

CHEMISTRY OF GEMINAL-DITHIOLATES DERIVED FROM CYANO-SUBSTITUTED
TETRATHIAFULVALENES

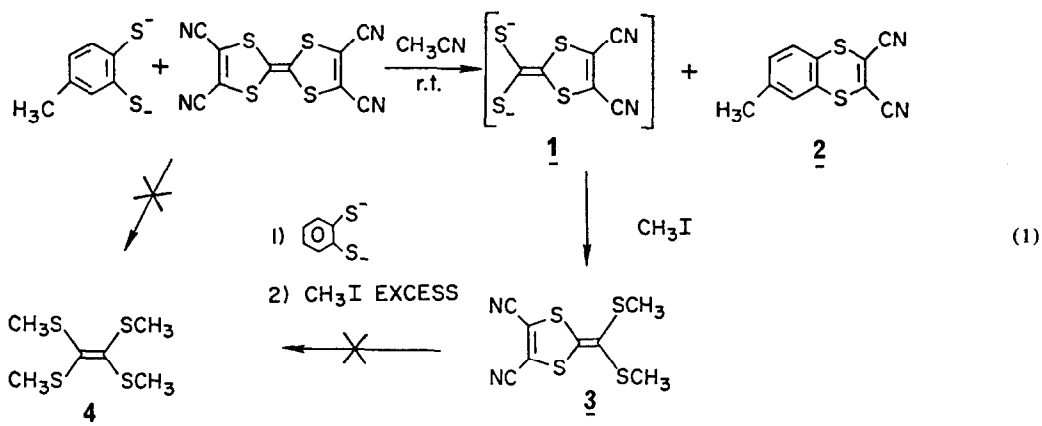
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Abstract: Tetracyanotetrathiafulvalene reacts with two equivalents of thiol salts (RS^-) to give 1,2-dicyano-1,2-di RS ethene and a geminal dithiolate intermediate which reacts with a variety of reagents to provide novel tetrathioethene derivatives, such as reaction with 3-chloro-2-butanone and acid to give dimethyldicyanotetrathiafulvalene.

The discovery of metal-like conductivity,¹ superconductivity² and reversible electrochromism³ in tetrathiafulvalene (TTF) derivatives has prompted considerable research on the chemistry⁴ of this interesting π -heterocycle. Most of this work has focused on coupling and synthesis of the key synthetic precursor, the 1, 3-dithiole ring system. Only recently has the direct modification of the tetrathiafulvalene ring itself^{5,6} been investigated as a means of elaborating new derivatives. In one such study, Cava and co-workers,^{6a} described the reaction of salts of o-dithiolbenzene with tetracarbomethoxytetrathiafulvalene which leads to substituent exchange through nucleophilic attack at the internal double bond in TTF. In a study aimed at extending this chemistry to other tetrathiafulvalenes that are substituted with electron-withdrawing substituents, we discovered an unexpected reaction which takes place when the salts of 3,4-dithioltoluene are reacted with tetracyanotetrathiafulvalene. Instead of attack at the internal bond, nucleophilic attack is now shifted to the more electron deficient external double bond as shown by equation 1 to provide 2,3-dicyano-5,6-tolu-1,4-dithiene (**2**: yellow needles; mp 180°C; ir (KBr, cm^{-1}): 2220 m, 1580 m, 1510 m, 1375 m, 1310 m, 805 s; nmr (δ , $CDCl_3$): 2.33 s, 1H, 7.2 multiplet, 1H) and an air-sensitive geminal-dithiolate intermediate (**1**) which was converted on treatment with methyl iodide to gem-dithiomethyl-(4,5-dicyano-1,3-dithioliden-2-yl)methylene (**3**: purple needles; mp 126-127°C; ir (KBr, cm^{-1}): 2900 br, 2210 m, 1570 m, 1525 s, 1465 s, 1450 sh, 1175 m, 820 m; nmr (δ , $CDCl_3$): 2.31 s).



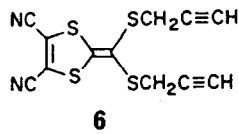
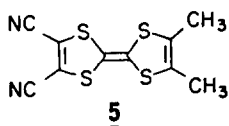
In contrast to Cava's reaction which involves refluxing in acetonitrile, nucleophilic attack on tetracyanotetrathiafulvalene occurs at room temperature, and is complete in a matter of minutes as seen by a distinct color change of the reaction mixture from dark-red to pale green-yellow. The reaction is run under nitrogen to prevent oxidation of 1 which is converted in situ to stable derivatives. The products are separated by chromatography in typical yields of 60-80%.

