A further study is in progress.[21]

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Registry No.—IV, 5938-06-7; OPNA, 4232-27-3; OPNH, 64252-81-9; OPND, 61063-34-1; OMND, 61063-35-2; PND, 1956-09-8; MND, 61063-38-5; hexanoyl chloride, 142-61-0; 2,4-dinitrophenol, 51-28-5.

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Syntheses of Electronegative Substituted Tetrathiafulvalene Derivatives

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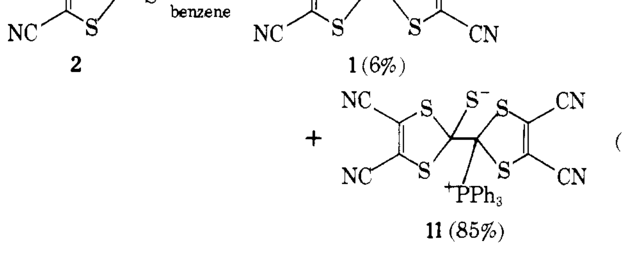
Tetracyano-, tetracarbomethoxy-, and tetraphenyltetrathiafulvalene have been prepared from 4,5-disubstituted 1,3-dithiole-2-thiones in the presence of triphenylphosphine and trialkyl and triphenyl phosphites. Acid- and base-catalyzed hydrolyses of tetracyano- and tetracarbomethoxytetrathiafulvalenes led to the formation of new derivatives. A new synthetic route to parent tetrathiafulvalene was established.

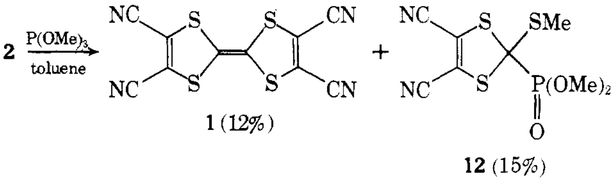
The phenomenon of high electrical conductivity[1] in the complex of tetrathiafulvalene (TTF) with tetracyanoquinodimethane (TCNQ) has recently aroused intense interests. Several synthetic methods[2] of TTF derivatives have been reported so far: (i) deprotonation of 1,3-dithiolium ions;[3] (ii) desulfurization of 1,3-dithiole-2-thiones with trivalent phosphorus compounds;[4] (iii) pyrolysis of orthothiooxalates;[5] (iv) reaction of acetylenes with carbon disulfide.[6,4b] As a series of our study[4f,7,8] on the reactions of thiocarbonyl compounds with trialkyl phosphites, we previously reported[4f] the successful synthesis of tetracyanotetrathiafulvalene (**1**) by the reaction of 4,5-dicyano-1,3-dithiole-2-thione (**2**) with triphenyl phosphite. In this paper, we wish to report the application of this synthetic method to the preparation of tetracarbomethoxytetrathiafulvalene (**3**) from 4,5-dicarbomethoxy-1,3-dithiole-2-thione (**4**) and tetraphenyltetrathiafulvalene (**5**) from 4,5-diphenyl-1,3-dithiole-2-thione (**6**). Tetracyano-,[4d-f] tetracarbomethoxy-,[4b,g] and tetraphenyltetrathiafulvalene[3b] have all been previously synthesized. By the acid hydrolyses of **1** and **3**, tetraamidetetrathiafulvalene (**7**) and dicarboxytetrathiafulvalene (**9**) were newly obtained, respectively. The alkaline hydrolysis of **3** led to the formation of tetracarboxytetrathiafulvalene (**8**), which was converted to its anhydride (**10**) and **9**. Pyrolysis of **9** provided a new synthetic route to parent tetrathiafulvalene in good yields.

