Organic Metals. A Study of the Hurtley–Smiles Tetrathiafulvalene Synthesis

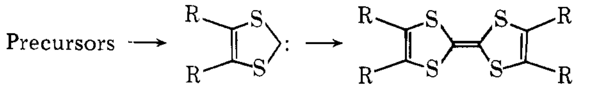
Masao Mizuno and Michael P. Cava*

Department of Chemistry and Laboratory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia, Pennsylvania 19104

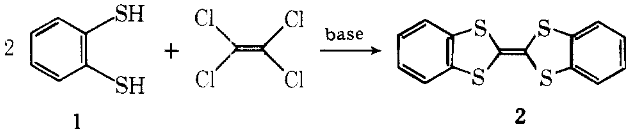
Received July 25, 1977

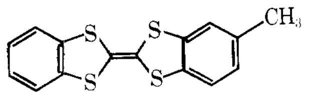
The reaction of excess tetrachloroethylene with *o*-benzenedithiol (**1**) and with disodium *cis*-ethenedithiolate (**6**) affords 2-dichloromethylene-4,5-benzo-1,3-dithiole (**4**) and 2-dichloromethylene-1,3-dithiole (**10**), respectively. Reaction of **1** with either **4** or **10** under basic conditions yields only dibenzotetrathiafulvalene (**2**). A similar reaction of **1** with tetrakis(carbomethoxy)tetrathiafulvalene (**12**) results in transdithiolation with the formation of **2** and 4,5-bis(carbomethoxy)-4′,5′-benzotetrathiafulvalene (**13**). Mechanisms of these reactions are discussed.

Since the first report on the high electrical conductivity of the charge-transfer salt of tetrathiafulvalene–tetracyanoquinodimethane (TTF–TCNQ) in 1973,[1] much interest has been generated in the synthesis of tetrathiafulvalene derivatives and analogues.[2] Almost all known tetrathiafulvalenes are symmetrical compounds, which are generally prepared by reactions involving the coupling of intermediary carbene or carbenoid monomers.[2]



In 1926, Hurtley and Smiles found that *o*-benzenedithiol (**1**) reacts with tetrachloroethylene under basic conditions to give dibenzotetrathiafulvalene (**2**).[3] This reaction, which represents the first synthesis of any tetrathiafulvalene, received no further attention until a half century later. At that time, improved reaction conditions were reported, and the reaction of tetrachloroethylene with a mixture of *o*-benzenedithiol and toluene-3,4-dithiol was found to give a mixture of products from which the pure mixed TTF derivative **3** could be crystallized.[4]





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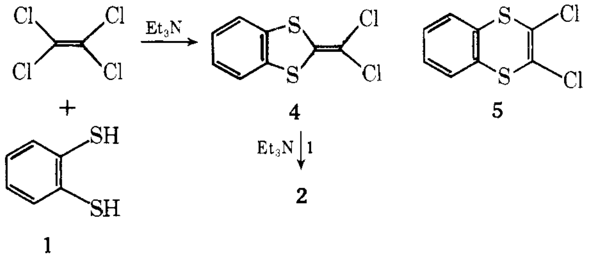
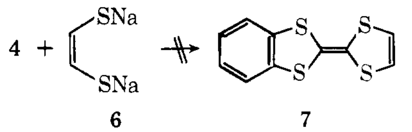
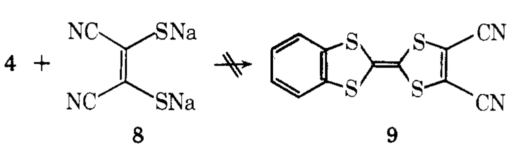
As part of a broad investigation of synthetic routes to unsymmetrical tetrathiafulvalenes,[5] we now report the results of a further study of the Hurtley–Smiles synthesis, aimed at its modification for the synthesis of monobenzotetrathiafulvalenes.[6]

Results

Dithiol **1**[7] was allowed to react with excess tetrachloroethylene and triethylamine in DMF at room temperature with the objective of isolating the intermediate dihalide in the Hurtley–Smiles reaction. Workup after 3 days afforded only a small amount of the symmetrical TTF **2** (5%), the major product (59%) being a colorless, crystalline compound, $C_8H_4S_2Cl_2$, mp 157–158 °C. This compound was assigned the structure 2-dichloromethylene-4,5-benzo-1,3-dithiole (**4**) rather than the isomeric benzodithiin structure **5**, since it was slowly converted in high yield to **2** on treatment with dithiol **1** and triethylamine in refluxing acetonitrile. On the other hand, attempts to convert **4** to monobenzotetrathiafulvalene (**7**) or its dinitrile **9** by reaction with disodium *cis*-ethenedithiolate (**6**)[8] or disodium *cis*-dicyanoethenedithiolate (**8**)[9] were unsuccessful, the starting dihalide being recovered unchanged.

