

the benzene was distilled off. The oily residue was dissolved in ether. The ethereal solution was washed with water, purified with activated charcoal, and dried over magnesium sulfate. The ether was distilled off to give 6.5 g (67.3%) phenol VIII as an oily liquid without impurities as indicated by thin-layer chromatography on Silufol plate with 20:1 chloroform-ethanol as eluent, R_f 0.68. IR spectrum: 1660 (CO), 3400 cm^{-1} (OH). PMR spectrum (C_6D_6 , ppm): 0.88 t (CH_3 , $J = 7$ Hz), 1.42 d (CH_3 , $J = 7$ Hz), 3.56 oct (1H, $J^1 = 7$ Hz, $J^2 = 0.6$ Hz), 3.90 m (CH_2). Found: C, 67.9; H, 7.2%; M^+ 194. Calculated for $\text{C}_{11}\text{H}_{14}\text{O}_3$: C, 68.0; H, 7.3%; M 194.

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MONOESTERS OF TETRATHIAFULVALENE-2,6(7)-DICARBOXYLIC ACID AND THEIR USE IN THE PREPARATION OF TETRATHIAFULVALENECARBOXYLIC ACID

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Monoesters of tetrathiafulvalene-2,6(7)-dicarboxylic acid were synthesized. Decarboxylation of these esters with subsequent hydrolysis gave tetrathiafulvalenecarboxylic acid. Pure mono- and diesters of tetrathiafulvalenedicarboxylic acids were isolated but their assignment to the 2,6- and 2,7-series requires further study.

Three carboxylic acids are known among the strong tetrathiafulvalene derivative electron donors: tetrathiafulvalenetetracarboxylic acid (I) [1], tetrathiafulvalene-2,6(7)-dicarboxylic acid (II) [2], and tetrathiafulvalenecarboxylic acid (III) [3]. Special interest lies in the not readily available monoacid III which contains an active functional group which permits various reactions while at the same time it is a strong electron donor [3]. Several good methods are known for the preparation of acids I and II [1, 2, 4, 5]. Thus, we found it useful to develop a synthesis for acid III from the more available dicarboxylic acid II.

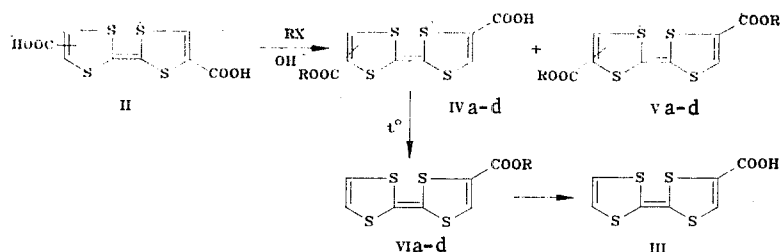
The direct conversion of II to III, as observed in the case of the conversion of I to II [2], is impossible since monocarboxylic acid III decarboxylates much more readily than acid II [6]. Thus, we protected one carboxylic acid function as an ester with subsequent decarboxylation and hydrolysis.

Monoesters of dicarboxylic acid II have not been reported. Alkylation of II using alkyl bromides and iodides according to Shaw et al. [7] leads to a mixture of monoester IV (~30%) and diester V (15-25%). In addition, we encounter <5% products of the decarboxylation of acids III and IV (tetrathiafulvene and alkoxy carbonyl tetrathiafulvalene VI) and the recovery of about 40% of starting acid II (Table 1).

Monoesters IVa-d decarboxylate above 160°C, for example, in refluxing diglyme, to give VIa-d in 70-90% yield: these products may be used to obtain acid III [8].

The spectral data for esters VIa-d which are reported for the first time in this communication are summarized along with the data for the known ester of tetrathiafulvalenecarboxylic acid [3] given for comparison (Table 2).

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IV-VI a R=CH₃; b R=C₄H₉; c R=CH₂C₆H₅; d R=CH₂-CH=CH₂

All the disubstituted tetrathiafulvalenes prepared were mixtures of the 2,6- and 2,7-isomers.

