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POLYSULFONYLETHYLENES.

COMMUNICATION 2. THE REACTION OF TETRAKISALKYLSULFONYLETHENES WITH WATER, ALCOHOLS, AND THIOLS

N. P. Petukhova, N. E. Dontsova, and E. N. Prilezhaeva

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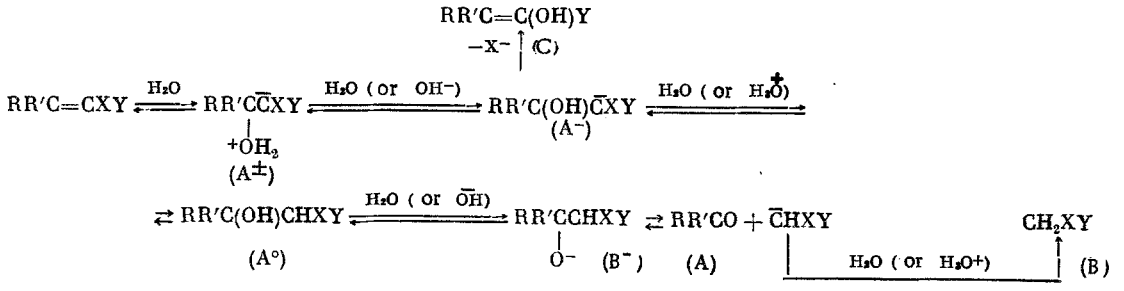
We have already [1] developed a synthesis of tetrakisalkyl(aryl)sulfonylethenes (TSE) by oxidation of tetrakisthioethenes with CF_3CO_3H in CH_2Cl_2. In the present communication, using the reaction of TSE with water, alcohols, and thiols as an example, we begin a systematic investigation of the chemical conversions of this new class of strongly electron-deficient ethylenes, in order to obtain tetrasubstituted unsaturated sulfones with various sets of substituents.

The presence of four electron-acceptor groups in the TSE molecules makes these compounds highly reactive. Thus, in aqueous solution TSE (Ia, b) easily hydrolyzes and which leads to scission of the C=C bond. Disulfonylmethanes (IIa, b), CO_2, and 2 equivalents of alkanesulfonic acid (identified as the Na salt) form in quantitative yield. This process proceeds over a wide pH range: neutral, acid, and especially easily in the presence of bases such as Et_3N or pyridine.

It is well known that in nucleophilic attack on an alkene, besides the formation of vinyl substitution products, fragmentation of the molecule at the multiple bond can also occur. The most frequently observed reactions are those that split out water; these are typical of unsymmetrical ethylenes that are activated by some electron-acceptor groups. Detailed study of the kinetics leads to the conclusion that these are all multistep processes that proceed by the same mechanism, which for the uncatalyzed splitting of alkene by water is shown in Scheme 1:

Scheme 1



Attack of the alkene by a water molecule yields a zwitterion $A^{\pm}$, which is then converted to the anion A^-. The latter is either stabilized to a monosubstituted ethylene C by splitting out of X^-, or is protonated to the neutral product A°, which undergoes, via deprotonation, a splitting-out reaction to form the final products A and B. This scheme is also valid for processes in acid or basic media. At different pH values, only the rate constants of the individual steps change [2-4].

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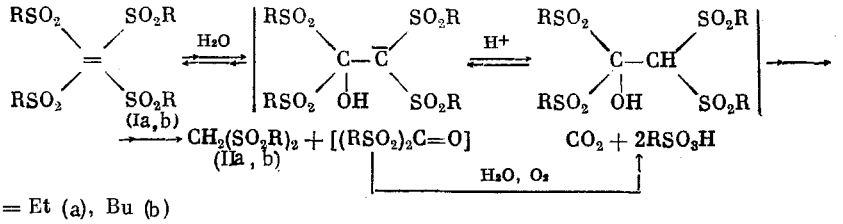
The reaction of tetrakissulfonylethylenes (Ia, b) with water is presented in simplified form in Scheme 2:

Scheme 2



R = Et (a), Bu (b)