Results and Discussion

The synthesis of tetracyanotetrathiafulvalene (**1**) by the reactions of 4,5-dicyano-1,3-dithiole-2-thione (**2**) with triphenylphosphine, trialkyl, and triphenyl phosphite was briefly reported in our preceeding communication.[4f] The procedure in detail is described in the Experimental Section of this paper. In the reaction of **2** with triphenylphosphine in benzene under reflux, **1** was obtained only in 6% yield and the betaine



(1)



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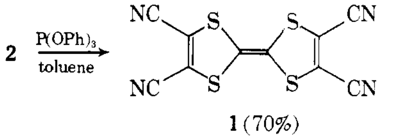

(3)

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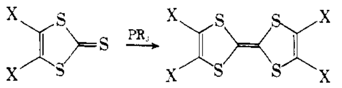
Table I. Desulfurizaton Reaction of Disubstituted 1,3-Dithiole-2-thiones



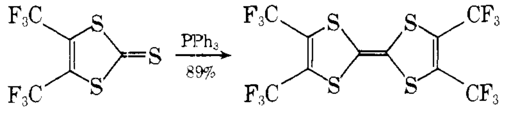
X	R	Product	Yield, %
CN	Ph	1	6
CN	OMe	1	12
CN	OPh	1	71
COOMe	Ph	3	90
COOMe	OMe	3	63
Ph	OMe	5	21

11 as the major product. Heating of 11 in dichlorobenzene afforded 1. The reaction of 2 with trimethyl phosphite gave 1 in 12% yield and the Arbuzov reaction type product which was formed by the methyl rearrangement. When triphenyl phosphite was used in order to inhibit the alkyl rearrangement, 1 was obtained in 70% yield.

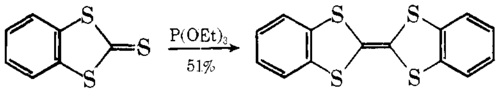
Similar desulfurization reaction of 4,5-dicarbomethoxy-1,3-dithiole-2-thione (4) successfully yielded tetracarbomethoxytetrathiafulvalene (3), which was firstly prepared from dimethyl acetylenedicarboxylate and carbon disulfide.[4b] Different from the reaction behavior of 2, the reaction of 4 with triphenylphosphine in toluene under reflux was found to lead the exclusive formation of 3. However, the reaction proceeded too slowly. After 30 h, 60% of 4 was recovered. The reaction of 4 with trimethyl phosphite, which proceeded faster than with triphenylphosphine, gave 3 in 63% yield and several unidentified products. Triphenyl phosphite also reacted with 4 to give 3, but the reaction rate was extremely low. The preparation of 3 in high yield (90%) was achieved by the reaction of 4 with triphenylphosphine in xylene under reflux for 10 h.

Tetraphenyltetrathiafulvalene (5) was also prepared from 4,5-diphenyl-1,3-dithiole-2-thione (6) and trimethyl phosphite in 21% yield, together with several unknown by-products. The results are summarized in Table I.

The synthetic studies of TTF derivatives using trivalent organophosphorus compounds have recently been reported by several groups. Tetrakis(trifluoromethyl)tetrathiafulvalene was prepared by the use of triphenylphosphine[4b] and dibenzotetrathiafulvalene by the use of triethyl phosphite.[4c,9] Desulfurization with trialkyl phosphite has also been reported for tetracyano-[4d-f] and tetracarbomethoxytetrathiafulvalenes.[4g] It is obvious from these results that 1,3-dithiole-2-thiones substituted by electron-withdrawing groups generally undergo desulfurization reaction with triphenylphosphine or trialkyl phosphites.



