mation of **3b** in the photosensitized oxygenation of **1** with methanol as solvent[5] lent credence to this supposition. Indeed, gas-phase singlet oxygenation of **1** and condensing the product stream onto a liquid nitrogen cold finger gave the monomeric endoperoxide **2**; but on warming above −30 °C it quickly polymerized with oxygen evolution.[6] We now provide evidence that the monomeric endoperoxide **2** can be formed quantitatively on photosensitized singlet oxygenation of **1** in CCl_4 or $CFCl_3$ at 0–5 °C, and contrary to previous reports[5,6] it is remarkably stable in solution even at room temperature (ca. 25–30 °C). Our evidence includes the following: (1) a 99.3% peroxide titer (iodometry) based on **2**; (2) low temperature bulb-to-bulb codistillation with CCl_4; (3) conversion into the hydroperoxide **3b** on treatment with methanol; and (4) quantitative deoxygenation into 1,2-diacetylethylene with triphenylphosphine. The experimental details are described below.

Experimental Section

Melting points are uncorrected. NMR spectra were run on a Hitachi Perkin-Elmer Model R-24B instrument and IR spectra on a Perkin-Elmer Model 237B Infracord. Solvents and reagents used were purified according to standard literature procedures.

2,5-Dimethylfuran Endoperoxide (2). The irradiation was carried out in a 50-mL, two-neck, round-bottom flask provided with a magnetic spinbar, a rubber septum, and a gas inlet tube which was connected to an oxygen-filled balloon. The flask was charged with a solution of 2,5-dimethylfuran (ca. 250 mg, 2.60 mmol) and tetraphenylporphyrin (0.5 mg) in 20 mL of CCl_4 (or $CFCl_3$), submerged in a water or ice bath, and positioned as close as possible (~10 cm) to a General Electric 150-W sodium street lamp. While the solution was vigorously stirred by magnetic action, the light source was activated and the required singlet oxygen was generated in situ. Within 120 min the photooxygenation was completed, as confirmed by monitoring the progress of the reaction by NMR. The characteristic furan proton resonances (CCl_4, Me_4Si) at δ 5.58 (olefinic, singlet, 2 H) and 2.17 (methyl, singlet, 6 H) were replaced by the characteristic peaks at δ 6.02 (olefinic, singlet, 2 H) and 1.70 (methyl, singlet, 6 H), respectively, of the endoperoxide **2**. The IR spectrum (CCl_4) showed bands at 3080 (olefinic CH), 2990, 2940 (aliphatic CH), 1450, 1390, 1330, and 1210 cm^{-1}. Iodometric analysis of the solution gave a 99.3 ± 0.5% peroxide titer based on the endoperoxide structure **2**. Attempted isolation by solvent removal even at subambient temperatures (~0 °C) afforded polymeric product. However, on flash distillation at −20 °C (0.10 mmHg) the volatile endoperoxide codistilled intact with the CCl_4.

2,5-Dimethyl-2-hydroperoxy-5-methoxy-2,5-dihydrofuran (3b). A solution of the endoperoxide **2** (7.47 mmol) in 20 mL of $CFCl_3$ was cooled to −78 °C by means of a dry ice–acetone bath, and under a N_2 atmosphere 5 mL of anhydrous CH_3OH was syringed in dropwise while the mixture was stirred. After 2 h at −78 °C, the reaction mixture was allowed to warm up to 0 °C and the solvent was removed at 0 °C (10 mm Hg) to afford 410 mg (93.5%) of crude hydroperoxide **3b**. The latter was purified by sublimation at 60–65 °C (0.15 mmHg), mp 74–75 °C (lit.[5] mp 75–76 °C). The ^1H NMR and IR data were identical with those of an authentic sample prepared directly by singlet oxygenation of 2,5-dimethylfuran in methanol.

Triphenylphosphine Deoxygenation of Endoperoxide 2. A solution of the endoperoxide **2** (2.50 mmol) in 20 mL of CCl_4 was cooled to −20 °C, and while under a N_2 atmosphere with stirring a solution of triphenylphosphine (2.50 mmol) in 5 mL of CCl_4 was syringed in at −20 °C for 1 h. The mixture was allowed to warm up to room temperature (ca ~30 °C) and was kept there for 12 h. The product showed the characteristic[4a] 1,2-diacetylethylene proton resonances (CCl_4, Me_4Si) at δ 6.60 (olefinic, singlet, 2 H) and 2.22 (methyl, singlet, 6 H) and IR (CCl_4) bands at 3050 (olefinic C–H), 1680 (C=O), 1430, 1360, 1280, and 1200 cm^{-1}.

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Registry No.—**1**, 625-86-5; **2**, 45722-89-2; **3b**, 13249-74-6; 1,2-diacetylethylene, 4436-75-8.

