Reactions of 1,3-Dithiolan-2-ylium and 1,3-Dithian-2-ylium Tetrafluoroborates and Ambident 2-Styryl Derivatives

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The ambident 2-styryl-1,3-dithiolan-2-ylium and 2-styryl-1,3-dithian-2-ylium cations react with preferential carbon-carbon bond formation at the β ethylenic carbon when treated with methylmagnesium iodide. In the lithium aluminum hydride reaction, reduction occurs at either electrophilic carbon center. Methanol and thiophenol react selectively with the β carbon of the side chain. The adduct formation with the heteroatom nucleophiles is readily reversed by acid catalysis. In the absence of the styryl group, the nucleophilic addition is at C-2. Dithioketals of symmetric 1,2-dicarbonyl derivatives are readily formed by zinc-induced reductive dimerization of 1,3-dithiolan- and 1,3-dithian-2-ylium salts.

Recently, we described a convenient synthesis of 1,3-dithiolan-2-ylium and 1,3-dithian-2-ylium tetrafluoroborates from an acid chloride and 1,2-ethanedithiol or 1,3-propanedithiol.[1] The former are cationic equivalents of the important lithium ylide synthons of 1,3-dithianes.[2] The corresponding 2-lithio-1,3-dithiolanes, however, have been less useful synthons, mainly because of difficulties encountered in the lithiation reaction; under the conditions used for metallation, extensive fragmentation reactions may occur,[3,4] but a successful series of reactions has been reported.[5]

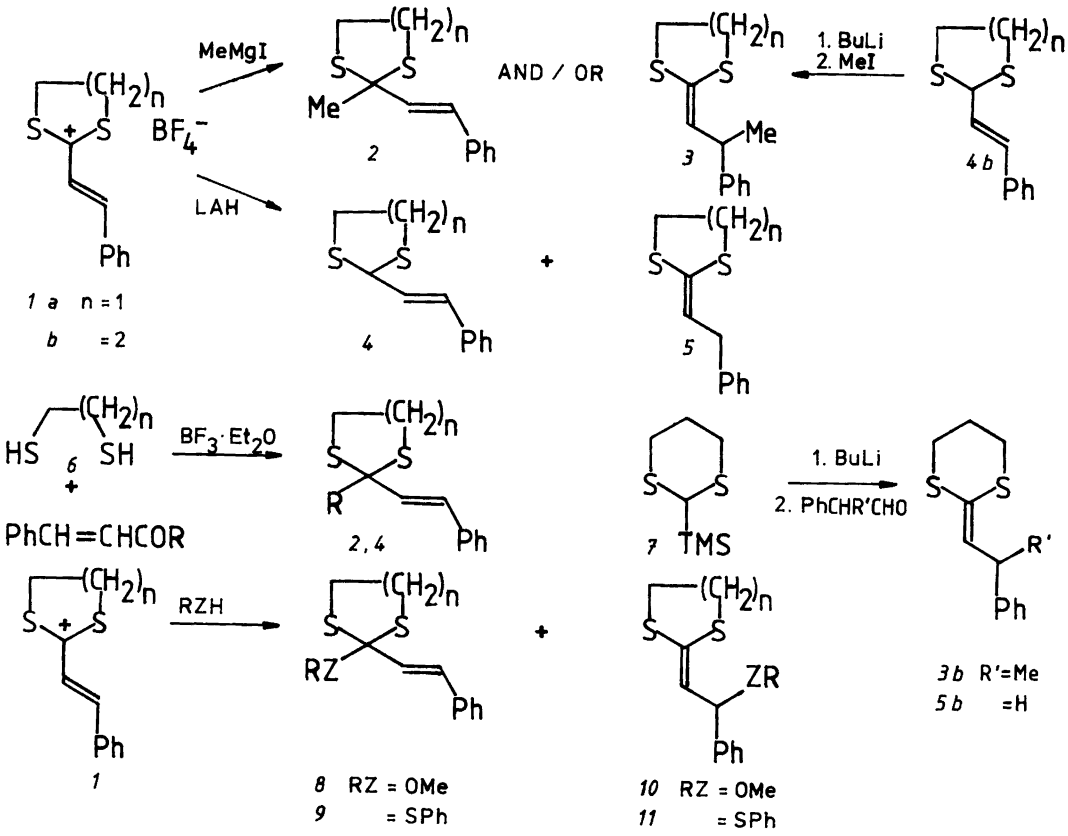
The ylides are complementary to the ylium salts in that treatment of the former with an electrophile or treatment of the latter with a nucleophile may lead to the same 2-substituted 1,3-dithiolane or 1,3-dithiane. It is apparent from the discussion above, however, that 2-substituted 1,3-dithiolanes are best obtained by way of ylium chemistry.