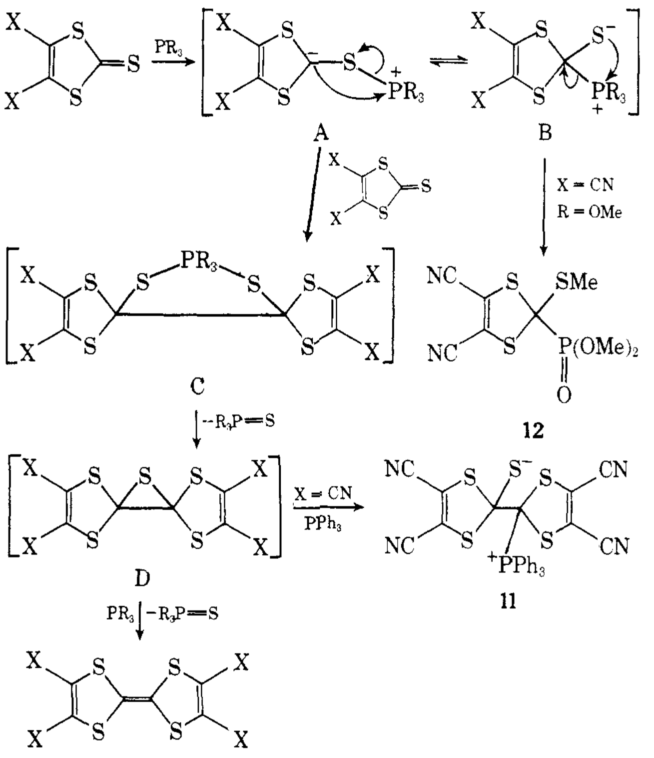
(4)[4b]



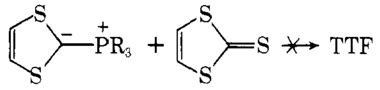
(5)[4c, 9]

On the other hand, the reactions of 1,3-dithiole-2-thiones substituted by electron-donating groups in the presence of trivalent phosphorus compounds were carried out, but the tetrathiafulvalene derivatives were not obtained. For example, the reaction of dimethyl-1,3-dithiole-2-thione with trimethyl phosphite in toluene at reflux temperature gave a variety of unidentified products but no TTF derivative.

Scheme I

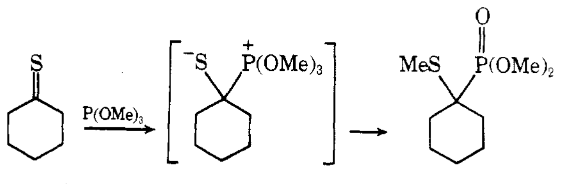


A mechanistic interpretation of the reaction of 2 and 4 with trivalent phosphorus compounds is shown in Scheme I. As seen in Scheme I, initial thiophilic attack of PR_3 at the thiocarbonyl sulfur atom of 1,3-dithiole-2-thione would afford ylide A (C^{-}–S–$P^{+}R_3$), which might isomerize to betaine B (S^{-}–C–$P^{+}R_3$). Similar ylide–betaine isomerization was suggested by Ogata et al.[10] in the reaction of thiobenzophenone with trialkyl phosphites. The intermediate A would react with another 1,3-dithiole-2-thione to give the intermediate C followed by the intermediate D and result in the formation of the TTF derivatives. When triphenylphosphine was used in the reaction of 4,5-dicyano-1,3-dithiole-2-thione, triphenylphosphine would attack at the carbon atom of the thiirane ring of D to afford the betaine 11. A similar reaction scheme via the ylide type intermediate A was mentioned by Schrowsky et al.[9] in the reaction of benzo-1,3-dithiole-2-thione with triethyl phosphite. Miles et al.[4e] proposed another mechanism for desulfurization via ylide intermediate E. However, Cava[11] has recently presented the experimental results that in the reaction of ylide E with 1,3-dithiole-2-thione no TTF was obtained. This finding lends more support for our proposed mechanism via the intermediate A.



