(2 H, br s, NH); mass spectrum, m/e (%) 510 (100), 437 (38), 255 (6); UV–vis λ_{max} (ϵ_M) 616 nm (2200), 563 (5500), 524 (5400), 492 (13 600), 395 (184 000). Anal. $C_{30}H_{30}N_4O_4$.

Method 2. 2,2'-Dipyrrylmethane (11, 146 mg) and 2,4-dimethyl-3-[2-(methoxycarbonyl)ethyl]-5-formylpyrrole (14,[21] 418 mg) were dissolved in 20 mL of methanol. This mixture was treated immediately with 48% HBr (0.6 mL). After 10 min, the dark orange-red solution was diluted with ether (50 mL) and the biladiene salts began to deposit. More ether (50 mL) was added and the solid product collected by filtration to give the a,c-biladiene dihydrobromide 13 (380 mg, 55%): mp 300 °C; NMR δ 2.28 (6 H , s, 1',8'-Me), 2.72 (6 H, s, 2,7-Me), 2.5–2.8 (8 H, m, CH_2Cl_2), 3.60 (6 H, s, OMe), 4.81 (2 H, s, b-CH_2), 6.98 (4 H, q, 3,4,5,6-H), 7.05 (2 H, a,c-CH), 13.45 (4 H, br, NH^+); UV–vis λ_{max} (relative absorbance) 439 nm (1), 504 (2.53). The biladiene salts and copper (II) chloride (3 g) were stirred in 20 mL of DMF at 140 °C for 10 min. The solution was poured into ice water (200 mL), and the precipitates were collected by filtration. The black solid was dried and pulverized with 10 mL of concentrated sulfuric acid. After 30 min, the mixture was cautiously diluted with anhydrous methanol (100 mL) and set aside for 2 days. The mixture was filtered, the solid washed with CH_2Cl_2 (150 mL), and the solution washed twice with water. The organic layer was filtered through a 1-in. silica gel pad and the red solution, after concentration, chromatographed on a 20 × 20 cm preparative TLC plate (Analtech, silica gel, 1.5 mm thick), using CH_2Cl_2–2% methanol as solvent; 6 mg of porphyrin was obtained (1.2% yield). This compound was characterized by UV–vis, mass spectrum, NMR, and TLC to be identical with the porphyrin 4 obtained by method 1.

6,7-Bis[2-(methoxycarbonyl)ethyl]porphine or Dimethyl 1,2-Porphinedipropionate (3). Method 1. Dipyrrylmethane 18 (490 mg) was heated on a steam bath in a solution of 0.35 g of KOH in water (10 mL) and ethanol (10 mL) for 4 h. The solution was then evaporated to dryness in vacuo. The residue was treated with trifluoroacetic acid (10 mL) and left at room temperature for 1 h to effect decarboxylation. [5,5'-Diformyl-2,2'-dipyrryl]methane (10,[11] 202 mg) was dissolved in acetic acid (15 mL). The two solutions were joined and diluted immediately with glacial acetic acid (400 mL) containing 56% hydriodic acid (4 mL); acetic anhydride (10 mL) was added and the reaction mixture was set aside in the dark for 4 h. Anhydrous sodium acetate (10 g) was added and the mixture aerated overnight. Water (250 mL) and 50 mg of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) were added to the mixture, and aeration was continued for 30 h. The solvent was then removed under reduced pressure and the residue esterified and purified by chromatography in the same manner as described above. The porphyrin fraction after rechromatography on silica gel plates gave the title porphyrin (28 mg, 6%): mp 196 °C; NMR δ 3.45 (4 H, t, CH_2CO), 3.80 (6 H, s, OMe), 4.51 (4 H, t, CH_2), 9.14 (2 H, s, 5,6-H), 9.43 (4 H, q, AX pattern, J = 4.4 Hz, 1,2,3,4-H), 10.18 (3 H, s, β, γ, δ), 10.26 (1 H, s, α), –4.18 (2 H, br s, NH); mass spectrum, m/e (%) 482 (100), 309 (41), 241 (4); UV–vis λ_{max} (ϵ_M) 618 nm (1700), 563 (5400), 521 (4900), 491 (14 100), 496 (218 000). Anal. $C_{28}H_{26}O_4N_4$.

