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Synthesis of Tetrathiafulvalene Derivatives by the Use of Organoaluminium Reagents

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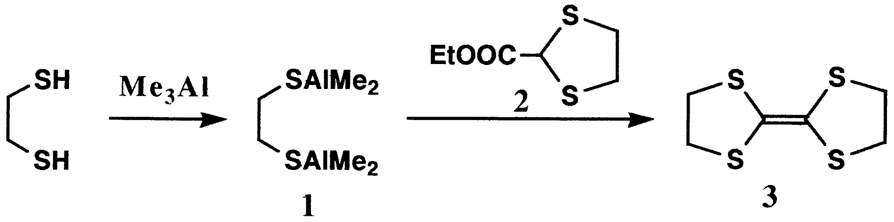
Bis(dimethylaluminium) salts of ethanedithiol, 1,2-benzenedithiol, and ethylenedithiol react with 1,3-dithiolane-2-carboxylate esters to give dihydro- and tetrahydro-tetrathiafulvalenes as well as tetrathiafulvalene derivatives.

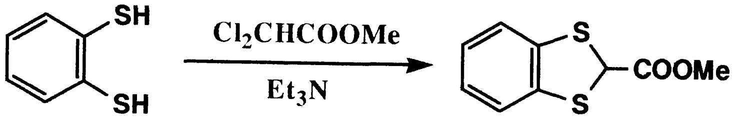
Synthetic chemistry of tetrathiafulvalenes (2-(1,3-dithiol-2-ylidene)-1,3-dithiole) has attracted a great deal of attention, because their radical cation salts exhibit high electrical conductivity and even superconductivity.1) Conventional syntheses of tetrathiafulvalenes are based on some kinds of coupling reactions, where the central C=C bond is constructed at the final step.2) On the contrary, synthetic routes that form the C-S bonds at the final step are very limited.3,4) In the course of our attempted synthesis of new extended tetrathiafulvalene derivatives, we recognized the necessity of such a non-coupling method. In order to explore the possibility of non-coupling routes, we have attempted to use Corey's ketene thioacetal synthesis by the reaction of bis(dimethylaluminium)-1,2-ethanedithiol (**1**) to esters.5) In the present paper, we report that this reaction is applicable to unsaturated dithiols, giving tetrathiafulvalene derivatives as well as dihydro- and tetrahydro-tetrathiafulvalenes.

A direct application of Corey's method for the synthesis of tetrahydrotetrathiafulvalene **3** is shown below: bis(dimethylaluminium) 1,2-ethanedithiolate (**1**), which is prepared from the reaction of trimethylaluminium to ethanedithol, reacts with ethyl 1,3-dithiolane-2-carboxylate (**2**) to afford tetrahydrotetrathiafulvalene (**3**).



All operations involving organoaluminium reagents were conducted in an argon atmosphere. Two mmol of trimethylaluminium (as 2 M hexane solution) was diluted with 10 ml of dry methylene chloride, cooled to 0 °C, and 1 mmol of ethanedithiol was dropwise added. After a 1.5 h reaction, ester **2**(6) was added. After being stirred for 15 h, 0.3 g of $Na_2SO_410H_2O$ was added at 0 °C, and when the gas evolution stopped (about 1 h at room temperature), the solution was dried over Na_2SO_4. The solid was filtered off, washed well with methylene chloride, and the solvent was removed by rotary evaporation to give a white solid **3**.(7)

As shown in Table 1, **1** reacts with various esters to give 1,3-dithiolanes (Entries 1 - 3). Similarly, 1,2-benzenedithiol instead of ethanedithiol reacts with trimethylaluminium to give bis(dimethylaluminium) 1,2-benzenedithiolate **7**, which successively reacts with the esters (Entries 4, 5 of Table 1). Ester **4**, which was used in these reactions, was prepared by the following reaction.



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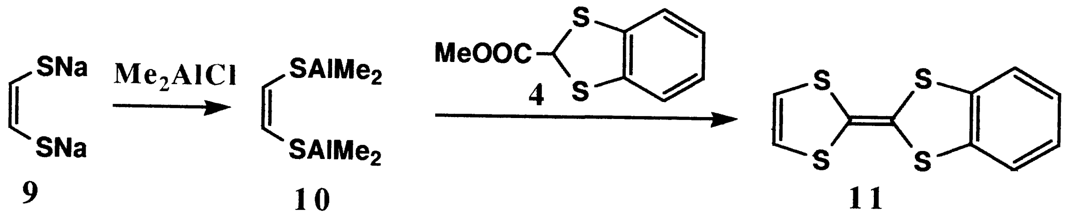
To a 20 ml benzene solution of 4 mmol 1,2-benzenedithiol and 4 mmol methyl dichloroacetate was dropwise added 8 mmol of triethylamine at 0 °C. After a 3 h reaction at room temperature, the white solid formed was filtered off, and the solvent was removed by rotary evaporation. Crystallization from methanol or column chromatography (silica gel, hexane : methylene chloride = 1 : 1) gave a white solid, **4**.(11) Yield 66 %.