In our recent report, we described studies on the introduction of carbon substituents at C-2 in 1,3-dithian-2-ylium salts by means of organometallic reagents.[6] Here, we describe some reactions with the ambident styryl cations *1a* and *1b*; the nucleophile may be added either at C-2 or at the β carbon of the ethylene substituent.

The NMR data of the products from the reactions of *1* with methylmagnesium iodide show that preferential addition of the methyl group is at the β carbon of the styryl function to form compound *3*. The presence of a small amount of its isomer *2* (<5 %), however, could also be detected by TLC. On TLC, the latter behaves as the *trans* products which were prepared by separate syntheses (see below). The high regio preference for the formation of *3* compares favourably with the course of the reaction when the reactants are oppositely polarized; the ylide of 2-styryl-1,3-dithiane reacts with methyl iodide to form the isomers *2b* and *3b* in almost equimolar amounts.[7]

In the lithium aluminum hydride reduction with the ylium salts *1*, the hydride ion adds to either electrophilic center. The ratio between *4a* and *5a* was 1:3; between *4b* and *5b* the ratio was 1:1. For comparison, it is pointed out that, on protonation of lithiated 2-styryl-1,3-dithiane, the proton is added on C-2 whereby *4b* is formed.[7]

For reference purposes, the styryl derivatives *2* and *4* and the ketene dithioacetals *3b* and *5b* have been prepared by other routes. Compound *2* was formed from the appropriate alkanedithiol and *trans*-4-phenyl-3-buten-2-one under the normal conditions for thioketalization; cinnamaldehyde furnished the dithioacetal *4*. The ketene dithio-