Method 2. Pyrrolepropionic ester 8 (506 mg) was heated on a steam bath in a solution of 0.35 g of KOH in water (10 mL) and ethanol (10 mL) overnight. The solvent was then removed in vacuo. The residue was dissolved in trifluoroacetic acid (10 mL); after 10 min, the acid solution was pumped to dryness at room temperature. The residue, taken in 10 mL of glacial acetic acid, was added to a solution of (5,5'-difromyl-2,2'-dipyrryl)methane (10,[11] 202 mg) in glacial acetic acid (10 mL). This mixture was treated immediately with 1 mL of 40% HBr in acetic acid, and after 20 min, the biladiene was precipitated by addition of ether (100 mL). The a,c-biladiene salt 12 has visible absorption maxima at 504 and 440 nm. This salt was redissolved in pyridine (40 mL), copper acetate (3 g) was added, and the mixture was stirred at room temperature for 10 min and then heated to 70 °C for 1 h. Fifty milliliters of water was added, the mixture was filtered, and the black precipitates, after being filtered and dried, were redissolved in concentrated sulfuric acid (10 mL). Methanol (100 mL) was added and the solution was set aside for 1 week. Purification of the porphyrin dimethyl ester by chromatography on silica gel TLC plates using CH_2Cl_2–2% MeOH as solvent gave

7 mg (1.5%) of 3, characterized by NMR, UV–vis, mass spectrum, and TLC to be identical with that obtained by method 1.

1,2,3,4,5,8-Hexamethyl-6,7-bis[2-(methoxycarbonyl)-ethyl]porphine (Dimethyl Ester of 2). Dipyrrylmethane 15 (204 mg) obtained by hydrogenolysis of [5,5'-bis[(benzyloxy)carbonyl]-3,3',4,4'-tetramethyl-2,2'-dipyrryl]methane,[12] followed by decarboxylation in trifluoroacetic acid, was dissolved in glacial acetic acid (10 mL) and mixed with another solution of pyrrole aldehyde 14[21] in glacial acetic acid (10 mL). This mixture was treated with 0.6 mL of 48% hydrobromic acid and after 10 min diluted with ether (50 mL) to complete the precipitation of the biladiene dihydrobromide. This salt was isolated by filtration and treated with copper(II) chloride in hot DMF as described above. Demetalation, methylation, and purification in the same manner gave 124 mg (22%) of 2 dimethyl ester: mp >300 °C; NMR δ 3.64 (3 H, s, OMe), 3.21 (4 H, t, CH_2CO), 4.30 (4 H, t, CH_2), 3.35, 3.38, 3.49 (6 H each, s, ring Me), 9.89 (1 H, s), 9.75 (2 H, s), 9.60 (1 H, s, meso protons), –4.0 (2 H, br s, NH); mass spectrum, m/e 566; UV–vis λ_{max} (ϵ_M) 620 nm (5200), 566 (6800), 531 (10 100), 497 (14 500), 497 (162 000). The data are consist with literature reports of 2 prepared by other methods.[5,6,23,24]

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Perdeuteriotetramethyltetraselenafulvalene

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Spin density wave (SDW) depinning was the original interpretation of the resurrection of spins (observed by solid-state ESR) and the reinstatement of metallic conductivity at low temperature and low electric fields in the organic superconductor bis(tetramethyltetraselenafulvalenium) hexafluorophosphate[1] [(TMTSF)$_2$PF$_6$]. There have been attempts to corroborate this interpretation[2] and to find other elucidations for the above observations.[3] There is, however, only one *definitive* way to confirm the existence of SDW's, and that is by means of neutron-scattering experiments. Since the background due to incoherent neutron scattering is much larger for protons than for deuterons and since SDW's would be expected to be of weak intensity,[4] they would be more easily observed in (TMTSF-d_{12})$_2$PF$_6$. Therefore, it was necessary to prepare the fully deuterated analogue of TMTSF. Also, since the carbon–deuterium bond is slightly shorter than the carbon–hydrogen bond, TMTSF-d_{12} is expected to be slightly smaller than TMTSF. This difference in size might have an effect on both the metal-to-semiconductor transition temperature and the metal-to-superconductor transition temperature (under pressure).[5] For the above reasons we decided to prepare TMTSF-d_{12}, and here we report on its preparation and spectroscopic properties.

