carried out on a Hewlett-Packard F & M 5752 gas chromatograph. The infrared spectra were recorded on a Beckman IR-8 instrument and the absorpton values are reported in microns.

1,3-Dioxacycloheptane, 1,3-dioxacyclohept-4-ene,[25] 2-methyl-1,4-butanediol,[26] and 1,4-pentanediol[27] were prepared as described in the literature.

1,3-Dioxacycloheptanes. General Procedure.—The preparation of 4-methyl-1,3-dioxacycloheptane is described as a representative example. A mixture of 10.4 g (0.1 mol) of 1,4-pentanediol, 3.0 g (0.1 mol) of paraformaldehyde, 100 ml of benzene, and 50 mg of *p*-toluenesulfonic acid was refluxed using a Dean–Stark distillation trap. The reaction was terminated when 1.8 ml of water was evolved. The mixture was fractionally distilled at atmospheric pressure to give 10.8 g (89%) of the desired product: bp 105–107° (760 Torr); n^{25}_{D} 1.4226; ir (neat) 3.41, 8.46, 8.71, 8.90 μ; *m/e* 116 (parent peak).

4,7-Dimethyl-1,3-dioxacycloheptane.—The mixture of isomers had bp 65° (760 Torr) and the yield was 37%. The relative concentrations of the isomers were 78% cis and 22% trans. The diastereoisomers were separated by glpc (8 ft 10% Apiezon–Chromosorb column). The trans isomer was the first peak: n^{25}_{D} 1.4269; ir 3.43, 3.49, 7.32, 8.68, 8.87, 9.09, and 9.26 μ; ^{1}H nmr CH_2(5,6) 8.27 ppm; *m/e* 130 (parent peak).

The cis isomer was the second peak: n^{25}_{D} 1.4214; ir (neat) 3.38, 3.44, 7.35, 8.68, 8.87, and 9.06 μ; *m/e* 130 (parent peak).

2-*tert*-Butyl-4-methyl-1,3-dioxacycloheptane.—The mixture of isomers was distilled at 35° (1 Torr) and the yield was 72%. The isomers were separated by glpc (8 ft 10% Apiezon–Chromosorb column) and the cis isomer was the first peak: n^{25}_{D} 1.4291; ir 3.43, 3.49, 6.74, 8.77, 9.15, and 9.52 μ; ^{1}H nmr *tert*-butyl 9.15, CH_2 (5,6) multiplet 8.30 ppm; ^{13}C nmr *tert*-butyl (C) 36.64, *tert*-butyl (CH_3) 25.10 ppm; *m/e* 116 (P − *tert*-butyl).

The trans isomer was the second peak: n^{25}_{D} 1.4304; ir (neat) 3.41, 3.49, 6.73, 8.82, 9.03, 9.21, and 9.47 μ; ^{1}H nmr (CCl_4) *tert*-butyl 9.15, CH_2(5,6) multiplet 8.33 ppm; ^{13}C nmr *tert*-butyl (C) 36.21, *tert*-butyl (CH_3) 25.36 ppm.

2-*tert*-Butyl-5-methyl-1,3-dioxacycloheptane.—The mixture of isomers was isolated in 45% yield: bp 44° (1 Torr); n^{25}_{D} 1.4323; ir (neat) 3.38, 3.48, 6.79, 6.90, 7.38, 8.33, and 8.93 μ; ^{1}H nmr (CCl_4) *tert*-butyl 8.92; ^{13}C nmr *tert*-butyl (C) 36.57, *tert*-butyl (CH_3) 25.17; *m/e* 116 (P − *tert*-butyl).

4-Methyl-1,3-dioxacycloheptane.—The product was isolated in 89% yield: bp 105° (760 Torr); n^{25}_{D} 1.4226; ir (neat) 3.41, 8.46, 8.71, and 8.90 μ; ^{1}H nmr (CCl_4) Me 8.83, OCH_2O 5.32, CH 6.15, OCH_2C multiplet at 6.26 ppm; *m/e* 116 (parent peak).

