SYNTHESIS OF 2,3-DIMETHYL-6-METHOXYCARBONYLTETRATHIAFULVALENE

Ya. N. Kreitsberga, R. B. Kampare,
and O. Ya. Nieland

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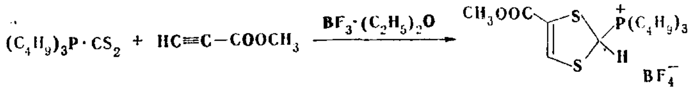
A method is proposed for the synthesis of an unsymmetrically substituted tetrathiafulvalene with an acceptor substituent, viz., 2,3-dimethyl-6-methoxycarbonyltetrathiafulvalene, from 2-tributylphosphonia-4-methoxycarbonyl-1,3-dithiole tetrafluoroborate.

Two methods for the synthesis of tetrathiafulvalenes that have one reactive functional group, i.e., asymmetrically substituted tetrathiafulvalenes, are known. The first method — direct introduction of substituents into lithiated tetrathiafulvalene [1] — gives monosubstituted tetrathiafulvalenes in rather high yields (30-40%), but the extreme sensitivity of the lithiated tetrathiafulvalene to moisture hampers the use of this method. The second method — the reaction of 1,3-dithioliatriphenylphosphoranes with 1,3-dithiolium salts [2] — has been used for the synthesis of benzotetrathiafulvalenes and tetramethylenetetrathiafulvalenes in 18-43% yields. The impossibility of the preparation of 1,3-dithiolium salts that contain electron-acceptor substituents restricts its use [3].

We have developed a modification of the latter method that makes it possible to obtain asymmetrically substituted tetrathiafulvalenes with one or two electron-acceptor substituents. For this, instead of a substituted 1,3-dithioliatriphenylphosphorane, which is obtained from the corresponding 1,3-dithiolium salt [2], a substituted 1,3-dithioliatributylphosphorane, which is readily formed in the reaction of acetylenes containing electron-acceptor substituents with the carbon disulfide—tributylphosphine adduct [4, 5], is used in the synthesis.

2-Tributylphosphonia-4-methoxycarbonyl-1,3-dithiole tetrafluoroborate (I) is obtained in the same way as 2-tributylphosphonia-4,5-dimethoxycarbonyl-1,3-dithiole tetrafluoroborate [4] by addition to the carbon disulfide—tributylphosphine adduct at —30°C to methyl propiolate in the presence of boron trifluoride etherate.



I

Salt I is a yellow oil that is stable in air; we were unable to crystallize it.

Tetrafluoroborate I reacts with butyllithium at —78°C to give phosphorane II, which does not undergo the Wittig reaction with 1,3-dithiol-2-one but reacts with 3,4-dimethyl-1,3-dithiolium tetrafluoroborate to give, after splitting out of tributylphosphine with triethylamine, tetrathiafulvalene III, which was isolated from the reaction mixture by means of column chromatography.

Tetramethyltetrathiafulvalene was also detected in the mixture. Compound III is a red crystalline substance, the spectral characteristics of which are in good agreement with the characteristics of analogous compounds [2-ethoxycarbonyltetrathiafulvalene and 2-methyl-6(7)-ethoxycarbonyltetrathiafulvalene] obtained by acylation of lithiated tetrathiafulvalene [1]. (Formula, top, following page.)

EXPERIMENTAL

The IR spectra of suspensions of the compounds in mineral oil were recorded with a Specord 75 IR spectrometer. The UV spectra were recorded with a Specord UV-vis spectrophotometer.

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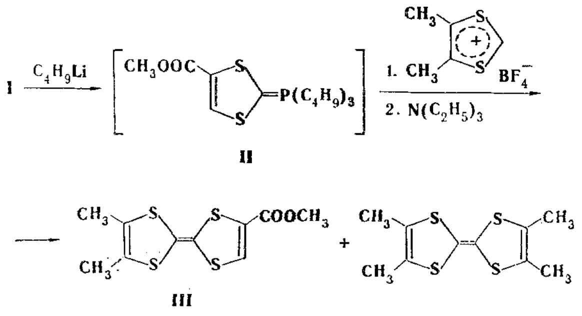

The PMR spectra were recorded with a WH-90/DS spectrometer (90 MHz) with hexamethyldisiloxane as the internal standard.

4,5-Dimethyl-1,3-dithiolium tetrafluoroborate was obtained from 4,5-dimethyl-1,3-dithiole-2-thione [6], tributylphosphine was obtained by the method in [7], and methyl propiolate was obtained from the potassium salt of acetylenedicarboxylic acid [8].

The syntheses of I and III were carried out in an argon atmosphere. Column chromatography was carried out with L 100/250 silica gel.

2-Tributylphosphonia-4-methoxycarbonyl-1,3-dithiole Tetrafluoroborate (I). A solution of 2 g (0.01 mole) of tributylphosphine and 0.6 ml (0.01 mole) of carbon disulfide in 25 ml of absolute ether was cooled to −35°C, and 1.52 ml (0.012 mole) of boron trifluoride etherate and 0.84 g (0.01 mole) of methyl propiolate were added to it. The red solution became colorless immediately, and a yellow oil was liberated. The oil was washed with ether and was reprecipitated twice from solution in acetonitrile by the addition of ether. The yield was 3.5 g (76%). IR spectrum: 1706 (CO); 1554 (C═C); 3050, 2951, 2931, 2971 cm^{-1} (C—H). PMR spectrum (in $CDCl_3$): 0.95 (t, 9H, 3-CH_3), 1.55 [m, 12H, 3-$(CH_2)_2$], 2.39 [t, 6H, $P(CH_2)_3$], 3.76 (s, 3H, OCH_3), 6.13 (s, 1H, S—CH═P—), and 7.13 ppm (s, 1H, CH═). Found: C 45.4; H 7.2; S 13.9%. $C_{17}H_{32}BF_4O_2PS_2$. Calculated: C 45.5; H 7.1; S 14.2%.

2,3-Dimethyl-6-methoxycarbonyltetrathiafulvalene (III). A solution of butyllithium (0.03 mole) in ether was added dropwise at −78°C in the course of 15 min to a suspension of 1.3 g (0.003 mole) of I and 0.63 g (0.003 mole) of 4,5-dimethyl-1,3-dithiolium tetrafluoroborate in 25 ml of absolute tetrahydrofuran (THF), after which stirring was continued for 1 h at the same temperature. Triethylamine (3 ml) was then added, and the mixture was stirred at −78°C for another 2 h. The mixture was passed through a column filled with silica gel (3.5 × 20 cm) by elution with benzene—hexane (5:1). The first fraction contained 0.2 g of tetramethyltetrathiafulvalene. Workup of the second fraction gave 0.18 g (21%) of III with mp 132-134°C (from acetonitrile). IR spectrum: 1720 (CO); 1555, 1527 (C═C); 2904, 2944 cm^{-1} (C—N). UV spectrum (in acetonitrile), λ_{max} (log ε): 292 (4.05), 313 (4.06), and 438 nm (3.27). PMR spectrum (in $CDCl_3$) 1.93 (s, 6H, 2-CH_3), 380 (s, 3H, OCH_3), 7.32 (s, 1H, HC═). Found: C 41.3; H 3.4; S 44.3%. $C_{10}H_{10}O_2S_4$. Calculated: C 41.4; H 3.4; S 44.2%.

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