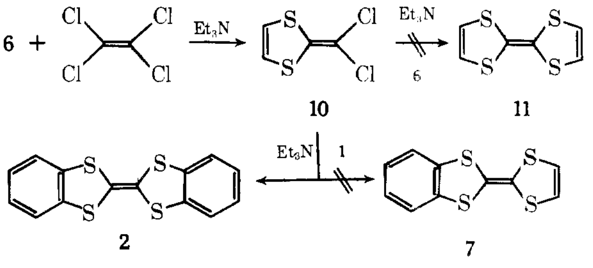






The dithiolate salt **6** was found to react with excess tetrachloroethylene in the presence of triethylamine to give a single isolable product (42%), mp 55–58 °C, assigned the structure 2-dichloromethylene-1,3-dithiole (**10**) by analogy with **4**. In contrast to **4**, which is quite stable to storage, dichloride **10** decomposes to a black tar on keeping overnight in the refrigerator; it rapidly turns blue on contact with silica, but it can be purified chromatographically on basic alumina. Attempts to convert **10** to tetrathiafulvalene (**11**) by further reaction with the salt **6** were unsuccessful, and led only to the destruction of **10**.

By contrast, dichloride **10** reacted with *o*-benzenedithiol (**1**) in the presence of triethylamine. The only isolable product (30%) was not, however, the expected monobenzotetrathiafulvalene (**7**),[6] but rather dibenzotetrathiafulvalene (**2**).



On the basis of mechanistic considerations of the above reaction (see Discussion), it seemed possible that each dichloromethylene unit of tetrachloroethylene might be re-

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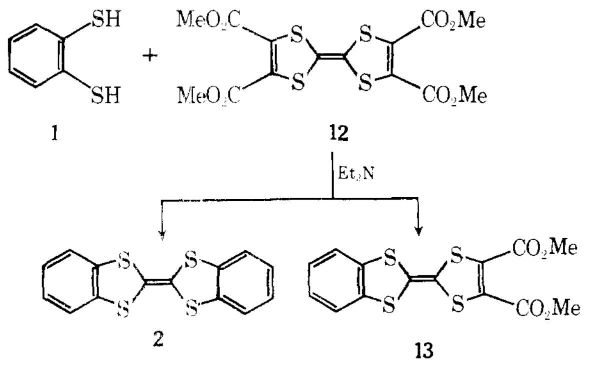
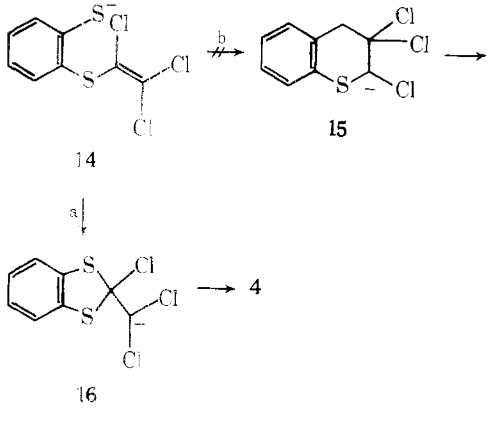
placeable by an electron-deficient 1,3-dithiole unit in the Hurtley–Smiles reaction. Indeed, reaction of excess *o*-benzenedithiol (1) with tetrakis(carbomethoxy)tetrathiafulvalene (12)[10] in the presence of triethylamine resulted in the quantitative conversion of tetraester 12 into dibenzotetrathiafulvalene (2). A similar reaction of equimolar quantities of 1 and 12 afforded a small amount (7%) of 2, along with a modest yield (19%) of 4,5-bis(carbomethoxy)-4′,5′-benzotetrathiafulvalene (13).[6] Since diester 13 is readily converted in one step to monobenzotetrathiafulvalene (7),[6] the latter is therefore accessible from readily prepared starting materials[7,10] by the use of this new "transdithiolation" synthesis.