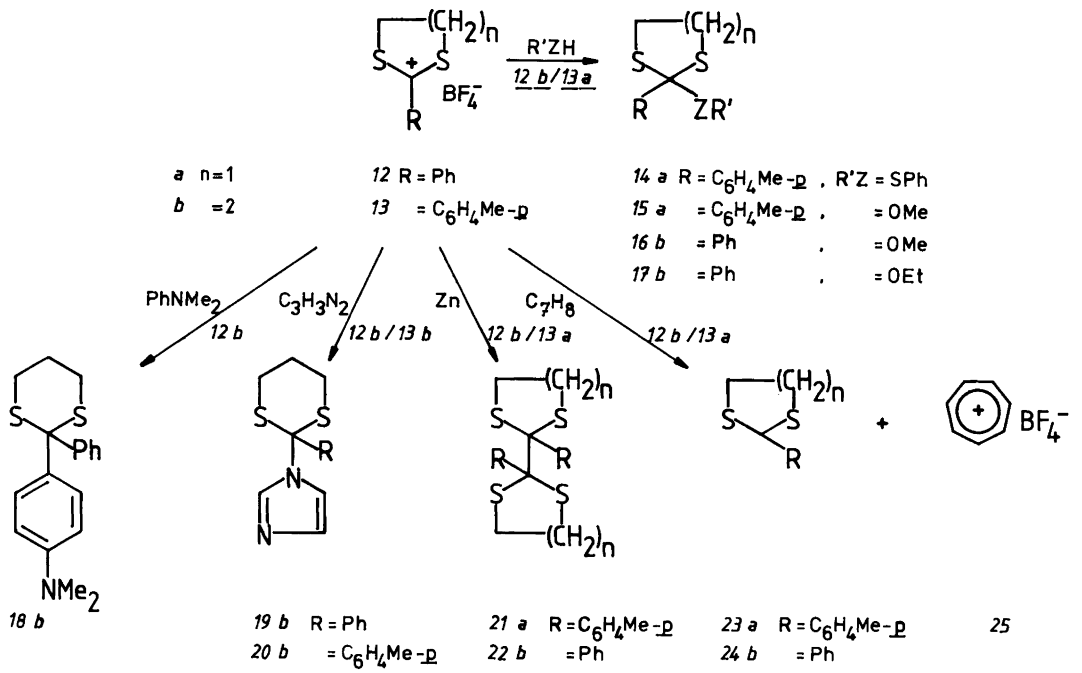
SCHEME 1

acetal *3b* was prepared by the reaction between the ylide of 2-trimethylsilyl-1,3-dithiane and 2-phenylpropanal; *5b* was similarly available from phenylacetaldehyde.

In the reaction of oxygen and sulfur nucleophiles with *1*, preferential addition on the β carbon was observed; *1a* reacted with methanol to furnish *10a;* whereas the reactions of *1* with thiophenol yielded *11*. C-2 of the 2-styryl cation *1* is a hard electrophilic center. From the literature, it is known that 2-dialkylamino-1,3-dithiolan-2-ylium salts react with hard nucleophiles at the carbonium site and with soft donors at the methylene carbon atoms, and similarly that the tris(methylthio)methyl cation reacts at the carbonium center with water, whereas soft ions attack the methyl group.[8a] It is also accepted that α,β unsaturated carbonyl compounds, which are ambident electrophiles, possess a hard carbonyl and a softer β carbon center.[8b] By analogy, the harder electrophilic center in the 2-styryl cation *1* is assigned to C-2. The reactions of the alcohol and the thiol are thus at the softer electrophilic β carbon.

The addition of the heteroatom nucleophiles to *1* is readily reversed by acid catalysis resulting in reformation of ylium ion; dissolution of *11* in TFA for ^{1}H NMR analysis led to complete dissociation to *1*. With HBF_4 in ether, the tetrafluoroborate salt is precipitated.

When the ambident nature of the ylium ion is abolished, such as in the case of *12* and *13*, rapid nucleophilic addition at C-2 occurs; with thiophenol or alcohols, the products *14–17* are formed. These findings agree with the results from a very recent mechanistic study of the behavior of the 2-(4-methoxyphenyl)-1,3-dithiolan-2-ylium ion in aqueous solutions,[9] and related reactions with ethanethiol.[10]



SCHEME 2

The electrophilic species *12* and *13* are expected to substitute electronically activated aryl derivatives whereby protected aryl ketones are formed. This was demonstrated for *12b* which reacts with *N,N*-dimethylaniline to furnish the *para* substituted product *18b*. With phenol, the reaction with *12b* was very slow (TLC). Compounds *12b* and *13b* react with imidazole to furnish the *N*-substituted products *19b* and *20b*. The ^{1}H NMR spectra contained three imidazole protons which were not exchangeable in deuterium oxide. 2-Chloro-1,3-dithiane, which has partial ionic character, reacts readily with phenols and with imidazole.[11,12]

Reductive dimerization of 1,3-dithiolan- and 1,3-dithian-2-ylium cations provides a synthetic route to dithioketals of symmetric 1,2-dicarbonyl compounds. Thus, *12b* and *13a* give the 2,2'-dimers *21a* and *22b* when treated with zinc dust in acetonitrile.