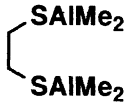
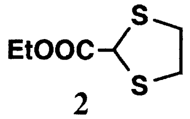
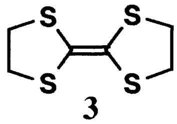
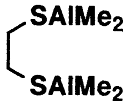
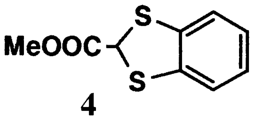
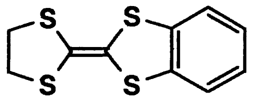
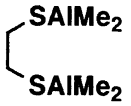
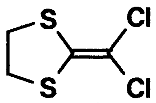
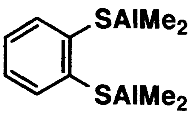
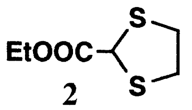
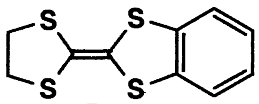
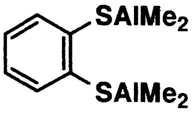
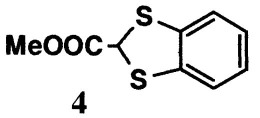
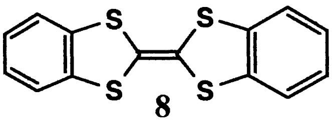
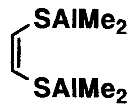
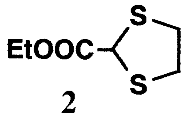
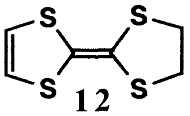
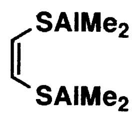
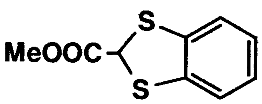
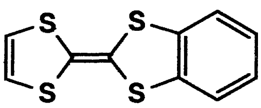
Though the above aluminium reagents were prepared from dithiols, dithiolate salt can be also used: disodium ethylenedithiolate **9** reacts with dimethylaluminium chloride to give bis(dimethylaluminium) ethylenedithiolate **10**. This reagent similarly reacts with the esters to form 1,3-dithioles (Entries 6, 7 of Table 1).



9 **10** **11**

Disodium ethylenedithiolate **9** (1.32 mmol)(12) was suspended in 15 ml dry methylene dichloride, and 2.65 mmol of dimethylalumimium chloride (1 M hexane solution) was added at 0 °C. After the white solid was completely consumed to give a white emulsion (typically 2.5 h at room temperature), ester **4** was added, and the mixture was further stirred for 17 h. The workup as described above gave an unsymmetrical tetrathiafulvalene **11**.

Table 1. Summary of attempted reactions

	Organoaluminium reagents	Esters	Products	Yield
1.	 1	 2	 3	96% 7)
2.	 1	 4	 5	86% 8)
3.	 1	$Cl_2CHCOOCH_3$	 6	22%[a] 9)
4.	 7	 2	 5	66% 8)
5.	 7	 4	 8	50% 10)
6.	 10	 2	 12	45%[a] 7)
7.	 10	 4	 11	29%[a] 3)

[a] After column chromatography (silica gel, hexane : methylene chloride = 1:1).

The reported synthesis of dihydrotetrathiafulvalene **12** is DDQ (2,3-dichloro-5,6-dicyano-1,4-benzoquinone) oxidation of 2,2'-bi(1,3-dithiolanyl).[7] This method, however, gives a mixture of dihydrotetrathiafulvalene **12** and tetrahydrotetrathiafulvalene **3**. On the contrary, the present method is a facile selective synthesis of these compounds.

1,2-Benzenedithiol is reported to react with tetrachloroethylene to give dibenzotetrathiafulvalene **8**.[3] This method was, however, not successfully applied to the synthesis of an unsymmetrical tetrathiafulvalene **11**.[4] The present method can be used for the preparation of this kind of unsymmetrical compounds.

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References

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8) Compound **5**: Mp 184 - 185 °C, ^{1}H NMR ($CDCl_3$) δ 3.47 (4H), 7.0 - 7.2 (4H); IR (KBr) 2928, 1444, 1276, 1119, 744 cm^{-1}; Mass *m/z* = 256 (M^+), 152, 108. Anal. Found: C, 46.73; H, 3.06 %: Calcd for $C_{10}H_8S_4$: C, 46.84; H, 3.14 %.
9) Compound **6**: Mp 24 - 25 °C, ^{1}H NMR ($CDCl_3$) δ 3.54; IR (KBr) 2930, 1282, 983, 879, 853, 770 cm^{-1}; Mass *m/z* = 187 (M^+), 152.
10) K. Spencer, M. P. Cava, and A. F. Garito, *J. Chem. Soc., Chem. Commun.*, **1976**, 966.
11) Compound **4**; Mp 77 °C, ^{1}H NMR ($CDCl_3$) δ 3.76 (3H), 5.28 (1H), 7.0 - 7.2 (4H); IR (KBr) 2952, 1741, 1450, 1433, 1293, 1162, 995, 756 cm^{-1}; Mass *m/z* = 212 (M^+), 153. Anal. Found: C, 51.00; H, 3.84 %: Calcd for $C_9H_8O_2S_2$: C, 50.92; H, 3.80 %.
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