Results and Discussion

We did not expect to be able to exchange the protons in TMTSF; therefore, the most logical approach was to

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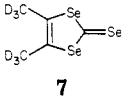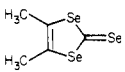
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Table I

|	IR ^{a,d}	UV–vis ^{b}	CV ^{c,d}
TMTSF	2970 (m), 2902 (s), 2840 (m), 1617 (m), 1434 (vs), 1145 (m), 1062 (s), 665 (s)	508 ± 5, ^{e} 299 ± 1 ^{e}	430 ± 10, 730 ± 10
TMTSF-d_{12}	2225 (m), 2190 (m), 2095 (m), 2050 (m), 1599 (m), 1170 (m), 1108 (m), 1036 (s), 1007 (m), 942 (vs), 748 (w), 658 (m)	508 ± 5, ^{d} 299 ± 1 ^{d}	430 ± 10, 730 ± 10
7	890 (vs), 706 (s) ^{d,g,h}	557 (250), 422 (17 500), ^{d,f} 325 (920), 280 (3180)	
	890 (vs), 762 (s) ^{d,g,h}	555 (224), 424 (14 800), ^{e,f} 328 (730), 266 (6200)	

^{a} Sublimed film on NaCl. ^{b} CH$_2$Cl$_2$ in nanometers. ^{c} Cyclic voltammetry: $E^{1/2}$, CH$_2$Cl$_2$, 0.1 M Bu$_4$NBF$_4$, vs. SCE, 200 mV/s. ^{d} This work. ^{e} Reference 6. ^{f} Hexane. ^{g} KBr disk. ^{h} C–H and C–D stretching too weak to be seen.
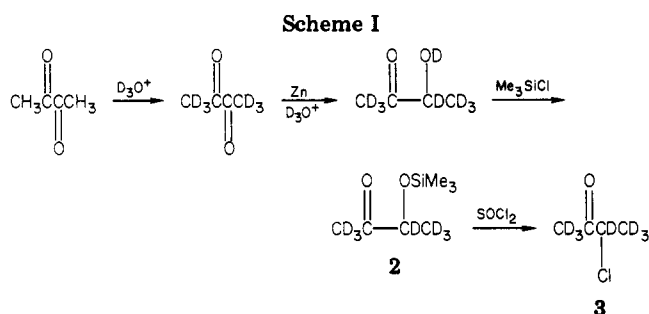
Scheme I

Scheme II

start with **3**, which could be carried on to the target by the route developed for the protio material (see Scheme II).[6,7] There are two principal approaches to such a labeled product: (a) to use deuterated starting materials and build up the carbon skeleton or (b) to exchange hydrogen for deuterium in a precursor containing the desired carbon skeleton (Scheme I).

The first approach (condensation of deuterioacetaldehyde) which involved attempts to prepare acetoin trimethylsilyl ether from *O*-(trimethylsilyl)acetaldehyde cyanohydrin **1** by sequential treatment with LDA and acetaldehyde according to the method of Hünig,[8a] failed to yield even a trace of the desired product. Wright and West have also attempted to prepare lithio-substituted **1** and reported only low yields (15–30%) of characterizable products after quenching with chlorosilanes.[8b] Therefore, in contrast to aryl-[8a] and vinyl-substituted[8c] *O*-trimethylsilyl cyanohydrins, the unstabilized alkyl substituted analogues do not appear to be synthetically useful. Attempts to use deuterioethyl acetate were abandoned because the acyloin coupling step could not be improved beyond ~30% yield.