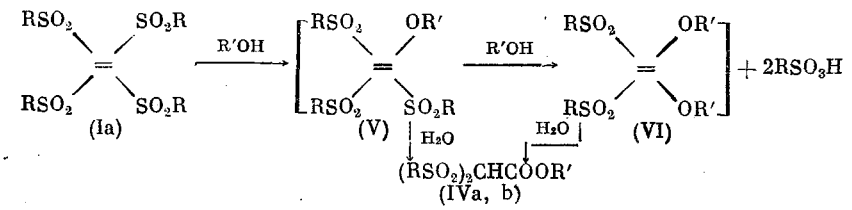
Because of the extremely easy fragmentation of TSE (I) in aqueous medium, these compounds can be synthesized only under anhydrous conditions [1]. Naturally attempts to obtain (I) from the respective sulfides using 30% H_2O_2 in CH_3CO_2H as oxidant yield upon heating only disulfonylmethanes of type (II), the products of hydrolytic splitting [5, 6].

When tetrasubstituted electrophilic ethylenes containing cyano groups, such as tetracyanoethylene or 1,2-dicyano-1,2-disulfonylethylenes, are hydrolyzed, fragmentation does not occur, but one CN or SO_2R group is replaced by hydroxyl to form enols of type C (see Scheme 1) which are characterized as the stable amine salts [7, 8].

Under the same conditions our attempts to obtain enol salts from (Ia, b) with tetramethylammonium chloride led only to the separation of disulfonylmethanes (IIa, b).

Alcohols also react readily with (I), but without forming fragmentation products. For example, from (Ia) in a solution of an alcohol (20°C, 0.5 h) in the presence of urea as catalyst we synthesized in high yield the esters of disulfonylacetic acids (IVa, b) (Scheme 3):

Scheme 3



R = Et, R′ = Me (IVa); R = R′ = Et (IVb)

We did not specifically study the paths by which esters (IVa, b) are formed. It can be presumed they are obtained by the action of water on the reaction mixture, by hydrolysis of the intermediate acetals or diacetals of the ketenes (V) or (VI). The latter are the products of nucleophilic vinyl substitution of one or two alkylsulfonyl groups in (Ia) by an OR′ group, by the usual scheme of addition and splitting out.

As is well known, ketene acetals and diacetals hydrolyze easily, some even under the influence of atmospheric moisture, to give esters [9]. When ethanol (which is more hygroscopic than CH_3OH) rendered absolute in the usual way is used, there is a competitive hydrolytic splitting of sulfone (Ia) and disulfonylmethane (IIa) is isolated in 10% yield.

The proposals concerning the course of the reaction of (I) with alcohols are confirmed to a considerable extent by the reactions with thiols. The ketone thioacetals and dithioacetals (VIIa-c) and (VIIIa-c) are isolated; in contrast to their oxygen analogs (V) and (VI), under these reaction conditions they are quite stable.

$$\underset{\text{(Ia, b)}}{(RSO_2)_2C{=}C(SO_2R)_2} \xrightarrow{R'SH} \underset{\text{(VIIa—c)}}{(RSO_2)_2C{=}C(SO_2R)(SR')} + \underset{\text{*(VIIIa—c)}}{(RSO_2)_2C{=}C(SR')_2}$$

R = R′ = Et (VIIa), (VIIIa); R = Et, R′ = Ph (VII b, (VIII b; R = Bu, R′ = Et (VII c, (VIII c)

TABLE 1. Conditions and Product Composition of Reaction of $(RSO_2)_2C{=}C(SO_2)$, (Ia, b) with R'SH

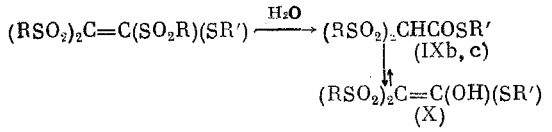
Test No.	R	R'	Reactions conditions			Reaction products, %			
			moles thiol/ moles (Ia, b)	solvent	reaction temp., °C (time, h)	(VII)	(VIII)	(IX)	(II)
1	Et	Et	1,5	CH_2Cl_2	30–35(1)	68,7	9,9	–	–
2	Et	Et	6	CH_2Cl_2	30–35(1)	57,8	28,9	–	–
3	Et	Et	6	CH_2Cl_2	30–35(5)	–	69,8	–	–
4	Bu	Et	1,2	CH_3CN	50(2)	26,7		23,5	9
5	Bu	Et	8	CH_2Cl_2	40(12)	–	70,3	–	–
6	Bu	Et	8	CH_3CN	50(3)	–	68,2	–	9
7	Et	Ph	1,2	CH_3CN	50(2)	26,2	6,5	33,3	6
8*	Et	Ph	1,2	ТГФ	50(2)	24,5	5,6	23,7	15,4
9	Et	Ph	3	CH_3CN	60(3)	–	63,5	–	10

*Reaction carried out in presence of urea.

