Organic Metals: a New Synthetic Route to Tetrathiafulvalenes

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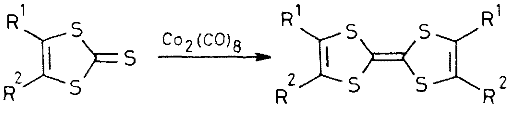
Summary We report here a new synthetic route to tetrathiafulvalenes in a simple one-step synthesis from 2-thioxo-1,3-dithioles.

TETRATHIAFULVALENE (TTF) and its derivatives have been a subject of great interest since the discovery of their π donor abilities to form charge-transfer complexes with suitable acceptors. The classical methods of synthesis commonly used to prepare tetrathiafulvalenes have been reviewed by Narita and Pittman.[1] These routes are convenient but involve three- or four-step syntheses. So far, few methods of synthesis have been described starting from 2-thioxo-1,3-dithioles.

It has been found[2-5] that triphenylphosphine and trimethyl phosphite react with 2-thioxo-1,3-dithioles to give the corresponding tetrathiafulvalenes, although the scope of the reaction is limited to compounds with electron withdrawing substituents (R = F_3C or CN), and unfortunately, yields are not always good. 2-Thioxo-1,3-benzodithiole has also been made using a phosphite.[6,7]



Our one-step synthesis affords tetrathiafulvalenes directly from 2-thioxo-1,3-dithioles in 20—45% yields when heated with dicobalt octacarbonyl in boiling benzene or toluene solutions. The desulphurization achieved with $Co_2(CO)_8$ has been applied to 2-thioxo-1,3-dithioles with various substituent (R) groups and seems general (Table).

TABLE

R^1	R^2	Solvent	Reaction time/h	Yield /%	M.p./°C (lit.[1] m.p.)
H	H	Toluene	0.5	35	119 (119)
Me	Me	Benzene	1	25	244 (244)
Ph	Ph	Benzene	2	42	262 (262)
CO_2Me	CO_2Me	Benzene	2	20	168 (170)
$[CH_2]_3$		Toluene	1	20	243 (244)
$[CH_2]_4$		Toluene	1	37	245 (247)
H	Ph	Toluene	1.5	25	208 (202—206)

During the boiling period a large amount of black precipitate was formed. This black pyrophoric material was filtered and the filtrate was chromatographed on alumina. Elution with benzene–light petroleum followed by concentration gave directly the corresponding TTF in pure crystalline form.

The reaction was also attempted with the 'carbonyl metals' bis(dicarbonylcyclopentadienyliron) $[(C_5H_5)Fe(CO)_2]_2$ and bis(triphenylphosphinyl)aminylium tetracarbonylcobaltate $(Ph_3P)_2NCo(CO)_4$, but these reagents seemed less effective than dicobalt octacarbonyl and the yields obtained were lower.

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[8] $Co_2(CO)_8$ has also been used in the desulphurization of thiocarbonyl compounds to give ethylenes, see H. Alder and H. N. Paik, *J. Org. Chem.*, 1977, **42**, 3522.