The chloro ketone **3** could be prepared most efficiently via the deuteration of biacetyl as shown in Scheme I. Reduction of biacetyl to the acetoin and conversion of the latter to the Me$_3$Si ether permitted preparation of the chloro ketone **3** in good yield. We could not reproduce the literature yields in the direct conversion of acetoin to the chloro ketone with thionyl chloride.[9] Attempts to displace
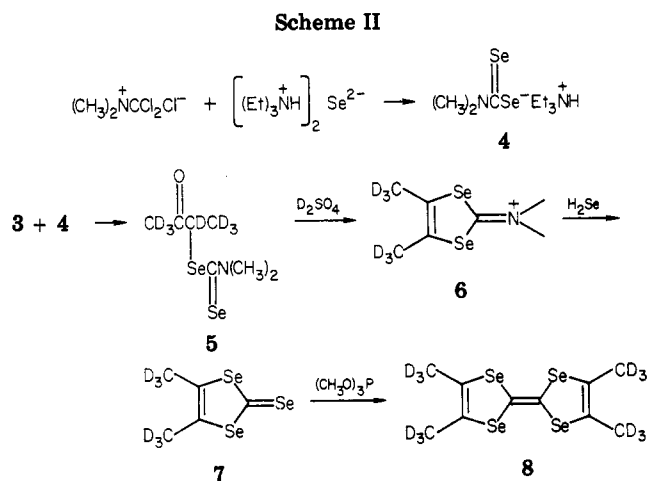
the trimethylsiloxy group in a model compound, benzoin trimethylsilyl ether, with sodium *N,N*-dimethyldithiocarbamate were not successful. Such a displacement with a Grignard reagent has been reported.[10]

The chloro ketone thus obtained was converted to TMTSF-d_{12} (**8**) via our modification of the usual synthesis.[6,7] Precautions were taken to always keep the reaction medium fully enriched in deuterium; for example, the cyclization of the diselenocarbamate **5** to the 2-(dimethylamino)-1,3-diselenolium ion **6** was performed in pure D$_2$SO$_4$ (Scheme II).

The final product (**8**) was twice gradient sublimed onto Teflon and analyzed spectroscopically. The UV–vis spectrum and cyclic voltammetry half-wave potentials were (within experimental error) identical with those for TMTSF. Infrared spectroscopy (cf. Table I) revealed that (within experimental error, ±5%) there was no absorption due to C–H stretching and only absorption due to C–D stretching (2225–2050 cm^{-1}) and bending vibrations. Good spectra could only be obtained when samples were sublimed directly onto sodium chloride plates.

The hexafluorophosphate and perchlorate salts were prepared electrolytically[5] in the usual manner and subjected to the usual physical measurements. Results of

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these[10] and neutron-scattering experiments will be reported elsewhere.

Experimental Section

3-Chloro-2-butanone-d_7 (3). Biacetyl-d_6 was prepared via the acid-catalyzed exchange of biacetyl (Aldrich) and deuterium oxide.[11] After four cycles (0.7 N D_2SO_4/D_2O, 95 °C, 48 h per exchange), the distilled product was 99% deuteriated (99.5% by comparative ^{1}H NMR;[12] 98.9% by mass spectroscopy).

Perdeuteriobiacetyl (9.2 g, 0.1 mol) was reduced with zinc in D_2SO_4 according to the literature procedure for biacetyl.[13] When methylene chloride was used to extract the hydrophilic product, only seven extractions (total volume 350 mL) were required rather than the continuous extraction necessary with ether.[13] The solution was dried (MgSO$_4$), and the solvent was distilled at atmospheric pressure. The residue (6.6 g, 70%) was used directly in the next step.

The crude perdeuterioacetoin was dissolved in 10 mL of dry pentane and cooled to 0 °C. A 1:1 (molar ratio) mixture of chlorotrimethylsilane and pyridine (17.9 g, 0.095 mol) was added dropwise with stirring at 25 °C. The pyridine hydrochloride which formed was separated by centrifugation and washed with pentane. The combined pentane extracts were distilled at atmospheric pressure until the bath temperature reached 95–100 °C. The resulting trimethylsilyl ether was used without further purification.

The neat trimethylsilylacetoin was heated to 95 °C (bath temperature) and titrated with distilled thionyl chloride containing a few drops of pyridine. When 6 mL of thionyl chloride had been added, NMR spectroscopy (of the analogous reaction on protio material) indicated clean, quantitative conversion to chloro ketone. Attempts to isolate the chloro ketone quantitatively have failed for both protio and deuterio compounds. Thus the fraction boiling at 67 °C (200 mm; pure 3) only amounted to 3.7 g (32.5% yield based on biacetyl, ~50% based on silylacetoin). This material was pure by GC/MS (parent peak m/e 113).