5-Methyl-1,3-dioxacycloheptane.—The product was isolated in 44% yield: bp 48° (0.3 Torr); n^{25}_{D} 1.4266; ir (neat) 3.41, 8.71, 8.90, and 9.43 μ; ^{1}H nmr (CCl_4) Me 9.33, OCH_2O 5.37, CH_2-OCH_2O multiplet 6.49, CH 8.41, CH_2 multiplet 8.35 ppm; *m/e* 116 (parent peak).

Equilibration of *cis*-2-*tert*-Butyl-4-methyl-1,3-dioxacycloheptane.—A 50-ml three-neck flask equipped with a condenser, thermometer, and drying tube was charged with 0.54 g of *cis*-2-*tert*-butyl-4-methyl-1,3-dioxacycloheptane, 5 mg of *p*-toluenesulfonic acid, and 10 ml of dry benzene. The mixture was heated to reflux for periods of 8, 24, and 148 hr and analyzed by glpc. The response ratio for the glpc was found to be 1.0. The equilibrium ratios were identical with those found by integrating the C(2) proton areas of the nmr spectra. The cis:trans equilibrium ratio was found to be 1.91:1.

Equilibration of *trans*-2-*tert*-Butyl-4-methyl-1,3-dioxacycloheptane.—The procedure for this equilibration was the same as described for the cis isomer. The cis:trans equilibrium ratio was 1.9:1.

Acknowledgment.—Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

Registry No.—1,4-Pentanediol, 626-95-9.

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[25] K. C. Branncock and G. Lappin, *J. Org. Chem.*, **21**, 1366 (1956).

[26] R. Rossi, P. Diversi, and G. Ingrosso, *Gazz. Chim. Ital.*, **98**, 391 1968).

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Nonclassical Condensed Thiophenes. III. Studies in the Benzo[1,2-*c*:4,5-*c'*]dithiophene System

M. P. CAVA* AND M. A. SPRECKER

Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19174

Received April 2, 1973

The reaction of phosphorus pentasulfide and xylene with 1,2,4,5-tetrabenzoylbenzene (**13**) and with 1,3,6,7-tetraphenyl-4,5-dibenzoylisothianaphthene (**19**) affords 4,8-dihydro-1,3,5,7-tetraphenylbenzo[1,2-*c*:4,5-*c'*]dithiophene (**14**) and 4,8-dihydrohexaphenylbenzo[1,2-*c*:4,5-*c'*]dithiophene (**20**), respectively. Dehydrogenation of **14** and **20** affords diketones **18** and **19**. The intermediacy of **9** and **10** in these transformations is consistent with similar reactions carried out on the recently synthesized compound **10**.

We have reported the synthesis of a number of nonclassical isocondensed thiophenes for which the only uncharged resonance contributors are those structures containing tetracovalent sulfur (**1–3**).[1] Other five-membered heterocycles containing tetracovalent sulfur have been reported. In these compounds, at least one sulfur is directly bonded to a heteroatom (**4–6**)[2,3] or is in conjugation with a heteroatom whose lone electron pair is not used in π bonding (**7** and **8**).[4] We have now examined an approach to the synthesis of several derivatives (**9** and **10**) of the benzo[1,2-*c*:4,5-*c'*]dithiophene system which, although unsuccessful, involves the generation of compounds **9** and **10** as reaction intermediates.[5]

Tetrakisbromodurene (**11**)[6] was converted to 1,2,4,5-tetrabenzylbenzene (**12**) by reaction with benzene in the presence of anhydrous ferric chloride.[7] Chromic acid oxidation of **12** afforded the corresponding tetraketone **13** in 70% yield.[8] Treatment of **13** with phosphorus pentasulfide in boiling xylene yielded, as the

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[1] (a) M. P. Cava and G. E. M. Husbands, *J. Amer. Chem. Soc.*, **91**, 3952 (1969), and references cited therein; (b) M. P. Cava and M. A. Sprecker, *ibid.*, **94**, 6214 (1972); (c) for a general review of this work see M. P. Cava, *Int. J. Sulfur Chem.*, in press.