The cations *12b* and *13a* were treated with cycloheptatriene to furnish the tropylium ion and the corresponding 1,3-dithiolane *23a* or 1,3-dithiane *24b*, but *12b* did not react with triphenylmethane. This suggests that the stability of *12b* lies between the stabilities of the tropylium and the trityl ion. In agreement with this finding, it has been reported that the 1,3-dithian-2-ylium salt can be prepared from 1,3-dithiane by treating the latter with triphenylmethyl tetrafluoroborate.[13] Rather surprisingly, this approach to the preparation of ylium salts from 2-substituted 1,3-dithiane was not successful.[1,14]

Experimental

The ^{1}H NMR spectra were recorded at 60 MHz and the ^{13}C NMR spectra at 15 MHz in deuteriochloroform unless otherwise stated. The mass spectra under electron impact conditions (MS) were recorded at 70 eV ionizing voltage. Isobutane was used for the chemical ionization (MSCI) unless otherwise stated.

TLC was performed on silica gel using toluene-light petroleum as developer. For GLC, a column consisting of 8 feet, 3 % SP2100 Supelcoport® 80/100 was used, working range 100–250 °C at 16 °C/min. Argon was used to generate an inert atmosphere in the organometallic reactions.

*Reaction between 2-*trans*-β-styryl-1,3-dithiolan-2-ylium tetrafluoroborate* 1a *and methylmagnesium iodide.* 2-*trans*-β-Styryl-1,3-dithiolan-2-ylium tetrafluoroborate[1] (2.96 g, 10.0 mmol) was added at 0 °C to vigorously stirred methylmagnesium iodide (50.0 mmol) in dry ether (70 ml). The mixture was stirred at 20 °C for 30 min and heated under reflux for 15 min. The cold mixture was treated with 0.5 M HCl (50 ml), the organic layer separated and the aqueous layer extracted with ether (3×50 ml). The combined ether solutions were shaken with saturated aqueous $NaHCO_3$ (2×50 ml), with water and the dried ($MgSO_4$) solution evaporated. There remained 2.38 g of a yellow oil. GLC analysis showed this to be *3a* containing ca. 1 % of *2a*. Compound *3a* was purified by chromatography on silica gel using toluene for elution. Anal. $C_{12}H_{14}S_2$: C,H. ^{1}H NMR: δ 1.40 (Me, d, *J* 7 Hz), 3.33 (CH_2CH_2, s), 3.4–3.8 H-β, m), 5.70 (CH=, d, *J* 9 Hz), 7.30 (Ph, s). MS: 222 (5, M), 207 (13), 147 (100).

*Reaction between 2-*trans*-β-styryl-1,3-dithian-2-ylium tetrafluoroborate* 1b *and methylmagnesium iodide.* 2-*trans*-β-Styryl-1,3-dithian-2-ylium tetrafluoroborate[1] (3.08 g, 10.0 mmol) was added at 0 °C to vigorously stirred methylmagnesium iodide (50 mmol) in dry ether (70 ml). The reaction conditions and the work-up of the mixture were as described above. The crude product (1.90 g) was *3b*, containing a small amount of the isomer *2b* (<5 %; TLC). The yield of *3b* was 60 %. It was purified by chromatography on silica gel with toluene as eluant.

*Reaction between 2-*trans*-β-styryl-1,3-dithiolan-2-ylium tetrafluoroborate* 1a *and lithium aluminum hydride; formation of* 4a *and* 5a. Lithium aluminum hydride (0.19 g, 5.0 mmol) was added with stirring to a suspension of 2-*trans*-β-styryl-1,3-dithiolan-2-ylium tetrafluoroborate (1.47 g, 5.0 mmol) in dry THF (100 ml) at room temperature. A colourless solution was gradually formed. The reaction was stopped after 15 min by cautious addition of water (150 ml), and most of the THF was removed by distillation at reduced pressure. The pH was adjusted to ca. 6 before extraction with ether (4×100 ml). Evaporation of the washed and dried ($MgSO_4$) ether solution gave a yellow oil which was found by ^{1}H NMR and TLC to be a mixture of compounds *4a* and *5a* in the ratio 1:3; yield 1.00 g (96 %). The isomers were separated on neutral alumina using benzene-light petroleum (1:2) for elution; *4a* eluted first.