3-[(N,N-Dimethylselenocarbamyl)seleno]-2-butanone-d_7 (5). A solution of 9.9 mL of freshly distilled triethylamine in 250 mL of chloroform (dried over alumina) was cooled to –10 °C (ice–acetone), deoxygenated with argon, and treated for ca. 10 min with a fast stream of hydrogen selenide. *Complete exclusion of the ambient atmosphere is required throughout this entire sequence.* The hydrogen selenide stream was then replaced by a fast stream of argon. The argon was purged through the reaction mixture for 2 h at room temperature, or until no more H_2Se could be detected in the effluent gas (a trace of triethylamine will produce smoke if there is H_2Se present). In quick succession, 9.9 mL of triethylamine and 5.72 g of phosgeniminium chloride (Aldrich) were added to the previously cooled (0 °C) triethylammonium hydrogen selenide. The deep orange reaction mixture was allowed to stir at room temperature for 2 h. It was cooled to 0 °C and treated with a solution of 3.4 g of 3 in 10 mL of dry chloroform (dropwise) over 10 min. The mixture was stirred at room temperature for 2 h, the solvent was removed under vacuum overnight, and the residue was extracted with six 100-mL portions of ether. The ether was evaporated to afford a yellow oil which quickly crystallized. Diselenocarbamate 5 (6.4 g, 73% yield), pure by NMR and mass spectra, was thus obtained. This material was subjected to the usual TMTSF synthesis (see below) without further purification.

Perdeuteriotetramethyltetraselenafulvalene. The above diselenocarbamate was added over 10 min to stirred, cooled (–10 °C) D_2SO_4 (18 mL, 99% deuterated Aldrich). After the addition was complete, the mixture was heated to 58 °C (internal temperature) over 5 min and stirred at that temperature for another 5 min, cooled in ice–acetone, and poured onto ~50 g of ice. The mixture was filtered rapidly three times (until the filtrate remained clear) and then treated with a filtered solution of excess sodium

hexafluorophosphate in 20 mL of water. The resulting precipitate was separated by suction filtration on a glass frit and was washed copiously with water. It was dissolved in methylene chloride, and the solution was dried (sodium sulfate) and evaporated to afford 5.9 g (64%) of tan salt 6.

This solid was immediately suspended in 200 mL of 70% aqueous methanol, and the suspension was cooled to –10 °C while being degassed with argon over 15 min. Hydrogen selenide was then passed through the suspension at that temperature for 15 min, which caused the solid slowly to turn orange. The reaction mixture was stirred at room temperature for 2 h while excess hydrogen selenide was allowed to vent through two KOH traps. The product was filtered, washed with water, and dried by being dissolved in methylene chloride–benzene and treated with MgSO$_4$. Filtration followed by evaporation yielded 4.15 g (96%) of the deuterio selenone 7 as a red solid. Recrystallization via multiple extraction with hexane gave red needles: mp 150–151 °C; spectroscopic properties as shown in Table I; mass spectrum, parent ion at m/e 312.

A suspension of 2.6 g of 7 was refluxed in 7 mL of benzene under argon, and 1.9 mL of distilled trimethyl phosphite was added in a fine stream. The mixture was refluxed for 45 min, cooled, filtered, washed with ether, and dried under argon to obtain 1.72 g (90% yield) of purple prisms. Recrystallization from chloroform (≤50 mL) gave 1.57 g of small needles. Vacuum gradient sublimation onto Teflon at 10^{-5} torr and an initial temperature of 165 °C afforded material for electrochemical crystal growth. Spectroscopic properties are shown in Table I. Comparative NMR showed 99.5% deuteration.

Practical, Catalytic Synthesis of Anthranilic Acids

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This paper describes a convenient new route to the substituted anthranilic acids 3. In order to meet our requirements for a technical synthesis of anthranilic acids, we considered use of nickel-[2] or palladium–phosphine complex[3] catalyzed carbonylations of 2-bromoanilines. We decided to investigate palladium catalysts, e.g., Pd(PPh$_3$)$_4$, Pd(PPh$_3$)$_2$(Cl)$_2$, etc., because these systems seemed to be more robust and easier to handle than the nickel analogues. Previous workers[4] had found that palladium–triphenylphosphine complex catalyzed substitution reactions of 2-bromoanilines gave poor results, apparently because of quarternization of triphenylphosphine by the substrate which gave the poor ligand [Ar(NH$_2$)PPh$_3$]$^+$. Two solutions to this problem, which were described by Heck,[5,6] are

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