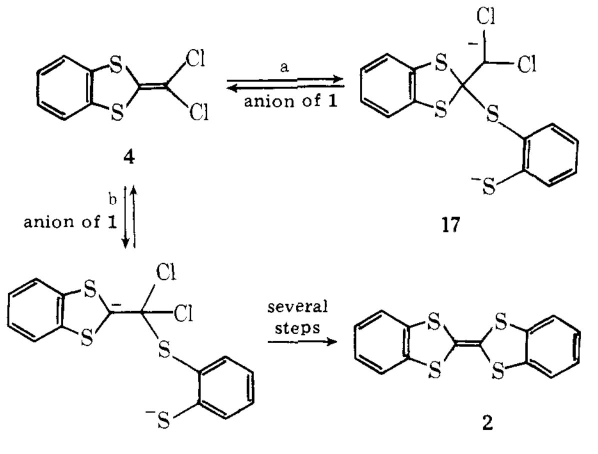
Discussion

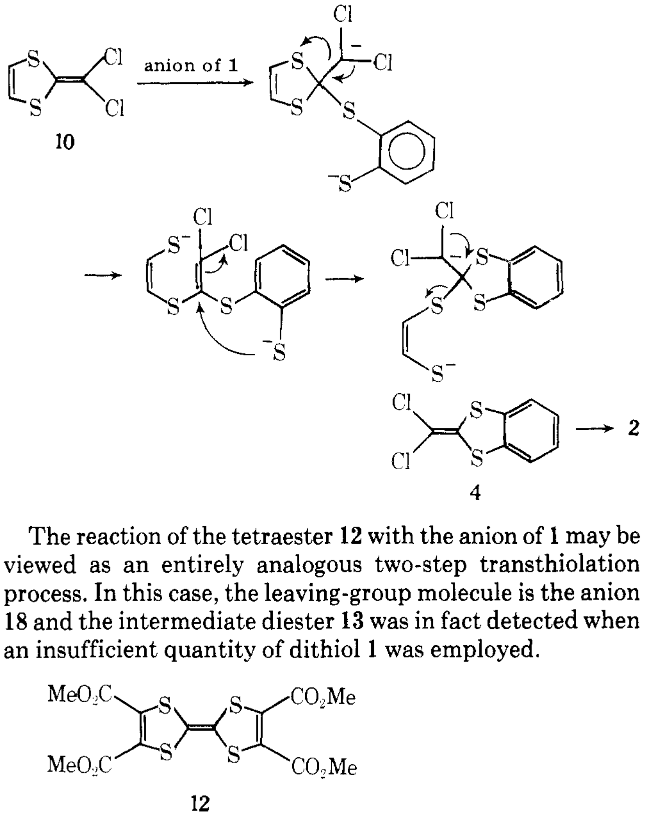
The formation of the five-membered ring heterocycles 4 and 10 from tetrachloroethylene, rather than six-membered isomers (e.g., 5), appears to fit formally within the framework of Baldwin's rules, although these rules are of doubtful predictive value when applied to anions of second-row elements.[11] The observed products are also explicable, however, on the basis of the greater electronegativity of chlorine as compared to sulfur. Thus, in the case of the reaction of *o*-benzenedithiol (1) with tetrachloroethylene, the structure of the final dichloride is determined by the point of attack (a or b) of the intermediary thiolate anion 14. Path a should be of lower energy than path b due to the greater stability of carbanion 16 over the isomeric carbanion 15.



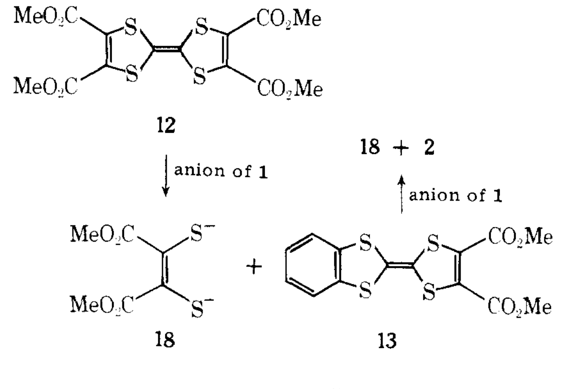
The electronegativity argument proposed above also explains why the anion of dithiol 1 reacts more slowly with dihalide 4 than it does with tetrachloroethylene. Thiolate attack on 4 should occur preferentially, *but reversibly*, by path a to give the more stable anion 17; attack at the chlorine-bearing carbon (path b) should occur less often, but it will eventually lead to the formation of dibenzotetrathiafulvalene (2).