Physical data for 2-(2-phenylethylidene)-1,3-dithiolane *5a:* Oily product. Anal. $C_{11}H_{12}S_2$: C,H. ^{1}H NMR ($CDCl_3$): δ 3.33 (2 CH_2, s), 3.45 (CH_2Ph, d, *J* 7 Hz), 5.68 (C=CH, t, *J* 7 Hz), 7.23 (Ph). MS: 208 (100, M^+), 180 (20), 179 (16), 148 (11), 147 (58), 131 (14), 116 (23), 115 (36).

*Reaction between 2-*trans*-β-styryl-1,3-dithian-2-ylium tetrafluoroborate* 1b *and lithium aluminum hydride; formation of* 4b *and* 5b. Lithium aluminum hydride (5.0 mmol) reduction of 2-*trans*-β-styryl-1,3-dithian-2-ylium tetrafluoroborate (5.0 mmol) was carried out as above. The product, 95 % yield, was a mixture of *4b* and *5b* in the ratio 1:1 (^{1}H NMR, TLC).

*2-Methyl-2-*trans*-β-styryl-1,3-dithiolane* 2a. Boron trifluoride diethyl etherate (2 ml) was added with stirring at room temperature to a solution of 1,2-ethanedithiol (5.22 g, 55 mmol) and *trans*-4-phenyl-3-buten-2-one (7.30 g, 50 mmol) in acetic acid (50 ml) and the mixture was stirred for 36 h. Water (150 ml) was then added, the mixture extracted with dichloromethane (3×100 ml), the combined extracts shaken with 5 % NaOH (2×50 ml) and water, the dried ($MgSO_4$) solution evaporated and the residue distilled; yield 9.0 g (81 %), b.p. 120–122 °C/0.01 mmHg. The yellow oil crystallized on standing, m.p. 50–54 °C. Anal. $C_{12}H_{14}S_2$: C, H. ^{1}H NMR: δ 1.94 (Me), 3.31 (2 CH_2), 6.40 (CH-1′, $J_{1',2'}$ 16 Hz), 6.55 (CH-2′), 7.0–7.4 (Ph). ^{13}C NMR: δ 29.7 (2 C-4,5), 40.1 (Me), 65.5 (C-2), 126.7–136.5 (Ph, C=C). MS: 222 (66, M), 194 (68), 170 (50), 161 (100), 129 (83).

*2-Methyl-2-*trans*-β-styryl-1,3-dithiane* 2b.[7] This compound was prepared as above from 1,3-propanedithiol in 78 % yield, b.p. 134–136 °C/0.04 mmHg; colourless oil which crystallized as colourless needles m.p. 32–34 °C. Anal. $C_{13}H_{16}S_2$: C, H. ^{13}C NMR: δ 24.8 (C-5), 27.5 (Me), 29.6 (2 C-4,6), 50.1 (C-2), 125.5–136.4 (Ph, C=C). MS: 236 (11, M), 162 (8), 161 (45), 43 (100).

2-β-Phenylpropylidine-1,3-dithiane 3b (previously obtained in mixtures[7]). 1.6 M butyllithium in hexane (14 ml, 22.0 mmol) was added dropwise with stirring to a solution of 2-trimethylsilyl-1,3-dithiane[15] (3.80 g, 20.0 mmol) in dry THF (40

ml) at −78 °C. The mixture was stirred at this temperature for 2 h and at 0 °C for 2 h. 2-Phenylpropanal (2.82 g, 20.0 mmol) in dry THF (20 ml) was added dropwise at 0 °C and the mixture stirred for 12 h at 20 °C before water (120 ml) was added. The resultant mixture was extracted with pentane (3×100 ml), the washed and dried ($MgSO_4$) pentane solution evaporated and the product isolated as a yellow oil from the residue by "Kugelrohr" distillation at 150 °C/0.01 mmHg; yield 2.60 g (55 %). Anal. $C_{13}H_{16}S_2$: C, H. ^{13}C NMR ($CDCl_3$): δ 21.3 (Me), 25.1 (C-5), 28.6 and 29.5 (2 C-4,6), 39.3 (C-2'), 125.4–145.1 (Ph, C=C). MS: 236 (41, M), 222 (18), 221 (89), 43 (100).