Attempts to react both external double bonds with two mole equivalents of salts of *o*-dithioltoluene did not provide the ethenetetrathiolate intermediate as judged by our inability to detect any tetrathiomethylethene (4) in the product mixture after adding methyl iodide. Also, further reaction of 3 with salts of *o*-dithioltoluene and treatment with methyl iodide did not afford 4. Tlc examination of the product mixtures from these reactions show a multitude of products which have not been further characterized.

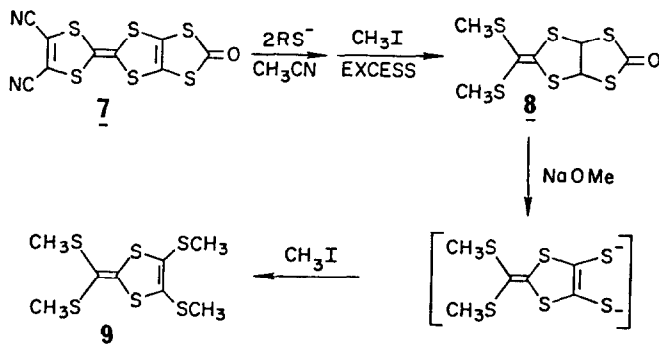
The reaction of thiol salts with tetracyanotetrathiafulvalene appears to be rather general. Alkyl (CH_3S^-), aryl ($\text{C}_6\text{H}_5\text{S}^-$) and acyl (CH_3COS^-) thiols react with tetracyano-TTF to give geminal-dithiolate 1. Also, selenol and tellurol salts are reactive as determined by the subsequent addition of methyl iodide to give dithiomethyl derivative 3, however, in lower yields. The selenium analog of tetracyano-TTF reacts in a similar fashion. Apparently, the chemistry described by equation 1 is specific for cyano-substituted tetrathiafulvalenes and its selenium analogs, since attempts to react tetratrifluoromethyl-TTF in an analogous fashion did not provide the expected products. A complex product mixture is obtained which has not been characterized beyond gpc/mass spectrum analysis which indicated the absence of the expected parent ions.

The synthetic importance of the geminal dithiolate intermediate lies in the varied types of tetrathioethene derivatives that can be elaborated from it. Most of our reactions of 1 have focused on reconstructing the TTF ring system. In this regard, ring closure in 1 by reaction with 1,2-dihalo-derivatives to provide dihydro-TTF derivatives, and with α -haloketones and acid to give TTF derivatives appear to be particularly promising routes to that end. For example, reaction of 1 with 3-chloro-2-

butanone, followed by dissolving the crude reaction mixture in concentrated sulfuric acid provided dimethyldicyanotetrathiafulvalene in 20% yield (**5**, purple needles; mp 230 °C; ir (KBr, cm⁻¹): 2220 m, 1500 s, 1180 s, 1050 s, 760 s; nmr (δ CDCl₃): 1.97 s). Reaction of **3** with propargyl bromide, in analogy with previous work⁷ on the malonitrile-carbon disulfide adduct, failed to undergo ring closure, but instead gave displacement product **6** in 33% yield (orange yellow needles; m.p. 165°C; ir (KBr, cm⁻¹): 2220 m, 2080 w, 1510 m, 1410 sh, 1225 m, 1175 m, 710 s; nmr (δ CDCl₃): 2.5 triplet 1H, 3.9 doublet, 2H).



An illustration of the synthetic utility of the reaction of thiol salts with cyano-substituted tetrathiafulvalenes is afforded by the reaction of unsymmetrically substituted TTF **7**.⁸ This compound possesses two base-sensitive functional groups. However, reaction of **7** with thiol salts at 0°C leads to attack preferentially at the cyano-substituted double bond to provide, after treatment with methyl iodide, product **8**. Subsequent reaction of **8** with stronger base (CH₃Li, NaOMe) leads to attack at the dithiocarbonate group to give a 1,2-dithiolate intermediate which can be reacted with methyl iodide to give **9** in 20% yield (yellow oil; ir (CCl₄, cm⁻¹): 2900 s, 2840 m, 1720 m, 1680 w, 1475 s, 1305 m, 960 m; nmr (δ, CDCl₃): 2.3 s, 1H, 2.4 s, 1H).



Part of our interest in some of these 1,2-dicyano heterocycles was based on their possible conversion to phthalocyanines.⁹ Preliminary studies have indicated that reaction of **3** and **5** with nickel octoate in refluxing quinoline did not provide the corresponding phthalocyanines, but rather underwent decomposition. Compound **2** is readily converted to the expected phthalocyanine derivative.

References and Notes

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