[2] M. Carmack, R. W. Street, and R. Y. Wen, 158th National Meeting of the American Chemical Society, New York, N. Y., Sept 1969, Abstract ORGN-54.

[3] J. D. Bower and R. H. Schlessinger, *J. Amer. Chem. Soc.*, **91**, 6891 (1969).

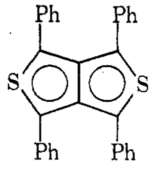
[4] K. T. Potts and D. McKeough, *J. Amer. Chem. Soc.*, **94**, 6215 (1972).

[5] The isolation of crystalline compound **10** was reported after the writing of the first draft of this paper: K. T. Potts and D. McKeough, *J. Amer. Chem. Soc.*, **95**, 2750 (1973).

[6] W. Reid and H. Boden, *Ber.*, **89**, 2328 (1956).

[7] The preparation of **12** from the less readily available tetrakischlorodurene has been reported: V. G. Drechler and W. Genill, *J. Prakt. Chem.*, **26**, 24 (1964).

[8] E. Profft, V. G. Drechler, and H. Oberender, *Chem. Abstr.*, **55**, 2564 (1961).



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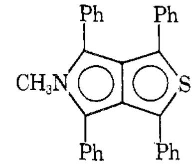

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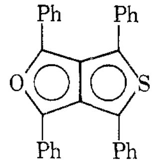

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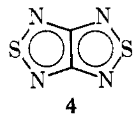

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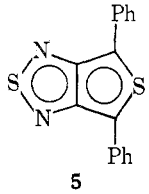

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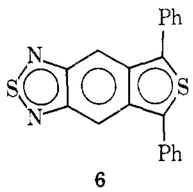

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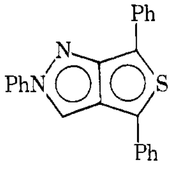

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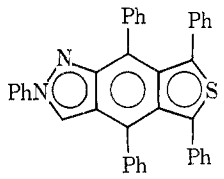

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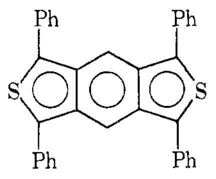

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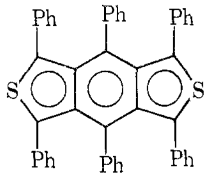
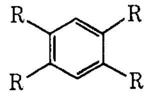


10

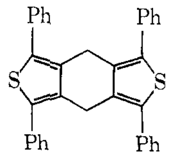
only isolable product (15%), 4,8-dihydro-1,3,5,7-tetraphenylbenzo[1,2-*c*:3,4-*c'*]dithiophene (**14**).

The assigned structure of dithiophene **14** was supported by its spectral properties, which were inconsistent with the anticipated isothianaphthene structure **15**. Compound **15** would be expected to show visible adsorption near 388 nm, which is the observed value for 1,3-diphenylbenzo[*c*]thiophene **16**.[9] The observed uv spectrum for **14**, however, is quite similar to that of 1,3-dihydrotetraphenylthieno[3,4-*c*]thiophene (**17**), which has a similar chromophore. Furthermore, the benzylic protons of **14** appear at δ 4.05 (four-proton singlet), as compared to the corresponding protons at δ 5.80 (two proton singlet) observed for the dihydrothienothiophene **17**, a model for the isomeric sulfide **15**.[10]

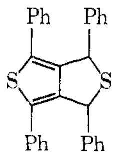
Attempted dehydrogenation of **14** to the fully aromatic compound **9** by DDQ in boiling *o*-dichlorobenzene resulted in the partial conversion of **14** to diketone **18**.[11] Similar treatment of degassed solutions of **14** with DDQ and tetracyanoethylene,[12] respectively, resulted only in the isolation of small amounts of starting material.