References and Notes

(1) Paper No. 80 in the "Cyclic Peroxide Series".
(2) NIH Career Development Awardee, 1975–1980.
(3) W. Adam, *Chem.-Ztg.*, **99**, 142 (1975).
(4) (a) T. Noguchi, K. Takayama, and M. Nakano, *Biochem. Biophys. Res. Commun.*, **78**, 418 (1977). (b) E. W. Kellogg and I. Fridovich, *J. Biol. Chem.*, **250**, 8812 (1975).
(5) C. S. Foote, M. T. Wuesthoff, S. Wexler, I. G. Burstain, R. Denny, G. O. Schenck, and K. H. Schulte-Elte, *Tetrahedron*, **23**, 2583 (1967).
(6) W. S. Gleason, A. D. Broadbent, E. Whittle, and J. N. Pitts, Jr., *J. Am. Chem. Soc.*, **92**, 2068 (1970).

New Syntheses of Tetrathiafulvalene

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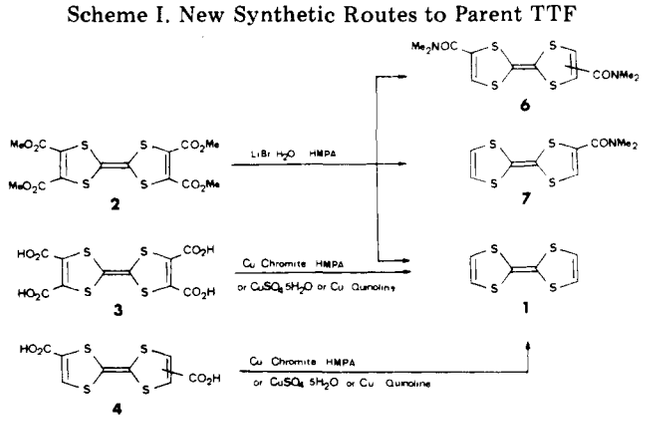
Tetrathiafulvalene (TTF, **1**) is known to be a superior π donor in the formation of highly conducting charge-transfer complexes.[1] Although this compound was first prepared by coupling of the 1,3-dithiolium cation,[2] although the method by Melby, Harzler, and Sheppard[3] seems to be suitable for preparing large amounts of TTF, and although the procedure by Wudl et al.[14] might be preferred for a small scale preparation, we report here new facile syntheses of TTF utilizing tetrakis(carbomethoxy)- (**2**),[5] tetracarboxy- (**3**),[5] and dicarboxytetrathiafulvalenes (**4**),[3,5] which have been prepared during the course of our systematic studies[6] on the reactions of isotrithiones with trialkyl phosphites.

A mixture of tetraester **2** and an excess of lithium bromide monohydrate in HMPA was gradually heated to 80 °C, and the temperature was maintained for 2 h (Scheme I). During this period the mixture was orange-red and gas evolution was observed. Treatment of the mixture with deaerated water gave TTF and bis(carbomethoxy)tetrathiafulvalene (**5**) in 11 and 53% yields, respectively.[7] Compound **5** was identified on the basis of its spectral data.[3,5]

Further reaction at 150–160 °C for 10 min, after the gas evolution ceased, afforded TTF (**1**, 13%), tetrathiafulvalene-bis(*N*,*N*-dimethyl)carbamide (**6**, 22.3%), and tetrathiafulvalene-*N*,*N*-dimethylcarbamide (**7**, 18.5%). The structures of **6** and **7** were determined by their analytical and spectral data. In the ^1H NMR spectrum of **6**, the methyl protons attached to the nitrogen atom and the olefin protons appeared as two singlets at δ 3.10 and 6.63, respectively. Generally, the methyl protons attached to the nitrogen atom of an amide group appear as a doublet because of the prominent contri-

Scheme I. New Synthetic Routes to Parent TTF



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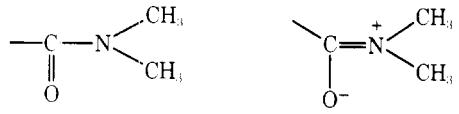
bution of the canonical structure B. However, in the ^1H NMR spectrum of **6**, only a singlet due to the *N*-methyl protons was observed, which indicates that the tetrathiafulvalene component of **6** has strong electron-donating properties.



A B

The ^1H NMR spectrum of **7** also showed a singlet due to *N*-methyl protons. The olefin protons of **7** appeared as two singlets at δ 6.34 and 6.61, which can be assigned to the olefin protons on the unsubstituted ring and the dimethylcarbamide-substituted ring, respectively, based on the correspondence of the chemical shifts noted above with those of TTF (δ 6.33) and **6** (δ 6.63). This is the first example of the synthesis of monosubstituted TTF from a tetrasubstituted one.[8]

The decarboxylation of acid derivatives, which are facilely derived from **2**,[5,6] gave parent TTF in better yields. Tetraacid **3** was heated with copper chromite in HMPA at 150 °C for 3 h, and the reaction mixture was treated with water. The benzene extracts, upon evaporation, gave a 57% yield of tetrathiafulvalene. This synthetic method is more available than the other method because of easy manipulation and no byproducts. Without copper chromite, **3** was recovered quantitatively. Diacid **4** also afforded parent TTF in 69% yield under similar reaction conditions. Copper(II) sulfate or copper powder in quinoline was also useful for decarboxylation of acid derivatives.

