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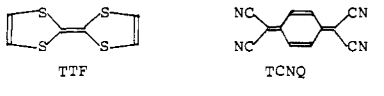
## Photodesulfurization by Distannane. Photochemical Synthesis of Tetrathiofulvalenes

*Sir:*

The recent discovery[1] of highly conductive organic charge transfer complexes which are formed from derivatives of tetrathiofulvalene (TTF) and the acceptor molecule, tetracyano-*p*-quinodimethane (TCNQ), has stirred interest in the discovery of a new synthetic method for TTF derivatives.[2]



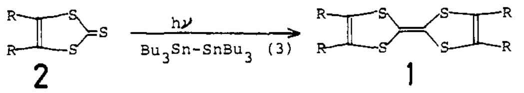
In connection with our previous work[3] on TTF and related compounds, we have investigated the one-step synthesis of TTF derivatives from 1,3-dithiole-2-thiones.

**Table I.** Photosynthesis of TTF derivatives **1**[a]

| | 2<br>R | (mmol) | 3<br>(mmol) | Solvent[b]<br>(ml) | Yield of 1[c]<br>(%) | |
|---|---|---|---|---|---|---|
| **2a** | Me | 0.5 | 0.5 | H (18) | **1a** | 56 |
| **2a** | Me | 0.5 | 1.0 | H (18) | **1a** | 77 |
| **2b** | $+CH_2+_2$ | 0.5 | 0.5 | B (18) | **1b** | 68 |
| **2c** | COOMe | 1.0 | 1.0 | H-B<br>(15-15) | **1c** | 73 |
| **2d** | Ph | 0.5 | 0.5 | H-B<br>(5-10) | **1d** | 50 |

[a] Reaction time is 5 h except **2d** (24 h). [b] H, hexane; B, benzene. [c] The yields have not been optimized in any case.

We wish to report here the first example of photochemical synthesis of the title compounds, using distannane. The procedure involves irradiation of 1,3-dithiole-2-thiones (**2**), in the presence of hexabutyldistannane (**3**), to give the corresponding TTF derivatives **1** in good yields.



The method has proven to be superior to the base catalyzed dimerization of 1,3-dithiolium ions, the method[4,5] initially used to synthesize TTF. The method also appears to be a more general preparation of TTF derivatives substituted with either electron-donating or -withdrawing groups.[6]

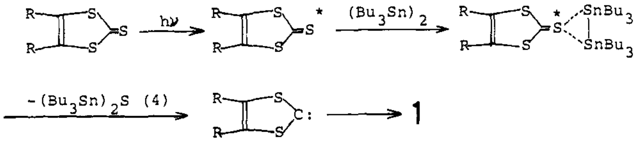
The general procedure is as follows. A benzene or hexane solution of an equimolar amount of **2**[5,6] and distannane **3**[7] in a quartz tube cooled by water was irradiated with a 300-W high-pressure mercury lamp for 5 h. After removing the solvent under reduced pressure, the residue was treated with a small amount of pentane to precipitate crystals of **1** (**1a, b, d**), or purified by column chromatography (alumina, benzene–EtOAc) (**1c**). The structure of the products was confirmed by comparison of their physical and spectral properties with those of authentic samples or with the data reported in the literature.[3,5,6]

As shown in Table I, a higher yield of **1a** was obtained when twice the molar amount of distannane **3** was employed.

Since there are very few reports on the photochemistry of distannane,[8] we have examined the photochemical behavior of distannane, which provided the following observations: (1) In the absence of **3**, or without irradiation, no reaction was observed. (2) TTF derivatives, **1**, were not obtained in the thermal reaction of **2** and **3** in the presence of azobisisobutyronitrile (AIBN) which was expected to cleave the tin–tin bond of distannane **3**.[8] (3) Bis(tributyltin) sulfide (**4**)[9] was isolated by column chromatography. (4) Hexabutyldistannane (**3**) apparently showed no absorptions in the uv and visible regions (210–700 nm). (5) The rate of the photoreaction varies with the wavelength of irradiating light. The relative rate of the second-order reaction of **2a** and **3** in cyclohexane at ca. 20 °C was estimated by monochromic irradiation (Table II).

The rate enhancement was observed at wavelengths especially in the uv range, which correspond to the absorptions of **2a**.

These facts suggest a possible reaction scheme as shown below.



The initial homolytic cleavage of the tin–tin bond is unlikely as a key step because of the ineffectiveness of AIBN. Instead,

**Table II.** Relative Rate[a] and Absorptions of **2a**

| Irradiated light (nm) | Rel rate[b] | $\lambda_{max}$ of **2a** (log ε)[c] |
|---|---|---|
| 233 | 39.1 | 233 (3.95) |
| 259 | 8.3 | |
| 273 | 18.1 | 273 (3.27) |
| 285 | 8.3 | |
| 312 | 5.3 | |
| 339 | 1.7 | |
| 372 | 2.6 | 372 (4.17) |
| 392 | 1.0 | |
| 433 | 0.0 | 433 (2.20) |

[a] Photolysis of solutions in a quartz cell with a 2-kW xenon-arc lamp. [b] Initial slope from plots of [**2a**] against time, [**2a**] determined spectrophotometrically. Reaction rates are normalized to overcome fluctuations in light intensity. [c] In cyclohexane.

the excited thione compound **2*** might interact with the tin-tin bond, followed by abstraction of sulfur to produce the *S,S*-carbene, which dimerized to **1**, presumably by attack to another carbene molecule or thione **2**.