11, $R = CH_2Br$
12, $R = CH_2Ph$
13, $R = COPh$



14



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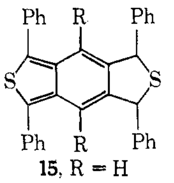
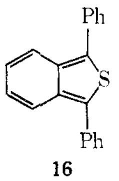
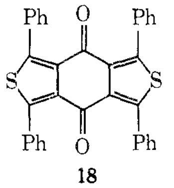


15, R = H
25, R = Ph



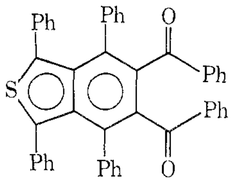
16



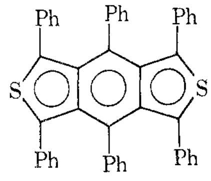
18

The reaction of dibenzoylacetylene with thienothiophene **1**[1a] yielded 4,5-dibenzoyltetraphenylisothianaphthene (**19**).[13] When diketone **19** was refluxed for a short time with phosphorus pentasulfide in xylene under nitrogen, the solution exhibited a deep blue color. The blue product, which was apparently benzodithiophene **10**, could not be isolated chromatographically owing to its sensitivity to oxygen. When the original reaction was run for several hours, the blue color slowly faded and the colorless 4,8-dihydrohexaphenylbenzo[1,2-*c*:4,5-*c'*]dithiophene (**20**) was formed in 70% yield.[14]

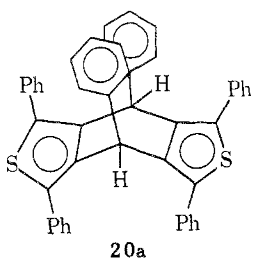
Molecular models indicate that the least hindered configuration of **20** is the *cis*-4,8-diphenyl isomer with the central phenyl groups occupying axial positions as shown in **20a**. The nmr exhibits a singlet at δ 5.80 (2 H) and two aromatic multiplets at 6.55–6.70 (10 H) and 7.02–7.42 (20 H). The benzylic protons absorb approximately 0.5 ppm downfield from the observed signal in 9,10-dihydro-9,10-diphenylanthracene, indicating that they are deshielded by adjacent phenyl groups.[15] Furthermore, the aromatic adsorptions correspond to four normal and two shielded (axial) phenyl groups, fully consistent with the structure assigned in **20a**.



19



20



20a

The attempted aromatization of **20** by DDQ in boiling *o*-dichlorobenzene resulted in partial oxidation to isothianaphthene **19**. Treatment of degassed solutions of **19** with DDQ and tetracyanoethylene, as before, resulted only in the isolation of small amounts of starting material.

Discussion

After the completion of the work described above, other workers reported that the reaction of diketone **19**

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[9] M. P. Cava and J. McGrady, *Chem. Commun.*, 1648 (1968).

[10] M. P. Cava, M. Behforouz, G. E. M. Husbands, and M. Srinivasan, *J. Amer. Chem. Soc.*, **95**, 2561 (1973).

[11] DDQ has been used to generate and trap pleiadene as a Diels–Alder adduct: J. W. Loun and A. S. K. Aidoo, *Can J. Chem.*, **49**, 1848 (1971).

[12] Tetracyanoethylene has been used to generate and trap anthracene from 9,10-dihydroanthracene: D. T. Longone and G. L. Smith, *Tetrahedron Lett.*, 205 (1962).

[13] The reaction of tetravalent thiophene derivatives with dienophiles is well documented. See ref 1 and 4.

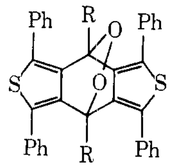
[14] The unsubstituted 4,8-dihydrobenzo[1,2-*c*:4,5-*c'*]dithiophene has been synthesized by D. W. H. MacDowell and J. C. Wisowaty, *J. Org. Chem.*, **37**, 1712 (1972).

[15] The benzylic protons of 9,10-dihydro-9,10-diphenylanthracene are found at δ 5.28: W. Theilacker, K. Albrecht, and H. Uffman, *Ber.*, **98**, 428 (1965).

