g, 4.3 mmol) and acetic anhydride (80 ml) was refluxed under nitrogen for 4 hr. After cooling to room temperature, filtration gave glistening, reddish-purple needles of thienothiophene **4** (1.70 g, 87%): mp 257–258°; nmr ($CDCl_3$) δ 7.12 (s); mass spectrum 444 (M^+, 100%); 222 (M^{2+}, 11%); uv–visible spectrum $\lambda_{max}^{C_2H_4Cl_2}$ 265 nm ($\log \epsilon$ 4.44), 295 (4.42), 553 (4.04).

Reduction of Thienothiophene 4. A. By Phosphorus Pentasulfide in Xylene. A mixture of thienothiophene **4** (0.050 g), phosphorus pentasulfide (0.050 g), and xylene (3 ml) was refluxed (nitrogen) for 3 hr. Colorimetric analysis (at 553 nm) showed that only 1.7% of the original **4** was present. The usual work-up, followed by crystallization from cyclohexane, afforded cis sulfide **7** (0.029 g, 58%), mp 196–198°. (The mother liquor was not worked up for the trans isomer.)

B. By Catalytic Hydrogenation. A solution of **4** (0.100 g) in benzene (100 ml) was shaken under hydrogen (room temperature) in the presence of 5% palladium–charcoal (1.0 g) until the purple-red color vanished. Evaporation of the filtered solution gave cis sulfide **7** (0.080 g, 80%), mp 196°.

Oxidation of Thienothiophene 4. A. By Chromium Trioxide. Finely ground chromium trioxide (0.10 g) was added to a suspension of thienothiophene **4** (0.10 g, 0.22 mmol) in acetic acid (5 ml). After heating for 5 min on the steam bath, the mixture was diluted with water. Extraction with chloroform, followed by the usual work-up, gave 0.080 g of yellow crystalline product. Purification by ptlc (benzene–chloroform 1:1 developer) and crystallization from cyclohexane gave pure 2,5-diphenyl-3,4-dibenzoylthiophene (**11**): mp 142–143°; ultraviolet spectrum $\lambda_{max}^{dioxane}$ 270 nm ($\log \epsilon$ 4.81); mass spectrum 444 (M^+); nmr ($CDCl_3$) δ 7.6–7.9 (m, 4 H), 7.0–7.5 (m, 16 H).

In an earlier oxidation experiment, in which all of the product was consumed for analysis, diketone **11** was obtained in a high-melting form, mp 184°.

B. By Oxygen and Light. A solution of thienothiophene **4** (0.10 g) in benzene (250 ml) was irradiated (Pyrex filter) by a high-pressure Hanovia lamp while oxygen was passed through the solution. When the solution became green, concentration followed by ptlc (benzene–chloroform 4:1 developer) allowed the isolation of the green product, thioketone **12**, mp 110–115°, mol wt (mass spectra) 460.0939.

In another experiment on the same scale, the photooxidation was continued until the green color faded to yellow (~25 min). Separation of the products by ptlc (benzene-chloroform 1:1 developer) gave diketone **11** (30 mg), and a pale yellow product, mp 55–100°, mol wt 476 (mass spectra), assumed to be sulfine **13**.

In a third experiment, photooxidation was continued for 7 hr. Isolation by ptlc revealed none of the presumed sulfine **13**; diketone **11** (mp 139–142°) was isolated in 50% yield.

Reaction of Thienothiophene 4 with Methanol. A. Under Acidic Conditions. A solution of sulfuric acid (4 drops) in methanol (4 ml) was added to a solution of thienothiophene **4** (0.100 g, 0.22 mmol) in benzene (10 ml). After stirring at room temperature (N_2) for 4 hr, the colorless solution was treated with 40% peracetic acid (5 ml). After a further 40 min of stirring, the mixture was heated on a steam bath for 5 min, neutralized (aqueous NH_4OH), and extracted with chloroform. Evaporation of the dried chloroform gave methoxy sulfone **16** (0.110 g, 96%), mp 215–220° dec. Crystallization from chloroform–ethanol gave analytically pure **16**: mp 228–229° dec; nmr ($CDCl_3$) δ 7.0–7.5 (m, 20 H), 5.60 (s, 1 H), 3.80 (s, 3 H).

B. Under Basic Conditions. A mixture of **4** (0.05 g), benzene (10 ml), and 10% methanolic KOH (3 ml) was stirred at room temperature (N_2) for 4 hr. Colorimetric analysis (at 553 nm) showed virtually no disappearance of **4**.

Addition of Dienophiles to Thienothiophene 4. A. *N*-Phenylmaleimide. A solution of thienothiophene **4** (0.200 g, 0.45 mmol) and *N*-phenylmaleimide (0.080 g, 0.45 mmol) was refluxed (N_2) in xylene (10 ml) for 1.5 hr. Concentration of the colorless solution and cooling gave 0.16 g of endo adduct **17**: mp 311–312°; mol wt (mass spectra) 617 M^+; nmr ($CDCl_3$) δ 7.5–7.8 (m), 7.4–6.8 (m), and 5.16 (s, 1 H).

The residues from the addition reaction were separated by ptlc ($CHCl_3$ developer) to give a further 0.040 g of **17** and 0.035 g of exo adduct **18**: mp 274–275°; mol wt (mass spectra) 617 (M^+); nmr ($CDCl_3$) δ 6.7–7.5 (m) and 4.27 (s, 1 H).

The total yield of **17** and **18** was 0.235 g (84%).

B. Dimethyl Acetylenedicarboxylate. A solution of thienothiophene **4** (0.200 g, 0.45 mmol) and dimethyl acetylenedicarboxylate (0.080 g, 0.56 mmol) in xylene (10 ml) was refluxed (N_2) for 7.5 hr. Concentration of the solution and cooling gave, in several crops, orange crystals (0.192 g, 80%), of isothianaphthene **20**, mp 255°. Recrystallization from cyclohexane–benzene gave yellow crystals of pure **20**: mp 255°; mol wt (mass spectroscopy) 554 (M^+); nmr ($CDCl_3$) δ ~6.9 (m, 20 H), 3.40 (s, 6 H); uv $\lambda_{max}^{dioxane}$ 273 nm ($\log \epsilon$ 5.01), 390 (4.00).

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