Other advantages of the present one-step synthesis, in addition to those mentioned in the introduction, include the convenience and safety of the procedure, and the ease of isolating the products, **1**, with high purity. We are continuing our investigations of the application of the present method. It is noteworthy that the desulfurization proceeds only under irradiation. The development of other useful processes involving the reaction of distannane with excited organosulfur compounds may be expected.

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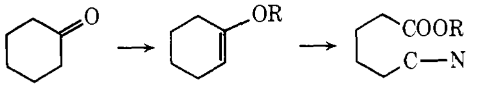
## Cleavage of Carbon–Carbon Bonds. Copper(II)-Induced Oxygenolysis of *o*-Quinones, Catechols, and Phenols

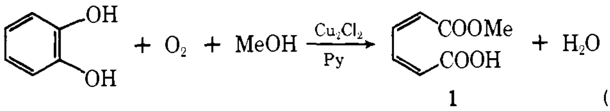
*Sir:*

Our interest in new synthetic approaches to caprolactam led us to explore carbon-carbon bond cleavage of various cyclic $C_6$-systems. We recently reported on a successful development of the nitrosolysis reaction—a carbon-carbon bond cleavage effected through nitrosation with a simultaneous introduction of a terminal carbon-nitrogen bond (eq 1).[1]



(1)

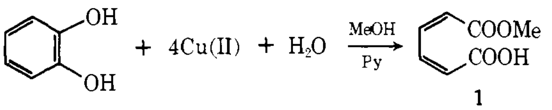
The remarkable ability of certain oxygenases to catalyze oxidative carbon-carbon bond cleavage of various aromatic substrates, most notably of phenols and catechols, is well known.[2] It is also recognized that a similar carbon-carbon bond cleavage of certain catechols can be effected with molecular oxygen and various transition metal ions.[3] The carbon-carbon bond cleavage of benzil to benzoic acid with molecular oxygen in the presence of certain copper(I) complexes was investigated by Kinoshita[4] more than 20 years ago, and very recently it has been claimed that the carbon-carbon bond cleavage of catechol to the *cis,cis*-muconic acid monomethyl ester, **1**, was achieved by oxidation with molecular oxygen activated by a particular copper(I)/pyridine/methanol system (eq 2).[5]



1 (2)

For reasons mentioned in the opening sentence, we too have investigated the carbon-carbon bond cleavage of catechol and of phenol in the presence of various transition metal ions and molecular oxygen. While we will present a full account of our work in this area in the near future, we would like to comment here on the role of the oxygen in the oxidative cleavage of catechol to *cis,cis*-muconic acid monoalkyl esters in the presence of copper(II).[5]

We have demonstrated that catechol reacts with cupric methoxy chloride in pyridine containing methanol and water *under anaerobic conditions* to give the *cis,cis*-muconic acid monomethyl ester (eq 3, Cu(II) = CuClOMe). Cupric methoxy chloride is a stable light yellow-green solid which readily reacts with atmospheric moisture. Hay, Endres, and their coworkers reported that cupric methoxy chloride reacts with pyridine to give a deep green complex, PyCuClOMe (I), which according to them exists as a dimer.[6] The pyridine cupric methoxy chloride complex I appears more stable and consequently it is more convenient to use than the cupric methoxy chloride itself (eq 3, Cu(II) = PyCuClOMe). The following experimental procedure is representative.



1 (3)

A three-neck flask equipped with a mechanical stirrer, and an addition funnel, protected with an inert gas atmosphere, was charged with solid I (6.26 g, 30 mmol), and a solution of methanol (0.3 ml) and water (0.27 g, ca. 15 mmol), in pyridine (60 ml). The green suspension was then freeze-pump-thaw degassed under nitrogen or argon. A similarly degassed solution of catechol (0.55 g, 5 mmol) in pyridine (10 ml) and methanol (0.5 ml) was added dropwise from the addition funnel at room temperature with stirring under anaerobic conditions. After complete addition (15-30 min) the reaction mixture was stirred an additional 15 min and then evaporated. The yellow-brown solid residue was hydrolyzed with dilute hydrochloric acid in the presence of chloroform under the inert atmosphere. Drying and evaporation of the chloroform solution afforded the *cis,cis*-muconic acid monomethyl ester, mp 80-80.5 °C, in an 80-85% yield.

While we think that the discussion of the mechanism of this carbon-carbon bond cleavage effected by the copper(II) sys-