SYNTHESIS OF TETRATHIAFULVALENE DERIVATIVES BY DIMERIZATION OF 1,3-DITHIOLSELENONES-2 USING TRIPHENYLPHOSPHINE

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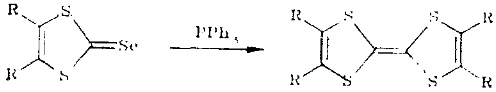
Tetrathiafulvalenes (I) are key compounds in the synthesis of materials with metallic conductivity and superconductivity [1, 2]. The principal method of synthesis is the dimerization of 2-derivatives of the 1,3-dithiol [3]. The combination of selenones and trialkylphosphites is rarely used for this purpose. Selenone dimerization by means of triphenylphosphine has been described only for the selenone analogs of 1,3-dithiol-2-selenone [3]. When alkylseleno-1,3-dithiolium salts react with PPh_3 they form derivatives of tetrathiafulvalenes in good yield [4].



II a-e I a-e

I, IIa R–R = $-SCH_2CH_2S-$; b R–R = $-S(CH_2)_3S-$; c R–R = $-S(CH_2)_4S-$; d R = Me; e R = Ph

We have established that PPh_3 is an excellent reagent for the dimerization of selenones (II). It works at a 1:(1.0-2.0) molar ratio of (II)—PPh_3, in various solvents (DMFA, pyridine, benzene, toluene), over a broad temperature range — from 2-3 days at room temperature to 60-90 min at 90°C at various concentrations of (II) (0.01-0.17 mole/liter). The reaction conditions affect the yield of (I), as was shown for the dimerization of (IIa).

The optimum (II)—PPh_3 ratio is 1:(1.5-2.0). The results presented below were obtained at a 1:2 ratio. Most of the tests were carried out in DMFA solution. At concentrations below 0.04 mole/liter in DMFA, dimerization at 4-70°C is unsatisfactory. At 0.15-0.17 mole/liter and 65-70°C for 90 min the yield of (Ia) reaches 85-90%. Raising the temperature to 90°C lowers the yield. At low concentrations of (IIa) carboxylic acids have a surprising effect on dimerization in DMFA. Thus at 0.035-0.040 mole/liter and 65-70°C acetic or formic acid [approximately fivefold excess with respect to (IIa)] increase the yield of (Ia) to 80-85%. But the stronger phosphoric acid prevents the formation of (Ia). At 0.15-0.20 mole/liter of (IIa) acetic acid has little effect.

Boiling in benzene for 3 h at 0.02-0.15 mole/liter of (IIa) forms (Ia) in 65-90% yield. Starting with 0.12 mole/liter of (IIa) in pyridine at 70°C for 90 min, (Ia) crystallizes out in 80% yield.

Bis(ethylenedithio)tetrathiafulvalene (Ia). Compound (IIa), 0.28 g, was dissolved in 6 ml of DMFA at 80-90°C and 0.3 ml of glacial acetic acid was added. Then 0.56 g of triphenylphosphine was added at 65-70°C, and the mixture was held at that temperature for 90 min. Then it was kept in the refrigerator for 1 day. Compound (Ia) was formed as coarse shiny red crystals in amount of 0.18-0.19 g (90-95%).

Tetrathiafulvalenes (Ib)(in DMFA, 70% yield), (Id) (in DMFA, 70% yield), and (Ie) (in benzene, 80% yield) were obtained analogously.

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