As shown previously for Va [1], such isomers have different solubility, which permits their separation, as well as different melting points. These authors note that the "only difference between the isomers is the band at 910 cm⁻¹ and that both isomers form acid II upon hydrolysis." However, the isomer structure was not elucidated and acid II is also a mixture of isomers with different physical and chemical properties.

We separated isomers IVb-A, IVb-B, Vb-A, and Vb-B by fractional crystallization, carried out their interconversions, and hydrolyzed these isomers to acids II-A and II-B. The isomer with lower solubility was termed A, while the more readily soluble isomer was termed B. A separate communication on the assignment to the 2,6- or 2,7-series will be submitted upon completion of an x-ray diffraction structural study.

TABLE 1. Mono- and Diesters of Tetrathiafulvalene-2,6(7)-dicarboxylic Acid.

Compound	Mp, °C	IR spectrum, cm ⁻¹			UV spectrum, λ _{max} , nm (log ε), in acetonitrile	Yield, %
		COOR	COOH	C=C		
IVa	224-225 (dec.)	1721	1645	1555	288 (4,05), 302 (4,10), 313 (4,14), 435 (3,41)	5
IVc*	196-198 (dec.)	1692	1653	1543	286 (4,21), 299 (4,21), 312 (4,20), 442 (3,52)	23
IVd	196-198 (dec.)	1688	1648	1538	286 (4,10), 300 (4,12), 313 (4,11), 428 (3,50)	21
Va †	238-242	1720		1555	290 (4,00), 302 (4,03), 315 (4,04), 444 (3,39)	45
Vc*	123-125	1698		1542	286 (4,19), 299 (4,18), 312 (4,19), 440 (3,50)	20
Vd	103-105	1691		1647, 1548	286 (4,12), 300 (4,13), 313 (4,12), 430 (3,47)	20

*The spectral characteristics for IVb and Vb are given in Table 3.

†Electronic spectrum of CH₂Cl₂ according to Melby et al. [4].

TABLE 2. Esters of Tetrathiafulvalenecarboxylic Acid

Compound	Mp, °C	IR spectrum, cm ⁻¹		UV spectrum, λ _{max} , nm (log ε), in acetonitrile	PMR spectrum, ppm			Yield, %
		COOR	C=C		3-H	6-H, 7-H	remaining protons	
VIa	102-104	1695	1565, 1545	292 (4,08), 302 (4,11), 313 (4,14), 430 (3,30)	7,24	6,26	3,77 (COOCH ₃)	80
VIb	74-76	1693	1545, 1567	289 (4,04), 304 (4,11), 315 (4,13), 435 (3,31)	7,30	6,30	4,18 (COCH ₂); 1,2-1,8[(CH ₂) ₂]; 0,93 (CH ₃)	78
VIc	77-79	1704	1558, 1536	290 (4,11), 299 (4,13), 313 (4,15), 430 (3,45)				70
VId	77-78	1697	1639, 1568, 1538	288 (4,11), 300 (4,12), 313 (4,12), 432 (3,29)				73
*		1690		292 (4,07), 303 (4,11), 314 (4,13), 424 (3,28)	7,30	6,30	4,25 (COCH ₂), J=7 Hz; 1,35 (CH ₃)	

*Ethyl ester of acid III according to Green [3].