In accord with this mechanism, dichloride 10 will react preferentially with the anion of 1 at the sulfur-bearing carbon, resulting in transthiolation with the formation of dichloride 4; further reaction of 4 with 1 then gives 2 as outlined above.





The reaction of the tetraester 12 with the anion of 1 may be viewed as an entirely analogous two-step transthiolation process. In this case, the leaving-group molecule is the anion 18 and the intermediate diester 13 was in fact detected when an insufficient quantity of dithiol 1 was employed.



Experimental Section

Melting points are uncorrected. NMR ($CDCl_3$ containing Me_4Si as internal standard), infrared (KBr), ultraviolet, and mass spectra were determined using Varian A-60, and Perkin-Elmer 137, 202 and 270B spectrometers, respectively.

2-Dichloromethylene-4,5-benzo-1,3-dithiole (4). *o*-Benzenedithiol[7] (3.6 g, 0.025 mol) and triethylamine (10.0 g, 0.10 mol) were dissolved in 100 mL of dimethylformamide, and tetrachloroethylene (16.8 g, 0.10 mol) was added dropwise with stirring at room temperature under an argon atmosphere. The reaction was allowed to proceed for 3 days at room temperature. The reaction mixture was poured into 300 mL of water and extracted with benzene. The benzene layer was washed with water, dried (Na_2SO_4), and evaporated to give a yellow oil. The oil was chromatographed on silica (hexane–benzene) to give 3.5 g of colorless needles of 2-dichloromethylene-4,5-benzo-1,3-dithiole (4, 59%) and 0.2 g of yellow crystals of dibenzotetrathiafulvalene (2, 5%). The water layer was acidified to pH 5 with hydrochloric acid and reextracted with benzene. The benzene layer was dried (Na_2SO_4) and concentrated to give 0.6 g of *o*-benzenedithiol (**1**, 17%).

2-Dichloromethylene-4,5-benzo-1,3-dithiole (**4**): mp 157–158 °C; UV (cyclohexane) λ_{max} 207 nm (ϵ 7700), 242 (15 000), 266 (9900), 277 (10 000), 314 (4200); NMR δ 7.16 (s); mass spectrum *m/e* (rel intensity) 238 (17), 236 (72), 234 (100), 199 (18), 164 (15).

Anal. Calcd for $C_8H_4S_2Cl_2$: C, 40.85; H, 1.70; S, 27.23; Cl, 30.21. Found: C, 40.84; H, 1.63; S, 27.00; Cl, 30.00.

The dibenzotetrathiafulvalene, mp 232–234 °C (lit.[3] 234 °C), was identical (IR) with an authentic sample.

Attempted Reaction of 2-Dichloromethylene-4,5-benzo-1,3-dithiole (4) with Disodium *cis*-Ethenedithiolate (6). 2-Dichloromethylene-4,5-benzo-1,3-dithiole (**4**, 60 mg, 0.25 mmol) and disodium *cis*-ethenedithiolate[8] (140 mg, 1 mmol) were dissolved in 10 mL of dimethylformamide, and the solution was stirred for 3 days at room temperature under an argon atmosphere. The reaction mixture was poured into 25 mL of water and extracted with benzene. The benzene layer was washed successively with dilute aqueous sodium hydroxide, water, dilute hydrochloric acid, and finally with water, dried ($MgSO_4$), and evaporated to give a brown solid. Chromatography on silica (hexane–benzene) afforded 55 mg of the starting material **4** as colorless needles, mp 157–158 °C.

2-Dichloromethylene-4,5-benzo-1,3-dithiole (60 mg) and disodium salt **6** (140 mg) were dissolved in 10 mL of acetonitrile, and the mixture was refluxed for 15 h under an argon atmosphere. The reaction mixture was worked up as above to give 57 mg of recovered starting material as colorless needles, mp 157–158 °C. Attempted reaction of **4** with salt **8**[9] led to similar results.