The replacement of one or two RSO_2 groups at the C=C bond depends on the proportion of components and the duration of the reaction. The process conditions are determined by the nature of the substrate and of the thiylating agent (Table 1). The more nucleophilic alkanethiols such as EtSH react with sulfone (Ia) with brief heating in CH_2Cl_2 medium. Under analogous conditions sulfone (Ib) (CH_2Cl_2, 35-40°C, 4h) is 80-85% unchanged; this may be related to the steric factor of the bulkier $BuSO_2$ group as compared with $EtSO_2$. Prolonged heating is needed to complete the reaction (see Table 1, test 5). An aprotic solvent such as MeCN shortens the reaction time considerably (tests 4, 6).

Thiophenol is less nucleophilic than ethanethiol and essentially does not react with sulfone (Ia) in CH_2Cl_2 even with prolonged heating (8 h, 35-40°C). This reaction can be carried out if an aprotic solvent (CH_3CN, THF) and urea catalysis are used. It should be noted that when these solvents, rendered absolute by the usual methods, are used, usually in the presence of urea, the competing hydrolysis of sulfones (Ia, b) becomes noticeable; this yields disulfonylmethanes (IIa, b), along with 6-15% yields of (VII) and (VIII).

In the chromatographic separation of reaction mixtures on silica gel (which always contains a certain amount of water), the ketone dithioacetals (VIIIb, c) were stable, but instead of the ketene monothioacetals (VIIb, c) their hydrolysis products (IX) and (X) were isolated.



$R = Bu; R' = Et$ (IXb); $R = Et; R' = Ph$ (IXc), (X)

According to the spectral data, (IXb), like (IVa, b), is in the ester form, whereas (IXc) is in the stable enol form; the IR spectrum contains the OH frequency at 3427 cm^{-1} and C=C at 1595 cm^{-1}, but lacks the typical C=O absorption.

The structures of the synthesized compounds were confirmed by elemental analysis and spectral data. The IR spectra of (VIIa-c) and (VIIIa-c) show frequencies at 1132-1145 and 1319-1330 cm^{-1} (SO_2 group). A feature of these IR spectra is the absence of absorption in the 1600-1500 cm^{-1} range that is typical of the C=C valence vibrations, and the presence of intense absorption in the 1431-1466 cm^{-1} range. Analogous spectral data were obtained for ketone S,S-acetals with other electron-acceptor groups. The absorption in the latter region probably corresponds to the vibration of the $C{=}C(SR)_2$ structure [10].

EXPERIMENTAL

PMR spectra were obtained on a DA-60 JL apparatus (60 MHz) and a Tesla BS-497 apparatus (100 MHz) with HMDS as internal standard; ^{13}C NMR spectra, on a Bruker WP-60 spectrometer. IR spectra were obtained in KBr on a UR-20 apparatus.

Absolute solvents were used. Tetrakissulfonylethenes were synthesized by the procedure of [1]. SiO_2, L 40/100 μm, was used for chromatography.

Hydrolysis of Tetrakisalkylsulfonylethenes (Ia, b). The tests were carried out with stirring in a current of Ar that was passed through Ascarite. Before the test, distilled water was boiled in an Ar stream for 15 min; CO_2 was collected in Ascarite.

(a) Sulfone Ia, 0.9940 g (2.5 mmole) was heated with 7 ml of water at 70-75°C until the sulfone dissolved (0.5 h). CO_2 recovery was 0.1060 g (96.3%). When the aqueous solution was cooled to 5°C, 0.49 g (98%) of (IIa) separated, mp 103-104°C [11]. IR spectrum (ν, cm^{-1}): 1125, 1330 (SO_2). PMR spectrum ($CDCl_3$, δ, ppm): 1.46 t (6H, $2CH_3$), 3.45 q (4H, $2CH_2$), 4.60 s (2H, CH_2SO_2). The aqueous solution was neutralized with 0.1 N NaOH. Evaporation yielded 0.61 g (92.3%) of $C_2H_5SO_3Na$. IR spectrum (ν, cm^{-1}): 1068, 1190, (SO_2 in sulfonate salts). Found: C 18.20; H 4.14; S 23.85; Na 17.36%. $C_2H_5O_3SNa$. Calculated: C 18.18; H 3.81; S 24.26; Na 17.40%.