TABLE 3. Spectral Data for II, IVb and Vb

Compound	IR spectrum, cm^{-1}			UV spectrum, λ_{max} , nm (log ϵ), in acetonitrile	PMR spectrum, ppm		
	COOR	COOH	C=C		3-H, 6(7)-H	COCH ₃	remaining protons
II-A		1663, 1643	1557	287* (4,20), 302 (4,26), 313 (4,28), 418 (3,55)			
II-B		1661, 1633	1535	288* (4,08), 304 (4,13), 315 (4,15), 404 (3,41)			
IVb-A	1688	1645	1545	289 (4,22), 302 (4,26), 313 (4,30), 439 (3,61)	7,76**; 6,76	4,14	1,72—1,27; 0,95
IVb-B	1693	1636	1546	287 (4,18), 301 (4,22), 313 (4,25), 432 (3,59)	7,74*; 6,74; 7,82; 7,70	4,14	1,72—1,27; 0,95
Vb-A	1708		1555	288 (4,21), 301 (4,23), 312 (4,26), 434 (3,60)	7,25	4,14	1,72—1,27; 0,95
Vb-B	1709		1555	288 (4,12), 300 (4,15), 312 (4,18), 415 (3,48)	7,21	4,14	1,72—1,27; 0,95

*In 0.01 N NaOH.

†The PMR spectrum of IVb in DMSO- d_6 .

The differences between the IR and PMR spectra of the isomers are slight but the electronic spectra differ significantly. Firstly, the long-wavelength band of isomers A are bathochromically shifted relative to the corresponding band of isomers B. Secondly, the absorption is stronger for isomers A. Both these differences indicate a longer conjugation chain in isomers A. Several chemical properties also differ such as the finding that isomers A of acids II and IVb decarboxylate more readily than the corresponding isomers B. Isomers A and B can be interconverted. For example, the alkylation of isomer A of acid II with butyl bromide in the presence of alkali gives not only isomers A of IVb and Vb, but also the corresponding isomers B in almost equal amounts.

EXPERIMENTAL

The IR spectra were taken on a Specord IR spectrometer in vaseline oil. The UV spectra were taken on a Specord UV-VIS spectrometer and the PMR spectra were taken on a Perkin-Elmer R-12A spectrometer at 60 MHz with HMDS as internal standard.

6(7)-Butoxycarbonyltetrathiafulvalene-2-carboxylic Acid (IVb) and 2,6(7)-Bis(butoxycarbonyl)tetrathiafulvalene (Vb). A sample of 21 ml (0.2 mole) butyl bromide and 10 ml (0.06 mole) 25% aq. NaOH were added to a solution of 18 g (0.06 mole) acid II in 300 ml hexamethylphosphorotriamide and stirred at room temperature for 1.5 h. The solution formed was poured into 1.5 liter water containing 300 ml hydrochloric acid. The precipitate was filtered off, washed with water, dried in the air, and crystallized from 1.5 liters acetonitrile. A total of 7.2 g (40%) acid II was recovered as the residue not soluble in acetonitrile. Upon cooling, 3.2 g dark red IVb-A was precipitated from acetonitrile, mp 184–186°C (dec.). After filtering off IVb-A, the acetonitrile was evaporated and the residue was dissolved in about 200 ml benzene. A total of 1.5 g IVb-B did not dissolve in benzene, mp 192–194°C (dec.). The total yield of IVb was 30%. Found: S, 36.6%. Calculated for $\text{C}_{12}\text{H}_{12}\text{O}_4\text{S}_4$: S, 36.8%.

The benzene solution was evaporated and the residue was recrystallized from hexane to give 5.1 g (18%) Vb-A, mp 108–110°C. After two crystallizations from about 250 ml hexane, this orange crystalline product has mp 114–115°C. Found: S, 32.1%. Calculated for $\text{C}_{16}\text{H}_{20}\text{O}_4\text{S}_4$: S, 31.7%.

Product Vb-A was filtered off and the hexane solutions were evaporated. Column chromatography on silica gel with benzene as eluent gave 0.9 g (4%) Vb-B. After two crystallizations from about 10 ml hexane, this orange-red crystalline compound had mp 69–70°C. Found: S, 31.4%. Calculated for $\text{C}_{16}\text{H}_{20}\text{O}_4\text{S}_4$: S, 31.7%.

Compounds IVa, IVc, IVd, Va, Vc, and Vd were obtained by analogy. Their separation into isomers was not investigated. The yields, melting points, and spectral data of these compounds are given in Table 1. The sulfur analyses corresponded to the calculated values.