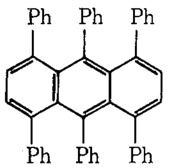
with phosphorus pentasulfide in pyridine afforded **10** as a blue, crystalline solid.[5] We have repeated the preparation of **10** and found that, when **10** was refluxed with phosphorus pentasulfide in xylene, decolorization took place with the formation of the dihydro compound **20**. This reaction is analogous to the reduction of the stable thienothiophene **1** under similar conditions.[10]

The reduction of **9** and **10** could theoretically proceed in either of two ways to yield isothianaphthenes (**25** and **15**) or dithiophenes (**14** and **20**). The formation of the dithiophenes as the only isolable products is a consequence of the greater delocalization energy of two isolated thiophene units as compared with a single isothianaphthene unit.[16] Thus the conversion of diketones **13** and **19** to the reduced dithiophenes provides good evidence for the intermediate formation of benzodithiophenes **9** and **10**.

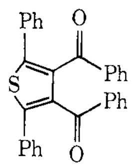
The oxidative dehydrogenation of dihydro compounds **14** and **20** to diketones **18** and **19** is also most readily explained as proceeding *via* benzodithiophenes **9** and **10**. In the tetraphenyl case, dehydrogenation to the fully unsaturated heterocycle **9**, followed by addition of oxygen across the central ring, would yield dione **18** *via* peroxide **21**, a process analogous to the photooxidation of anthracene to anthraquinone.[17] In the hexaphenyl case, the addition of oxygen could proceed reversibly to afford the corresponding peroxide (**22**), as is observed for hexaphenylanthracene (**23**).[18] However, addition of oxygen across either five-membered ring would yield diketone **19** *via* the formation of an unstable thioozonide intermediate.[19] A similar reaction is observed in the oxidation of thienothiophene **1** to the dibenzoylthiophene **24**.[10]



21, R = H
22, R = Ph



23



24

With the recent availability of crystalline **10**, we investigated the behavior of this compound under our oxidation conditions. When a benzene solution of **10** was warmed with DDQ in the presence of air, rapid oxidation was observed with the formation of diketone **19**. Indeed, a solution of **10** in xylene was oxidized slowly to **19** by air alone at room temperature.[20]

In view of the high reactivity of the isolable hexaphenyldithiophene **10**, it is not surprising that the less substituted tetraphenyl analog, **9**, would be an even more reactive species. Indeed, an attempted synthesis of **9** from tetrabenzoylbenzene (**13**) and the phosphorus pentasulfide–pyridine reagent gave only a complex mixture of unidentified yellow products under conditions which convert **19** into **10** in virtually quantitative yield.

Experimental Section

General.—Melting points are uncorrected. Elemental analyses were carried out by Midwest Microlabs, Indianapolis, Ind. Spectra were recorded on a Perkin-Elmer Model 137 ir spectrophotometer, a Perkin-Elmer Model 202 uv–visible spectrophotometer, a Varian Model HA-100D nmr spectrometer, a Perkin-Elmer Model 270B mass spectrometer, and a Varian V-4502 esr spectrometer. Recovered starting materials were identified (ir, tlc) by comparison with authentic samples.

1,2,4,5-Tetrabenzylbenzene (**12**).—A mixture of anhydrous ferric chloride (1.0 g) and **11** (10 g) in benzene (150 ml) was refluxed overnight. Evaporation and chromatography (300 g of neutral grade I alumina, 10% benzene–hexane) yielded **12** as a white, crystalline solid (4.9 g, 48%), mp 132–135° (lit.[7] mp 140°).

1,2,4,5-Tetrabenzoylbenzene (**13**).—The oxidation of **12** to **13** has been previously reported, but without experimental details.[8]

A slurry of **12** (1.79 g, 3.9 mm) and chromium trioxide (3 g, 30 mm) in acetic acid (200 ml) was refluxed for 2 hr. Upon addition of water, a light green powder was recovered. Recrystallization from acetic acid yielded **13** as colorless plates (1.25 g, 70%), mp 259–261° (lit.[8] mp 261–263°).