(b) To 0.1980 g (0.5 mmole) of Ia in 5 ml of H_2O was added one drop of CF_3CO_2H; after one hour the evolved CO_2 weighed 0.001 g (49%). From the aqueous solution, as described above, 0.47 g (47%) of (IIa) and 0.06 g (46.3%) of $C_2H_5SO_3Na$ were isolated.

(c) to 0.9940 g of (Ia) in 30 ml of acetone at 0°C were added 1 g of pyridine and 2 ml of H_2O. After 1 h at 20°C 0.1031 g of CO_2 (93.7%) was obtained. Evaporation of the acetone solution yielded 0.63 g (96%) of (IIa) and 0.24 g (96.3%) of $C_2H_5SO_3Na$.

(d) To 0.5047 g of (Ib) in 20 ml of acetone were added 1 ml of H_2O and one drop of triethylamine. An exothermic reaction occurred. After 10 min the acetone was evaporated, the mixture was diluted with CH_2Cl_2, washed with $NaHCO_3$ solution and water, and dried with $MgSO_4$. Evaporation of CH_2Cl_2 yielded 0.22 g (84.6%) of (IIb), mp 99°C (pentane–ether) (cf. [12]).

REACTION OF SULFONE (Ia) WITH ALCOHOLS

Tests were carried out with stirring in a current of dry nitrogen.

Methyl Disulfonylacetate (IVa). To 1 g of (Ia) in 10 ml of CH_3OH at 10°C was added 0.2 g of urea. The mixture was stirred for 5 h at 20°C and evaporated. The residue was dissolved in $CHCl_3$, washed with water until neutral, and dried over $MgSO_4$. Evaporation yielded 0.5 g (81.3%) of (IVa), mp 97.5-98°C (cf. [13]).

Ethyl Disulfonylacetate (IVb). From 1 g of (Ia), 10 ml of C_2H_5OH, and 0.2 g of urea under conditions as described above, after evaporation of $CHCl_3$ and crystallization from ether, there was obtained 0.25 g of (IVb), mp 88.5-89°C (cf. [14]), and 0.40 g of a mixture of (IIa) and (IVb). The mixture was separated on a column of 15 g of SiO_2; gradient elution in a system of CCl_4–1% acetone → CCl_4–5% acetone yielded 0.47 g (69.7%) of (IVb).

REACTION OF SULFONES (Ia, b) WITH THIOLS

The tests were carried out with stirring in a nitrogen atmosphere.

Reaction of (Ia, b) with Ethanethiol. (a) To 0.99 g (2.5 mmole) of sulfone (Ia) in 5 ml of CH_2Cl_2 at 20°C was added 0.23 g (3.75 mmole) of ethanethiol. The mixture was heated for 1 h at 30-35°C and evaporated and ether was added to the residue. The yellow crystals that precipitated at 5°C were filtered off. There was obtained 0.59 g (68.7%) of (VIIa), mp 165.5-166°C (CH_2Cl_2–ether). Found: C 33.30; H 5.54; S 35.04%. $C_{10}H_{20}O_6S_4$. Calculated: C 32.96; H 5.53; S 35.18%. PMR spectrum ($CDCl_3$, δ, ppm): 1.36-1.61 m (12 H, 4 CH_3), 3.23-4.05 m (8 H, 3 CH_2SO_2 and CH_2S). ^{13}C NMR spectrum ($CDCl_3$, δ, ppm): 148.22, 169.05 (C_α, C_β). The ether solution was washed with water and dried with Na_2SO_4. Evaporation of the solvent yielded 0.09 g (9.9%) of (VIIIa), mp 63.5-64°C (pentane–ether). Found: C 36.25; H 6.04; S 38.28%. $C_{10}H_{20}O_4S_4$. Calculated: C 36.12; H 6.06; S 38.56%. ^{13}C NMR spectrum ($CDCl_2$, δ, ppm): 134.2, 177.3 (C_α, C_β). PMR spectrum ($CDCl_3$, δ, ppm): 1.26-1.56 m (12 H, 4 CH_3), 2.69-3.73 m (8 H, 2 CH_2SO_2 and 2 CH_2S). For yields of (VIIa) and (VIIIa) under other reaction conditions, see Table 1, tests 2, 3. In test 3, the reaction mixture was diluted with CH_2Cl_2, washed with $NaHCO_3$ and water, and dried, and (VIIIa) was isolated.