2-trans-β-Styryl-1,3-dithiolane 4a. Boron trifluoride diethyl etherate (2 ml) was added with stirring at 20 °C to a solution of 1,2-ethanedithiol (5.22 g, 55.0 mmol) and cinnamaldehyde (6.60 g, 50.0 mmol) in acetic acid (50 ml). A precipitate was rapidly formed. The mixture was stirred at 20 °C for 12 h before water (150 ml) was added. The product was isolated by filtration and was washed well with water; yield 8.10 g (78 %), m.p. 64–65 °C (Lit. [16a] m.p. 59–59.5 °C). ^{13}C NMR: δ 39.5 (2 C-4,5), 54.4 (C-2), 126.5–136.0 (Ph, C=C).

2-trans-β-Styryl-1,3-dithiane 4b.[7] This compound was prepared as above from 1,3-propanedithiol (2.2 g, 20.0 mmol) and cinnamaldehyde (2.6 g, 20.0 mmol) in acetic acid (20 ml). The product, a yellow oil, was purified by "Kugelrohr" distillation at 140 °C/0.15 mmHg; yield 2.30 g (52 %). ^{13}C NMR: δ 25.2 (C-5), 30.2 (2 C-4,6), 47.2 (C-2), 126.0–133.4 (Ph, C=C).

2-(2-Phenylethylidene)-1,3-dithiane 5b. This compound was prepared in the same way as *3b* from 2-trimethylsilyl-1,3-dithiane (3.80 g, 20.0 mmol) and phenylacetaldehyde (2.65 g, 20.0 mmol). The product, a yellow oil, was purified by "Kugelrohr" distillation at 140 °C/0.05 mmHg; yield 2.10 g (44 %). Anal. $C_{13}H_{16}S_2$: C, H. ^1H NMR: δ 1.9–2.4 (CH_2-5), 2.7–3.1 (2 CH_2-4,6), 3.55 (CH_2-2', d, *J* 8 Hz), 6.08 (CH-1', t, *J* 8 Hz), 7.20 (Ph). ^{13}C NMR: δ 25.1 (C-5), 29.5 and 30.2 (2 CH-4,6), 35.5 (CH_2-2'), 126.1–153.3 (Ph and C=C). MS: 222 (55, M), 148 (19), 147 (70), 120 (14), 119 (19), 115 (22), 91 (100).

2-(2-Methoxy-2-phenylethylidene)-1,3-dithiolane 10a. 2-*trans*-β-Styryl-1,3-dithiolan-2-ylium tetrafluoroborate (1.00 g, 3.4 mmol) was added to methanolic (100 ml) sodium methoxide (3.4 mmol) at 20 °C and the mixture stirred at this temperature for 30 min. The solution was evaporated, the residue extracted with chloroform (100 ml) and the filtered chloroform solution evaporated; yield 0.59 g (73 %). Attempts to carry out recrystallizations led to partial decomposition. ^1H NMR: δ 3.0–3.4 (2 CH_2-4,5, OMe), 4.81 (CH-2', d, *J* 8 Hz), 5.63 (CH-1', d, *J* 8 Hz), 7.20 (Ph).