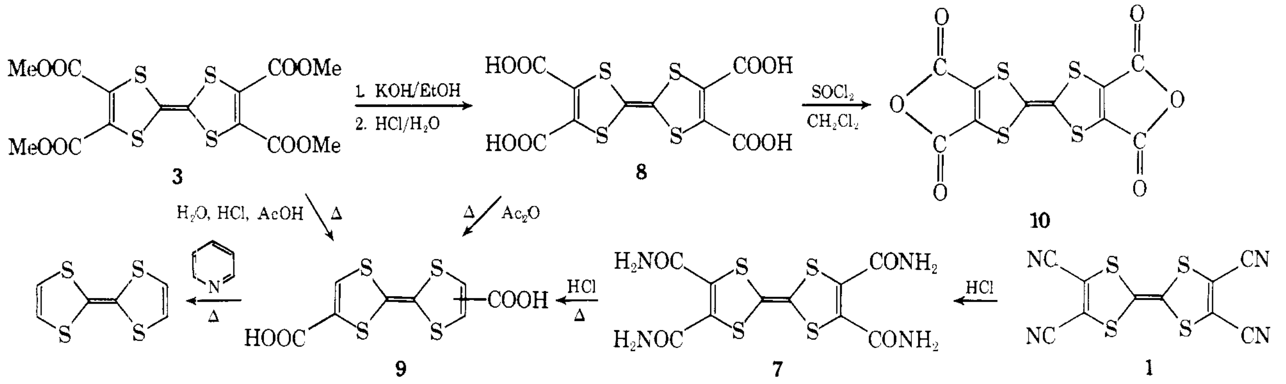
E

The phosphonic acid ester 12 is considered to be obtained from the betaine type intermediate B by the alkyl rearrangement. Such alkyl rearrangement has been reported from this laboratory[7] in the reaction of alicyclic thiones with trialkyl phosphites.



Hydrolysis of 1 in concentrated hydrochloric acid at room temperature afforded light purple crystallines melting at high temperature (>360 °C). The elemental analysis and spectral data were all consistent with the formation of tetraamidetetrathiafulvalene (7). Hydrolysis of 3 gave two different acid

Scheme II



derivatives depending on the reaction condition: tetracarboxytetrathiafulvalene (8)[4g] under basic condition and dicarboxytetrathiafulvalene (9)[12] under acidic condition, respectively. It is noteworthy that 9 was directly synthesized in high yield by refluxing aqueous acetic acid solution of 3 in the presence of hydrochloric acid, since 1,3-dithiole-2-thiones substituted with carboxy groups did not react with trivalent phosphorus compounds to give tetrathiafulvalenes and moreover parent tetrathiafulvalene was directly synthesized from 9 as seen in Scheme II.

On the other hand, refluxing an ethanol solution of 3 with potassium hydroxide followed by acidification afforded light purple tetracarboxytetrathiafulvalene (8). The reaction of 8 with thionyl chloride in methylene chloride gave bis(anhydride)tetrathiafulvalene (10) quantitatively, which was identified by its infrared absorptions at 1850 and 1870 cm^{-1} characteristic for unsaturated five-membered anhydride and its mass spectrum. Attempts to prepare 10 as usual by refluxing of 8 in acetic anhydride resulted in the formation of 9 in good yield, in connection with which the decarboxylation of 8 has been reported not to be attained in basic solvent such as pyridine.[4g]

The parent TTF is well known to be easily air-oxidized, while the TTF derivatives obtained in this work, **1, 3, 7, 8, 9,** and **10**, are very stable against air oxidation, which is consistent with the calculated results by HMO method that the energy levels of highest occupied molecular orbitals of those derivatives are quite low compared with that of the parent TTF.

Although parent TTF was first prepared by deprotonation of 1,3-dithiolium cation,[3a] the Du Pont group's synthesis[12] is by far the best method for preparing large amounts of TTF, and the procedure of Wudl et al.[3f] is easy to carry out for smaller scale reactions. We tried to prepare TTF by combining our facile preparation of dicarboxytetrathiafulvalene (9) and the decarboxylation of 9 by Hartzler et al.[12] This route to TTF including only three steps (4 → 3 → 9 → TTF) with a total yield of 53% based on 4.[13] Scheme II shows the synthetic route and the relating experimental results.