(b) Sulfone (Ib), 1 g (2 mmole), and 1 g (16 mmole) of ethanethiol in 10 ml of CH_2Cl_2 were heated at 40°C for 12 h. After the treatment described above for (VIIIa), 0.52 g (70.2%) of (VIIIc), mp 47.5-48.5°C (pentane–ether). Found: C–43.28; H 7.26; S 33.00%. PMR spectrum (CCl_4, δ, ppm): 0.98-1.75 m (20 H, $2CH_3$ and $2[CH_3(CH_2)_2]$), 2.95-3.52 m (8 H, 2 CH_2S and 2 CH_2SO_2).

When (Ib) was reacted with ethanol in CH_3CN (see Table 1, test 6), after separation of (VIIIc) and column chromatography of the mother liquor (eluent hexane–ether 5:1), 9% of (IIb) was obtained.

(c) Sulfone (Ib), 1 g (2 mmole) and 0.15 g (2.4 mmole) of C_2H_5SH in 5 ml of CH_3CN were heated for 2 h at 50°C. The solution was evaporated and the residue was treated with CH_2Cl_2, washed with $NaHCO_3$ and water, and dried with $MgSO_4$. The CH_2Cl_2 was evaporated and pentane was added. The yellow crystals that precipitated at 20°C were filtered off. There was obtained 0.24 g (26.7%) of (VIIc), mp 100-101°C (pentane–ether). Found: C 43.07; H 7.25; S 28.31%. $C_{16}H_{32}O_6S_4$. Calculated: C 42.83; H 7.18; S 28.58%. PMR spectrum ($CDCl_3$, δ, ppm): 0.96-1.60 m (24 H, 4 CH_3 and 3 CH_2CH_2), 3.35-3.71 m (8 H, 3 CH_2SO_2 and CH_2S).

The mother liquor was separated on a column of 15 g of SiO_2 by gradient elution in a system of petroleum ether → petroleum ether–ether (6:1) to yield 0.26 g (23.5%) of (IXb), mp 78-79°C. Found: C 42.05; H 7.00; S 27.78%. $C_{12}H_{27}O_5S_3$. Calculated: C 41.87; H 7.02; S 27.91%. IR spectrum (ν, cm^{-1}): 1125, 1333 (SO_2), 1665 (CO, in thiol esters). PMR spectrum (C_6H_6, δ, ppm): 0.95-1.55 m (17 H, 3 CH_3 and 2 CH_2CH_2), 2.95 q (2 H, CH_2S), 3.69-3.96 m (4 H, 2 CH_2SO_2), 5.50 s (1 H, CH).

Further elution with 5:1 petroleum ether–ether yielded 0.03 g (9%) of (IIb).

Reaction of (Ia) with Thiophenol. (a) (Ia), 0.99 g (2.5 mmole) in 10 ml of CH_3CN was heated with 0.33 g (3.0 mmole) of thiophenol (see Table 1, test 7). After treatment as described for procedure (c), the reaction mixture was washed 3 times by decantation with pentane, then passed through a column (20 × 250 mm) of 10 g of SiO_2, L 100/160 μm, and rapidly (10-15 min) eluted with $CHCl_3$ with air pressure. The orange zone was collected. There was obtained 0.28 g (26.2%) of orange crystals of (VIIb), mp 133-133.5°C (hexane–CH_2Cl_2). Found: C 40.55; H 4.93; S 30.93%. $C_{14}H_{20}O_6S_4$. Calculated: C 40.75; H 4.88; S 31.08%. PMR spectrum ($CDCl_3$, δ, ppm): 1.33-1.61 m (9 H, 3 CH_3), 3.67-3.95 m (6 H, 3 CH_2SO_2), 7.45 m (5 H, C_6H_5S). Further rapid elution with ether yielded 0.48 g of a mixture containing, by TLC, (VIIb), (VIIIb), and (IIa). This mixture of orange crystals was separated on a column of 30 g of SiO_2. Gradient elution* with a system of hexane → hexane–$CHCl_3$ (4:1) yielded, in the following sequence: 0.07 g (6.5%) of (VIIIb), mp 162-163°C (ether–$CHCl_3$); 0.03 g (6%) of (IIa); and 0.28 g (33.3%) of (X), mp 164-165°C. Found for (VIIIb): C 50.23; H 5.06; S 29.66%. $C_{18}H_{20}O_4S_4$. Calculated: C 50.44; H 4.70; S 29.92%; PMR spectrum ($CDCl_3$, δ, ppm): 1.43 m (6 H, 2 CH_3), 3.49 q (4 H, 2 CH_2SO_2), 7.11 m (10 H, 2 C_6H_5S). Found for (X): C 42.57; H 5.15; S 28.32%. $C_{12}H_{16}O_5S_3$. Calculated: C 42.83; H 4.79; S 28.58%.