1,3,5,7-Tetraphenyl-4*H*,8*H*-benzo[1,2-*c*:4,5-*c'*]dithiophene (**14**).—A mixture of tetrabenzoylbenzene (2 g) and phosphorus pentasulfide (2 g) was refluxed (N_2) in 200 ml of xylene for 3 hr. The solvent was evaporated *in vacuo* and the residue was dissolved in a small portion of benzene and chromatographed on neutral grade I alumina (100 g) using benzene–hexane (1:10) as the eluent. The resulting yellow solution afforded **14** as colorless prisms (290 mg, 14.5%) after recrystallization from benzene: mp >320°; nmr (C_4Cl_6 at 180°) δ 4.05 (s, 4 H), 7.02–7.46 (m, 20 H); uv ($C_2H_4Cl_2$) λ_{max} 262 nm (log ϵ 4.53), 306 (4.50); mass spectrum *m/e* 496 (M^+).

Anal. Calcd for $C_{34}H_{24}S_2$: C, 82.24; H, 4.87; S, 12.89. Found: C, 82.50; H, 4.98; S, 13.17.

1,3,5,7-Tetraphenyl-4*H*,8*H*-benzo[1,2-*c*:4,5-*c'*]dithiophene-4,8-dione (**18**).—A solution of DDQ (150 mg, 0.5 mmol) and dithiophene **14** (100 mg, 0.2 mmol) was refluxed overnight in 15 ml of *o*-dichlorobenzene. The solvent was removed *in vacuo* and the black residue was dissolved in a small portion of benzene and chromatographed (40 g of grade I neutral alumina). Benzene elution yielded **14** (10 mg, 10%). Chloroform elution afforded an orange solution which upon evaporation and crystallization from benzene yielded yellow crystals of **18** (40 mg, 37.5%): mp >320°; uv ($C_2H_4Cl_2$) λ_{max} 275 nm (log ϵ 4.52), 348 (3.96); ir (KBr) 6.05 μ (C=O); mass spectrum *m/e* 524 (M^+).

Anal. Calcd for $C_{34}H_{20}S_2O_2$: C, 77.85; H, 3.84. Found: C, 77.60; H, 4.06.

1,3,4,7-Tetraphenyl-5,6-dibenzoylisothianaphthene (**19**).—A solution of thienothiophene **1** (100 mg, 0.23 mmol) and dibenzoylacetylene (61 mg, 0.26 mm) in 25 ml of xylene was refluxed under nitrogen for 6 hr. The xylene was evaporated and a yellow solid was recovered (silica gel ptlc, benzene). Crystallization from benzene yielded yellow needles of **19** (90 mg, 61%): mp 296–297°; uv (dioxane) λ_{max} 240 nm (log ϵ 4.37), 261 (4.58), 280 (4.35), 400 (3.92); ir (KBr) 6.0 μ (C=O); mass spectrum *m/e* 646 (M^+).

Anal. Calcd for $C_{46}H_{30}SO_2$: C, 85.43; H, 4.68; S, 4.95. Found: C, 85.14; H, 4.81; S, 5.09.

Hexaphenyl-4*H*,8*H*-benzo[1,2-*c*:4,5-*c'*]dithiophene (**20**).—A mixture of isothianaphthene **19** (1.00 g) and P_2S_5 (3 g) was refluxed in 100 ml of xylene for 4 hr. The reaction was filtered and the dark residues were extracted with hot benzene. Chromatography (neutral grade I alumina, benzene) yielded white needles of **20** (736 mg, 73.6%): mp 302°; nmr ($CDCl_3$) δ 5.80 (s, S H), 6.55–6.70 (m, 10 H), 7.02–7.42 (m, 20 H); uv ($C_2H_4Cl_2$) λ_{max} 233 nm (log ϵ 4.31), 258 (4.32), 300 (4.34); mass spectrum *m/e* 648 (M^+).