Reaction of 2-Dichloromethylene-4,5-benzo-1,3-dithiole (4) with *o*-Benzenedithiol (1). *o*-Benzenedithiol (40 mg, 0.28 mmol) and triethylamine (100 mg, 1 mmol) were dissolved in 10 mL of acetonitrile, and dichloride **4** (60 mg, 0.25 mmol) was added with stirring at room temperature under an argon atmosphere. The reaction was allowed to proceed for 15 h at reflux. The reaction mixture was poured into 50 mL of water and extracted with benzene. The benzene layer was washed several times with water, dried (Na_2SO_4), and evaporated to give a yellow solid. The solid was chromatographed on silica using hexane–benzene to give dichloride **4** as colorless needles (25 mg, 42%), mp 157–158 °C, and dibenzotetrathiafulvalene (**2**) as yellow crystals (35 mg, 47%), mp 232–234 °C.

2-Dichloromethylene-1,3-dithiole (10). Disodium *cis*-ethenedithiolate (140 mg, 1.0 mmol) was dissolved in 10 mL of dimethylformamide. The solution was stirred at room temperature under an argon atmosphere, and tetrachloroethylene (510 mg, 3.0 mmol) was added dropwise. The reaction was allowed to proceed for 4 h at room temperature, and then the solution was poured into 30 mL of water and the mixture was extracted with benzene. The benzene layer was washed several times with water, dried (Na_2SO_4), and concentrated to give a dark brown oil. Chromatography on basic (I) alumina (hexane) gave 2-dichloromethylene-1,3-dithiole (**10**) as slightly yellow needles (80 mg, 42%), mp 55–58 °C; NMR δ 6.35 (s); mass spectrum *m/e* (rel intensity) 186 (74), 184 (100), 149 (62), 126 (32). This compound was not sufficiently stable to obtain an elementary analysis. It also decomposed readily on plates of silica gel or acid alumina, giving an initially colorless spot which turned blue and finally yellow.

Reaction of 2-Dichloromethylene-1,3-dithiole (10) with *o*-Benzenedithiol (1). *o*-Benzenedithiol (50 mg, 0.35 mmol), dichloride **10** (40 mg, 0.22 mmol), and triethylamine (100 mg, 1.0 mmol) were dissolved in 10 mL of acetonitrile. The solution was stirred for 15 h at reflux under an argon atmosphere. The reaction mixture was poured into 30 mL of water and extracted with benzene. The benzene layer was washed several times with water, dried (Na_2SO_4), and evaporated to give a brown oil, which was chromatographed on a dry silica column (hexane–benzene) to give yellow crystals of dibenzotetrathiafulvalene (**2**, 20 mg, 30%), mp 232–234 °C.

Reaction of Tetrakis(carbomethoxy)tetrathiafulvalene (12) with an Excess of *o*-Benzenedithiol (1). Tetraester **12**[10] (220 mg, 0.5 mmol), *o*-benzenedithiol (355 mg, 2.5 mmol), and triethylamine (505 mg, 5.0 mmol) were dissolved in 10 mL of acetonitrile. The solution was stirred for 15 h at reflux under an argon atmosphere. The reaction mixture was poured into 100 mL of water and extracted with benzene. The benzene layer was washed several times with water, dried (Na_2SO_4), and evaporated to give a yellow solid. Recrystallization from benzene gave yellow plates of dibenzotetrathiafulvalene (**2**, 140 mg, 92%), mp 231–233 °C.

Reaction of Tetraester 12 with an Equimolar Amount of *o*-Benzenedithiol (1). Tetraester **12** (220 mg, 0.5 mmol), *o*-benzenedithiol (75 mg, 0.5 mmol), and triethylamine (100 mg, 1.0 mmol) were dissolved in 10 mL of acetonitrile. The solution was stirred for 15 h at reflux under an argon atmosphere. The reaction mixture was poured into 50 mL of water and extracted with benzene. Workup as above, followed by chromatography on a dry silica column (hexane–benzene), gave yellow crystals of dibenzotetrathiafulvalene (**2**, 10 mg, 7%, mp 232–234 °C) and the reddish-brown diester **13** (35 mg, 19%). The latter solid was recrystallized from methanol to give reddish-brown needles (25 mg), mp 171–173 °C (lit.[6] 171–173 °C), identical (IR, mass spectrum) with authentic material.[6]

Acknowledgment. This work was supported by the National Science Foundation MRL program under Grant DMR 76-00678.

Registry No.—**1**, 17534-15-5; **2**, 24648-13-3; **4**, 64188-91-6; **6**, 17934-70-2; **10**, 64188-90-5; **12**, 26314-39-6; **13**, 62921-53-3; tetrachloroethylene, 127-18-4.

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