Experimental Section

Melting points were determined using a Büchi melting point apparatus in sealed tubes and are uncorrected. The infrared spectra were determined on a Hitachi grating IR spectrophotometer, Model 215, the mass spectra were determined on a Hitachi RMU-6C or RMS-4 mass spectrometer, and the ^1H NMR spectra were recorded on a Varian HA-100 spectrometer. Elemental analyses were carried out at the Elemental Analytical Center of Kyoto University.

$\Delta^{2,2'}$-Bis[4,5-bis(carbomethoxy)-1,3-dithiolidene] (**2**), $\Delta^{2,2'}$-bis(4,5-dicarboxy-1,3-dithiolidene) (**3**), and $\Delta^{2,2'}$-bis[4(5)-carboxy-1,3-dithiolidene] (**4**) were prepared as described in our previous paper.[6d]

Reaction of 2 with Lithium Bromide. A mixture of 436 mg of **2**, 3.0 g of lithium bromide monohydrate, and 10 mL of hexamethylphosphoramide was heated gradually to 80 °C. Gas evolution and a considerable lightening of color occurred. When gas evolution ceased, the mixture was cooled and treated with deaerated water to give a red solid. After filtration, the solid was subjected to column chromatography on silica. The first yellow fraction upon evaporation gave 22 mg of **1**: yield 11%; mp 117–119 °C (lit.[3] 119–119.5 °C); ^1H NMR ($CDCl_3$) δ 6.33 (s, =CH); MS *m/e* 204 (M^+).

The second red fraction gave bis(carbomethoxy)tetrathiafulvalene (**5**, 166 mg): yield 53%; mp 226–228 °C dec[9] (lit.[3] 244–245 °C); ^1H NMR ($CDCl_3$) δ 3.85 (s, 6 H, OCH_3) and 7.30 (s, 2 H, =CH); IR (KBr) 1708 (C=O), 1548 (C=C), 1440 and 1255 (C–O) cm^{-1}; MS *m/e* 320 (M^+). Anal. Calcd for $C_{10}H_8O_4S_4$: C, 37.48; H, 2.52; O, 19.97. Found: C, 37.45; H, 2.64; O, 20.09.

After gas evolution ceased, the temperature was raised to 150–160 °C for 10 min. The cooled mixture was diluted with water and extracted with benzene. The orange organic extract was washed, dried over Na_2SO_4, and after concentration subjected to chromatography on silica, eluting with methylene chloride. The first yellow fraction gave 27 mg of orange-yellow crystals of **1**, yield 13%.

The second yellow fraction gave 51 mg of tetrathiafulvalene-*N*,*N*-dimethylcarbamide (**7**): yield 18.5%; mp 162.5–163.5 °C; IR (KBr) 3050 (C=CH), 1603 (C=O), 1580, 1540, and 1395 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.09 (s, 6 H, $N-CH_3$), 6.34 (s, 2 H, HC=CH), and 6.61 (s, 1 H, HC=CC=O); MS *m/e* 275 (M^+). Anal. Calcd for $C_9H_9NOS_4$: C, 39.25; H, 3.29; N, 5.09; S, 46.57. Found: C, 39.46; H, 3.02; N, 5.06; S, 46.44.

The third orange-red fraction afforded 77 mg of tetrathiafulvalenebis(*N*,*N*-dimethyl)carbamide (**6**) as orange crystals after recrystallization from methylene chloride–ether: yield 22.3%; mp 231–232 °C; IR (KBr) 3090, 1602 (C=O), 1550 (C=C), and 1400 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.10 (s, 12 H, $N-CH_3$) and 6.63 (s, 2 H, HC=C-C=O); MS *m/e* 346 (M^+). Anal. Calcd for $C_{12}H_{14}N_2O_2S_4$: C, 41.59; H, 4.07; N, 8.08; S, 37.01. Found: C, 41.58; H, 3.80; N, 8.05, S, 37.00.

Decarboxylation of 3 with Copper Chromite. A mixture of 760 mg of **3**, 300 mg of copper chromite, and 15 mL of HMPA was heated at 150–160 °C for 3 h. The cooled mixture was diluted with water and extracted with benzene. The yellow organic extract was washed, dried over Na_2SO_4, and evaporated to afford orange-yellow crystals, which were recrystallized from hot hexane to give orange needles of **1** (231 mg): yield 57%; mp 118.5–119.2 °C. No byproducts were observed.