The colors of 1 (deep purple), 3 (brown), 7 (light purple), 8 (light pruple), 9 (red), and 10 (dark brown) indicate that they have absorption in longer wavelength than parent TTF (yellow orange). The absorption band at the longest wavelength of 1 exhibits a blue shift by changing solvents: λ_{max} 502 nm (benzene), 500 (methylene chloride), 492 (acetonitrile), 493 (DMF), and 480 (methanol), which can be explained in terms of intramolecular charge transfer. The band of 3 also exhibits a similar solvent shift to short wavelength: λ_{max} 461 (*n*-hexane), 462 (benzene), 455 (methylene chloride), 446 (DMF), and 445 (ethanol).

Experimental Section

Melting points were determined using a Büchi melting point apparatus in sealed capillary tubes and are uncorrected. The electronic absorption spectra were measured on a Hitachi ESP-3T recording photometer, 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, the ^{1}H NMR spectra were recorded on a Varian HA-100 spectrometer, and the ^{13}C NMR spectra were recorded on JEOL FX-60. Elemental analyses were carried out at the Elemental Analytical Center of Kyoto University.

4,5-Dicyano-1,3-dithiole-2-thione (2) was prepared as described by Klingsberg,[14] and **4,5-dicarbomethoxy-1,3-dithiole-2-thione (4)** was prepared as described by O'Connor et al.[15] The phosphine and phosphites were commercial materials and were used as received.

Reaction of 2 with Triphenylphosphine. To a boiling solution of **2** (0.200 g) in 15 mL of dry benzene under nitrogen was added a solution of triphenylphosphine (0.450 g) in 10 mL of benzene. After several minutes the orange solid began to precipitate. The resulting solid was filtered, washed with cool benzene, and recrystallized from methylene chloride–ether to give 0.270 g (85%) of orange crystals (**11**): mp 169–172 °C dec; IR (KBr) 2210, 2170, 1415 cm^{-1}. Anal. Calcd for $C_{28}H_{15}N_4PS_5$: C, 56.17; H, 2.53; N, 9.36. Found: C, 56.27; H, 2.56; N, 9.42.

The filtrate was concentrated and column chromatographed on silica. The red band upon evaporation gave 0.018 g (6%) of dark purple needles after recrystallization from methylene chloride–ether: mp 264–265 °C dec; IR (KBr) 2208, 1535, 1182, 1066 cm^{-1}; *m/e* 304.

Anal. Calcd for $C_{10}N_4S_4$: C, 39.46; N, 18.41; S, 42.14. Found: C, 39.04; N, 18.38; S, 42.37.

Reaction of 2 with Trimethyl Phosphite. A mixture of 1.00 g of **2** and 1.50 g of trimethyl phosphite in 50 mL of toluene was heated under reflux for 6 h under nitrogen. The resulting dark solution was concentrated and chromatographed on silica eluting with benzene. The yellow band upon evaporation gave 0.117 g (15%) of yellow crystals **12:** mp 140–141 °C; IR (KBr) 2220, 1547, 1240 (P=O stretching), 1180 (P–O–Me), 1054–1012 cm^{-1} (P–O–R); ^{1}H NMR ($CDCl_3$) δ 2.75 (s, 3 H, SMe), 3.83 (d, $J_{c\text{-}p}$ = 11.2 Hz, 6 H, P–O–Me). Anal. Calcd for $C_8H_9N_2O_3PS_3$: C, 31.16; H, 2.94; N, 9.09; P, 10.05. Found: C, 31.32; H, 2.70; N, 9.11; P, 10.31.

In this reaction, 1 was obtained in 12% yield.

Reaction of 2 with Triphenyl Phosphite. A mixture of 1.008 g of **2** and 15 mL of triphenyl phosphite in 50 mL of toluene was heated under reflux overnight and concentrated. The dark residue was subjected to chromatography on silica eluting with benzene. The red band upon evaporation gave 0.603 g (71%) of 1.