Anal. Calcd for $C_{46}H_{32}S_2$: C, 85.16; H, 4.97; S, 9.87. Found: C, 84.90; H, 5.12; S, 9.67.

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[16] Dewar has calculated that the resonance energy of thiophene is 6.5 kcal/mol as compared with 9.3 kcal/mol calculated for isothianaphthene: M. J. S. Dewar and N. Trinajstić, *J. Amer. Chem. Soc.*, **92**, 1453 (1970).

[17] A. Schönberg, "Preparative Organic Photochemistry," Springer-Verlag, New York, "N. Y., 1968," p 389.

[18] Y. Lepage and O. Pouchot, *Bull. Soc. Chim. Fr.*, 2342 (1965).

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

[20] Both crystalline **10** and its dark blue toluene solution exhibited an esr signal at liquid nitrogen temperatures. A referee has pointed out that this signal (sharp peak, g = 2.0024) is almost certainly not that of the thermally excited triplet of **10**, but is most likely due to a small amount of a radical formed by oxidation of the easily oxidized **10**.

Reaction of 20 with DDQ.—A solution of DDQ (71 mg, 0.31 mmol) and **19** (100 mg, 0.155 mm) in 20 ml of *o*-dichlorobenzene was refluxed overnight. The black solution was filtered and evaporated *in vacuo*. Chromatography on grade I neutral alumina yielded **20** (20 mg, 20%) upon benzene elution and **19** (65 mg, 65%) upon chloroform elution.

Attempted Reaction of 14 with DDQ in the Absence of Oxygen.—A thoroughly degassed solution of **14** (100 mg, 0.2 mm) and DDQ (150 mg, 0.6 mm) in *o*-dichlorobenzene (15 ml) was heated at 180° overnight in a sealed tube. The dark solution was filtered, reduced in volume (*in vacuo*), and chromatographed on neutral grade I alumina. Benzene elution yielded **14** (20 mg, 28% recovery) as the only isolable compound.

Reaction of 14 with Tetracyanoethylene in the Absence of Oxygen.—A degassed solution of **14** (150 mg, 0.3 mmol) and TCNE (96 mg, 0.75 mmol) in *o*-dichlorobenzene (10 ml) was heated in a sealed tube as above. Work-up yielded **14** (110 mg, 73%) as the only product.

Reaction of 20 with TCNE in the Absence of Air.—The above procedure carried out using **20** (150 mg, 0.23 mmol) and TCNE (74 mg, 0.58 mmol) resulted in the recovery of **20** (80 mg, 53%).

Reaction of 20 with DDQ in the Absence of Air.—Reaction of **20** (100 mg, 0.125 mmol) and DDQ (106 mg, 0.4 mmol) was carried out as above, resulting in the recovery of 28 mg of starting material.

Reaction of Pure 10 with Phosphorus Pentasulfide and Xylene.—A mixture of crystalline **10**[5] (200 mg), phosphorus pentasulfide (400 mg), and xylene (10 ml) was refluxed for 30 min (N_2). Alumina chromatography (benzene) yielded white needles of **20** (145 mg, 73%).

Oxidation of Pure 10 with DDQ in the Presence of Air.—A solution of **10** (100 mg) and DDQ (70 mg) in benzene (10 ml) was warmed for 2 min on a steam bath. Chromatography (silica, benzene) yielded diketone **19** (53 mg, 53%).

Air Oxidation of Pure 10.—A stream of air was passed through a suspension of **10** (50 mg) in xylene (20 ml) at room temperature for 2 hr with the exclusion of light. Chromatography (silica, benzene) yielded diketone **19** (22 mg, 44%).

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Registry No.—**1**, 36516-81-1; **10**, 41947-66-4; **13**, 3867-56-9; **14**, 41947-68-6; **18**, 41947-69-7; **19**, 41947-70-0; **20**, 42080-44-4; dibenzoylacetylene, 1087-09-8.