Butoxycarbonyltetrathiafulvalene (VIb). A sample of 3.5 g IVb in 70 ml diglyme was heated at reflux for 1 h in an argon atmosphere. The solution was cooled, 300 ml water was added and the mixture was extracted with ether. After distilling off the ether, the residue was crystallized from 30 ml hexane to give 2.4 g (78%) orange crystalline VIb, mp 74–76°C. Found: S, 41.8%. Calculated for $\text{C}_{11}\text{H}_{12}\text{O}_2\text{S}_4$: S, 42.1%.

Products VIa, VIc, and VI_d were obtained by analogy (Table 2).

Tetrathiafulvalenecarboxylic Acid (III). A solution of 1.2 g NaOH in 90 ml water was added to a solution of 3 g (0.01 mole) IVb in 60 ml ethanol. The mixture was heated at 40-50°C in an inert argon atmosphere for 2-3 h and then acidified with hydrochloric acid. The red crystalline precipitate was filtered off, dried in vacuum, and recrystallized from benzene-hexane to give 1.6 g (66%) acid III, mp 183-184°C (dec.) (mp 182-184°C [3]). IR spectrum: 1655 (C=O), 1558, 1534 cm⁻¹ (C=C). UV spectrum in acetonitrile (λ_{max} (log ϵ)): 288 (4.08), 302 (4.14), 313 (4.15), 431 nm (3.30). PMR spectrum (CDCl₃ + DMSO-d₆, ppm): 6.33 s (2H, 6-H, 7-H), 7.27 s (1H, 3-H), 10.3 br. s (OH).

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REACTIONS OF 1,5-DIKETONES WITH HYDROGEN SELENIDE IN THE PRESENCE OF TRIFLUOROACETIC ACID

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Two competing pathways were found in the transformations of 1,5-diketones and the 4H-selenopyrans formed from these diketones upon reaction with CF₃CO₂H in the presence of hydrogen selenide entailing disproportionation and the electrophilic addition of hydrogen selenide.

In our previous work [1, 2], we found that 1,5-diketones react with hydrogen selenide and hydrogen chloride in acetic acid in an inert atmosphere to give the corresponding 4H-selenopyrans or 2,6-di(hydroseleno)-1-selenocyclohexanes, depending on the structure of the starting diketones. A complex mixture of products, from which separated selenopyridilium salts in 13-30% yield, was obtained under the same conditions but in the presence of oxygen.

In order to elucidate the probable mechanism for the formation of 2,6-di(hydroseleno)-1-selenocyclohexanes (IIa and IIb), we studied the reaction of 1,5-diketones with hydrogen selenide in trifluoroacetic acid. The reaction of 1,5-diketones with hydrogen sulfide in the presence of acids gives the corresponding 4H-thiopyrans [4] or the products of their disproportionation into thiapyrilium salts and thiacyclohexanes. Trifluoroacetic acid facilitates the disproportionation reaction [5, 6]. We might have expected that the reaction of 1,3,5-triphenyl-1,5-pentanedione (Ia) with hydrogen selenide in trifluoroacetic acid would yield 2,4,6-triphenylselenopyrilium salt (IVa) and 2,4,6-triphenyl-1-selenocyclohexane (IIIa). However, in addition to expected IIIa and IVa, 2,4,6-triphenyl-2,6-di(hydroseleno)-1-selenocyclohexane (IIa) gives the corresponding 2,6-diphenyl-2,6-di(hydroseleno)-1-selenocyclohexane (IIb), in addition to the products of the disproportionation of 4H-selenopyrans IIb and IVb. The poor solubility of IIa and IIIb in CF₃CO₂H likely plays a significant role in the formation of these compounds as they are removed from the reaction medium.

We have found that 2,4,6-triphenyl-4H-selenopyran (V) may disproportionate in the presence of CF₃CO₂H to form IIIa and IVa. It was important to learn whether 4H-selenopyrans in addition to the disproportionation products are capable of forming 2,6-di(hydroseleno)-1-

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