$\Delta^{2,2'}$-Bis(4,5-dicarbomethoxy-1,3-dithiolidene) (3). A. A mixture of 0.250 g of **4** and 0.416 g of triphenylphosphine in 20 mL of toluene was heated under reflux for 30 h. The red solution was concentrated and chromatographed on silica eluting with chloroform. The initial colorless band contained triphenylphosphine and triphenylphosphine thioxide. The yellow band led to recovery of 0.150 g of **4.** The subsequent red band upon evaporation gave 0.082 g (92%) of brown crystals: mp 168–169 °C (lit. 169–170 °C[4b]); IR (KBr) 1745, 1716, 1576, 1290, 1260 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.83 (s); *m/e* 436. Anal. Calcd for $C_{14}H_{12}O_8S_4$: C, 38.52; H, 2.77; O, 29.32. Found: C, 38.54; H, 2.94; O, 29.57.

B. A mixture of 0.506 g of 4 and 1.00 g of trimethyl phosphite in 30 mL of toluene was allowed to reflux for 5 h. A dark residue after concentration was chromatographed on silica to give 0.222 g (62%) of **3.**

C. A mixture of 0.250 g of 4 and 0.530 g of triphenylphosphine in 10 mL of xylene was heated under reflux for 10 h. A dark residue after evaporation of solvent was chromatographed on silica to give 0.195 g (90%) of **3.**

$\Delta^{2,2'}$-Bis(4,5-diphenyl-1,3-diphenyl-1,3-dithiolidene) (5). A mixture of 286 mg of 4,5-diphenyl-1,3-dithiole-2-thione (**6**), 0.5 mL of trimethyl phosphite, and 10 mL of toluene was heated under reflux under nitrogen for 24 h. The red solution was evaporated and the residue was recrystallized from acetonitrile to give 54 mg (21%) of orange crystals, mp 261.5–263 °C (lit. 262–263 °C).[3b] Spectral data were identical with authentic sample.

$\Delta^{2,2'}$-Bis(4,5-dicarbamide-1,3-dithiolidene) (7). A mixture of 76 mg of finely ground **1** and 10 mL of concentrated hydrochloric acid was allowed to stand for 2 weeks at room temperature under stirring. The solid was filtered and washed with water and with ethanol. After drying 74 mg (79%) of purple solids was obtained: mp > 360 °C; IR (KBr) 3600–2900, 1670, 1390–70 cm^{-1}; UV (DMF) λ_{max} 449 nm (log ϵ 3.31), 319 (4.18); *m/e* 376. Anal. Calcd for $C_{10}H_8N_4O_4S_4$: C, 31.90; H, 2.14; N, 14.88; O, 17.00. Found: C, 31.67; H, 2.29; N, 14.57; O, 17.10.

$\Delta^{2,2'}$-Bis(4,5-dicarboxy-1,3-dithiolidene) (8). A mixture of 0.637 g of **3**, 1.0 g of potassium hydroxide, and 40 mL of ethanol was heated under reflux for 1 h. The resulting orange potassium salts were filtered and dissolved in 15 mL of water. Neutralization with hydrochloric acid yielded purple solids. These were filtered and dried without washing, because of water solubility. Recrystallization from DMF–ether gave 0.590 g (100%) of light purple crystals: mp > 360 °C; IR (KBr) 3600–2700, 1550, 1503, 1360 cm^{-1}; UV (DMF) λ_{max} 477 nm (log ϵ 3.33), 311 (4.17), 302 (4.10). Anal. Calcd for $C_{10}H_4O_8S_4$: C, 39.25; H, 9.41; O, 29.88. Found: C, 39.21; H, 9.56; O, 29.97.