Decarboxylation of 4 with Copper Chromite. A mixture of 146 mg of **4**, 150 mg of copper chromite, and 7 mL of HMPA was treated as above to afford 70 mg of **1**, yield 69%.

Decarboxylation of 3 with Copper(II) Sulfate. A mixture of 130 mg of **3**, 300 mg of copper(II) sulfate pentahydrate, and 4 mL of quinoline was heated at 100–200 °C for 0.5–1 h. Workup afforded 35 mg of **1**, yield 50%.

Decarboxylation of 3 with Copper Powder. Using 150 mg of copper powder instead of the 300 mg of $CuSO_4 \cdot 5H_2O$ in the above case, **1** was obtained in 40% yield.

Registry No.—**1**, 31366-25-3; **2**, 26314-39-6; **3**, 59269-79-3; **4**, 69440-12-6; **5**, 69440-11-5; **6**, 69440-13-7; **7**, 69439-76-5.

References and Notes

(1) (a) J. P. Ferraris, D. O. Cowan, V. Walatka, Jr., and J. H. Perlstein, *J. Am. Chem. Soc.*, **95**, 948 (1973); (b) L. B. Coleman, M. J. Cohen, D. J. Sandman, F. G. Yamagishi, A. F. Garito, and A. J. Heeger, *Solid State Commun.*, **12**, 1125 (1973); (c) *Science*, **180**, 1041 (1973).

(2) (a) H. Prinzbach, H. Berger, and A. Lüttringhaus, *Angew. Chem., Int. Ed. Engl.*, **4**, 435 (1965); (b) K. M. Pazdro, *Rocz. Chem.*, **43**, 1089 (1969); (c) F. Wudl, G. M. Smith, and E. J. Hufnagel, *Chem. Commun.*, 1453 (1970); (d) J. P. Ferraris, T. O. Poehler, A. N. Bloch, and D. O. Cowan, *Tetrahedron Lett.*, 2553 (1973).

(3) L. R. Melby, H. D. Harzler, and W. A. Sheppard, *J. Org. Chem.*, **39**, 2456 (1974).

(4) F. Wudl and M. L. Kaplan, *J. Org. Chem.*, **39**, 3608 (1974).

(5) C. U. Pittman, Jr., M. Narita, and Y. F. Liang, *J. Org. Chem.*, **41**, 2855 (1976).

(6) (a) Z. Yoshida, T. Kawase, and S. Yoneda, *Tetrahedron Lett.*, 235 (1975); (b) *ibid.*, 331 (1975); (c) S. Yoneda, T. Kawase, M. Inaba, and Z. Yoshida, *J. Org. Chem.*, **43**, 595 (1978); (d) S. Yoneda, T. Kawase, and Z. Yoshida, *ibid.*, **43**, 1980 (1978); (e) Z. Yoshida, S. Yoneda, T. Kawase, and M. Inaba, *Tetrahedron Lett.*, 1285 (1978).

(7) A similar procedure for removing carbomethoxy substituents was used in the preparation of tetraselenafulvalene: M. V. Lakshmikantham and M. P. Cava, *J. Org. Chem.*, **41**, 882 (1976).

(8) Another synthesis of monosubstituted TTF's has been reported: D. C. Green, *J. Chem. Soc., Chem. Commun.*, 161 (1977).

(9) The large difference in melting point from the literature value is probably due to a variation in the "cis/trans" isomer ratio.

1,2-Bis(diphenylphosphino)-1-phenylethane: A Chiral Ditertiary Phosphine Derived from Mandelic Acid Used as a Ligand in Asymmetric Homogeneous Hydrogenation Catalysts

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During the last few years rhodium(I) complexes of chiral phosphines have been shown to be effective catalysts for the asymmetric hydrogenation of prochiral olefins.[1,2,3] The optical yields in such reactions have been shown to be particularly high when chiral ditertiary phosphines are used which form rigid five-membered chelate rings. Examples of such chiral ditertiary phosphines include the ligand (−)-(*o*-$CH_3OC_6H_4$)-(C_6H_5)$PCH_2CH_2P(C_6H_5)(C_6H_4OCH_3$-*o*) of Knowles et al.[4] and the ligands (−)-(2*S*,3*S*)-$(C_6H_5)_2PCH(CH_3)CH(CH_3)P(C_6H_5)_2$ ("(*S*,*S*)-chiraphos")[5] and $(C_6H_5)_2PCH(CH_3)CH_2P(C_6H_5)_2$ ("*R*-prophos")[6] of Fryzuk and Bosnich.

An attractive synthetic objective is the development of methods for the synthesis of chiral ditertiary phosphines forming rigid five-membered chelate rings using as raw ma-

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