Seven-Membered Heterocycles. VII. The Synthesis and Properties of 1-Benzothiepin and Its Chlorinated Derivatives[1a,b]

VINCENT J. TRAYNELIS,* YOICHIRO YOSHIKAWA,[1c] JOHN C. SIH,[1c] AND LARKEY J. MILLER

Department of Chemistry, West Virginia University, Morgantown, West Virginia 26506

JOEL R. LIVINGSTON, JR.[1d]

Department of Chemistry, University of Notre Dame, Notre Dame, Indiana 46556

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The reaction of 2,3-dihydro-1-benzothiepin (**7**) and sulfuryl chloride at low temperatures gave approximately equal amounts of *cis*- (**10**) and *trans*-4,5-dichloro-2,3,4,5-tetrahydro-1-benzothiepin (**11**), characterized as their corresponding sulfones **12** and **13**, respectively. Chromatography of *cis*-**12** or reaction with KOH produced 5-chloro-2,3-dihydro-1-benzothiepin (**14**). Elimination reactions and nmr spectra were used to assign stereochemistry. When **7** was treated with 1 or 2 equiv of *N*-chlorosuccinimide, 2-chloro- (**8**) or 2,2-dichloro-2,3-dihydro-1-benzothiepins (**19**) were formed and converted to their sulfones **18** and **20**, respectively. An explanation for the different outcome of these two reactions is presented. The reaction of **8**, **19**, or 2,4-dichloro-2,3-dihydro-1-benzothiepin (**24**) with strong base gave 1-benzothiepin (**9**), 2-chloro-1-benzothiepin (**27**), and 4-chloro-1-benzothiepin (**28**). All of these compounds decomposed slowly at room temperature with extrusion of sulfur and formation of naphthalene. The 1-benzothiepins were oxidized to their corresponding sulfones **25**, **31**, and **32**, which were also prepared by dihydrochlorination of the α-chloro sulfones **18**, **20**, and 2,4-dichloro-2,3-dihydro-1-benzothiepin 1,1-dioxide (**33**). The thermal stability, mass spectra, and nmr spectra are discussed for both the 1-benzothiepins and their sulfones. The structure of these compounds appears to contain a puckered thiepin ring.

Several literature reports[2-4] have appeared in recent years which described the isolation of substituted 1-benzothiepins **1–6**. Most of these compounds **1–4**[2,3] were enol derivatives in which the parent enol preferentially tautomerizes to the keto structure. One exception is **6**,[4] obtained by mild hydrolysis of **5**, which exists in the enol form, most likely owing to intramolecular H bonding with the adjacent methoxycarbonyl group. These 1-benzothiepin derivatives appear to be stable at room temperature but extrude sulfur at elevated temperatures.

In this paper we wish to report the successful synthesis of the parent heterocycle 1-benzothiepin (**9**) and some of its chlorinated derivatives and their subsequent conversion to the corresponding 1-benzothiepin 1,1-dioxides. These synthetic approaches reflect a general method for producing this class of condensed thiepins.

The key precursor in these synthetic schemes was 2-chloro-2,3-dihydro-1-benzothiepin (**8**). In a previous publication[5] we examined the use of sulfuryl chloride for the α-chlorination[6] of 2,3-dihydro-1-benzothiepin (**7**). When these reactants were refluxed in petroleum ether (bp 30–60°) and $NaHCO_3$, the products isolated were sulfur (3–5%), naphthalene (5–10%), and unidentified chlorinated compounds. The origin of sulfur

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[1] (a) For part VI in this series see V. J. Traynelis, J. C. Sih, and D. M. Borgnaes, *J. Org. Chem.*, **38**, 2629 (1973). (b) Presented in part before the Organic Division at the 164th National Meeting of the American Chemical Society, New York, N. Y., Aug 1972, and at the 160th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1970. (c) Abstracted from a portion of the Ph.D. Dissertation submitted by Y. Y. in May 1973 and by J. C. S. in Dec 1971 at West Virginia University. (d) Abstracted from a portion of the Ph.D. Dissertation submitted by J. R. L., Jr., in March 1962 at the University of Notre Dame.

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