$\Delta^{2,2'}$-Bis(4(5)-carboxy-1,3-dithiolidene) (9). A. 8 (63 mg) was suspended in 5 mL of acetic anhydride and heated under reflux for 0.5 h. Red crystals precipitated and were filtered and dried to give 36 mg (76%) of **9:** mp > 360 °C; IR (KBr) 3400–3200, 1650, 1540, 1425, 1295 cm^{-1}; ^{13}C NMR (DMSO-d_6) δ from TMS 160.0 ($C^*{=}O$), 132.6 ($=C^*CO$), 128.7 ($=C^*H$), 110.1 ($S_2C{=}CS_2$). Anal. Calcd for $C_8H_4O_4S_4$: C, 32.86; H, 1.38; O, 21.89. Found: C, 32.84; H, 1.49; O, 22.08.

B. A mixture of 0.400 g of **3**, 18 mL of water, 18 mL of concentrated hydrochloric acid, and 50 mL of glacial acetic acid was heated under reflux for 3 h. The resulting solids were filtered and dried and yielded 0.250 g (92%) of red crystals **9**.

$\Delta^{2,2'}$-Bis(4,5-dicarboxy anhydride-1,3-dithiolidene) (10). A mixture of 60 mg of **8**, 0.5 mL of thionyl chloride, and 3 mL of methylene chloride was heated under reflux for 1 h. The dark solution was evaporated to give the dark residue, which was crystallized from *n*-hexane to give 53 mg (100%) of **10** as dark brown needles: mp > 360 °C; IR (KBr) 1850, 1780, 1560, 1255 cm^{-1}; *m/e* 344.

Anal. Calcd for $C_{10}O_6S_4$: C, 34.88; O, 27.88. Found: C, 35.01; O, 27.92.

Tetrathiafulvalene, $\Delta^{2,2'}$-Bis(1,3-dithiolidene). A mixture of 141 mg of **9** and 4 mL of pyridine was sealed in a heavy wall glass tube under argon. The tube was heated at 250 °C for 1.5 h. After cooling, the solvent was evaporated. The dark residue was extracted with three 10-mL portions of acetonitrile. The extracts were evaporated and the residue was sublimed at 110 °C (0.3 mmHg) to give 63 mg of orange product (63%). The structure was identified by the ^1H NMR spectra.

Registry No.—**1**, 55052-32-9; **2**, 1005-10-3; **3**, 26314-39-6; **4**, 7396-41-0; **5**, 23780-79-2; **6**, 17534-37-1; **7**, 64414-04-6; **8**, 59269-79-3; **9**, 51751-19-0; **10**, 64414-03-5; **11**, 64414-02-4; **12**, 55513-26-3; triphenylphosphine, 603-35-0; trimethyl phosphite, 121-45-9; triphenyl phosphite, 101-02-0; TTF, 31366-25-3.

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Carbon Acidity. 55. Acidity of 8,8-Dimethyl-8,12b-dihydrobenz[*a*]fluoranthene. Conjugating Effect of a Coplanar Phenyl[1]

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The preparation of the title compound (DDF) is described. Its anion is of the 9-phenylfluorenyl type with the phenyl group constrained to coplanarity with the fluorenyl moiety by the *gem*-dimethyl bridge. The pK_{CsCHA} of DDF, 15.45, is 3.0 p*K* units more acidic than 9-phenylfluorene. Of the total ΔpK_{CsCHA} of 7.6 units from fluorene itself, about one-third is attributed to polar effects and two-thirds to conjugation.

The phenyl group in 9-phenylfluorenyl anion (PF^-) is known to conjugate only weakly with the fluorene nucleus, undoubtedly because interactions with the 1- and 8-fluorene hydrogens prevent coplanarity. 9-Fluorene substitutents that exert inductive effects only have been shown to give a linear correlation in a plot of the relative acidity (pK_{CsCHA}) in the cesium cyclohexylamide (CsCHA) system against the polar substituent constant σ^*.[2] According to this correlation, the phenyl substituent with $\sigma^* = 0.600$[3] would provide a pK_{CsCHA} of 19.5 for a 9-phenylfluorene (PF) in which the phenyl group exerted a polar effect only.

In an important recent paper, Bordwell and McCollum[4]

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