For the product composition of the reaction of (Ia) with a large excess of thiophenol, and also in THF solution, see Table 1, tests 8, 9. In test 9, after the raction mixture was treated as in method (c) and the solvent was evaporated, part of (VIIIb) was precipitated with ether. Chromatography of the mother liquor on a SiO_2 column under the conditions described above yielded more (VIIIb) and (IIa) (see Table 1).

CONCLUSIONS

1. Tetrakisalkyl(aryl)sulfonylethenes (TSE) in neutral, acid, and especially basic media easily undergoes hydrolysis; this causes fragmentation of the molecule to form disulfonylmethanes, CO_2, and sulfonic acids.

2. By the reaction of TSE with alcohols, disulfonylacetate esters are obtained in high yield; they are probably the products of the hydrolysis of intermediate unstable acetals or diacetals of disulfonylketenes.

3. Depending on reaction conditions and reagent proportions, the reaction of TSE with thiols causes the replacement of one or two SO_2R groups by SR groups.

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*As materials advance along the column, the orange zone disappears.

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TRANSFORMATION OF THIOPHENES INTO NONTHIOPHENE DERIVATIVES

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Since the discovery of thiophene 100 years ago, extraordinary advances have been made in the chemistry of this compound. Until the 1950's thiophene chemistry was developed in parallel to benzene chemistry but reactions without analogy for benzene derivatives have been steadily acquiring greater significance. Greatest interest now lies in reactions which reveal the specific features of thiophene as a special heteroaromatic system with unequal ring elements. Such reactions include opening of the thiophene ring leading to nonthiophene compounds.

Reductive methods now hold greatest interest among the methods for the conversion of thiophenes into aliphatic and carbocyclic compounds as well as other heterocyclic compounds. Two approaches are possible for this transformation. In the first variant, thiophene compounds are reduced to di- and tetrahydrothiophenes, which hold interest in themselves, and may serve as intermediates in the synthesis of various nonthiophene compounds. For example, methods are known for the opening of tetrahydrothiophene compounds leading to bifunctional aliphatic compounds [1, 2]. The elimination of sulfur upon the photolysis of dihydrothiophenes [3] or the thermal ring opening of the corresponding sulfones [4, 5] opens a pathway to open-ring diene systems.

The second approach which formally involves one-step opening of the thiophene ring by the breakage of one or two C—S bond has acquired greater significance. In the present work, we limit ourselves to a brief examination of the hydrogenation of thiophenes and give a more detailed examination of these "one-step" reactions, which, however, in essence, are consecutive reactions. In some of these reactions, dihydrothiophenes are initially formed, which then undergo reductive ring opening.

1. Hydrogenation of Thiophene Compounds with the Formation of Dihydro- and Tetrahydrothiophene Derivatives. The feasibility of using catalytic hydrogenation of the thiophene ring as a method for the synthesis of dihydro- and tetrahydrothiophenes is very limited due to poisoning of the catalysts and uncontrolled destruction of the ring under catalytic hydrogenation conditions. Only a few catalysts are suitable for the hydrogenation of the thiophene ring though their use is often limited by high cost, vigorous conditions, and low selectivity. An exception is the palladium catalyst described by Mozingo et al. [6] which permits hydrogenation under mild conditions. However, catalyst poisoning leads to a large consumption of palladium which, by weight, is close to the amount of hydrogenated thiophene compound. Thus, this reaction is justified only in special cases such as in the stereospecific synthesis of biotin through thiophene precursors [7]. High yields of tetrahydrothiophenes may be obtained using rhenium heptasulfide [8, 9] although the vigorous reaction conditions (250-500°C, 100-300 atm) and high cost of this catalyst prevent its common use.

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