2-(2-Phenyl-2-phenylthioethylidene)-1,3-dithiolane 11a. A solution formed from thiophenol (1.10 g, 10.0 mmol) and triethylamine (1.50 g, 15.0 mmol) in dry acetonitrile (5 ml) was added dropwise with constant stirring during 5 min to a solution of 2-*trans*-β-styryl-1,3-dithiolan-2-ylium tetrafluoroborate (2.95 g, 10 mmol) in dry acetonitrile (30 ml) at 0 °C. The cooling bath was removed and the mixture allowed to reach 20 °C before water (50 ml) was added. The resultant mixture was extracted with chloroform (3×50 ml) and the dried ($MgSO_4$) chloroform solution evaporated. The yellow product was obtained in 88 % yield (2.79 g), m.p. 89–91 °C (MeOH-H_2O). Anal. $C_{17}H_{16}S_3$: C, H. ^1H NMR: δ 3.25 (2 CH_2-4,5), 4.98 (CH-2', d, *J* 10 Hz), 5.81 (CH-1', d, *J* 10 Hz), 7.3 (2 Ph). ^{13}C NMR: δ 37.0 and 38.0 (2 CH-4,5), 56.5 (CH-2'), 115.5 (CH-1'), 126.0–140.5 (C-2, 2 Ph). MSCI: 317 (1, M+H), 209 (53), 208 (44), 207 (100, M-PhS), 131 (59), 111 (99).

2-(2-Phenyl-2-phenylthioethylidene)-1,3-dithiane 11b. This compound was prepared as above from 2-*trans*-β-styryl-1,3-dithian-2-ylium tetrafluoroborate (3.11 g, 10.0 mmol), thiophenol (1.10 g, 10.0 mmol) and triethylamine (1.50 g, 15.0 mmol) in dry acetonitrile (20 ml). White crystalline material m.p. 100–101 °C (MeOH), yield 2.82 g (85 %). Anal. $C_{18}H_{18}S_3$: C, H. ^1H NMR: δ 1.8–2.2 (CH_2-5), 2.5–3.0 (2 CH_2-4,6), 5.42 (CH-2', d, *J* 10 Hz), 6.18 (CH-1', d, *J* 10 Hz), 7.25 (2 Ph). ^{13}C NMR: δ 24.7 (C-5), 29.4 and 29.8 (2 C-4,6), 51.9 (CH-2'), 126.7–139.6 (C=C, 2 Ph). MS: 222 (19), 221 (100, M-SPh). MSCI: 331 (2, M+H), 223 (12), 222 (17), 221 (100).

Behavior of 2-(2-phenyl-2-phenylthioethylidene)-1,3-dithiolane 11a *towards acid catalysis.* 54 % HBF_4 in ether (0.5 ml) was added dropwise with stirring to a solution of *11a* (0.20 g, 0.63 mmol) in dry ether (10 ml) at 20 °C. A solid precipitate was formed during the addition. The mixture was stirred for 10 min before filtration. The product was washed with dry ether and recrystallized from acetic acid. The yield of 2-*trans*-β-styryl-1,3-dithiolan-2-ylium tetrafluoroborate was 41 % (80 mg).

The ready cleavage of *11a* to form *1a* was also evident from NMR experiments. After dissolution of *11a* in TFA, the NMR spectra showed the formation of *1a*. ^{1}H NMR (TFA): δ 4.25 (2 CH_2-4,5), 7.1–8.0 (CH-1′, 2 Ph), 8.35 (CH-2′, d, *J* 16 Hz). ^{13}C NMR (TFA): δ 44.1 (2 CH_2-4,5), 122.0–168.0 (C=C, 2 Ph), 225.5 (C-2).

Behavior of 2-(2-phenyl-2-phenylthioethylidene)-1,3-dithiane 11b *towards acid catalysis.* When compound *11b* was treated as above, 2-*trans*-β-styryl-1,3-dithian-2-ylium tetrafluoroborate *1b* was isolated in 86 % yield (0.32 g).

Dissolution of *11b* in TFA for NMR analysis resulted in the formation of *1b*.^{1}H NMR (TFA): δ 2.0–2.7 (CH_2-5), 3.3–3.8 (2 CH_2-4,6), 7.1–8.0 (CH-1′, 2 Ph), 8.20 (CH-2′, d, *J* 16 Hz).

2-Phenylthio-2-(4-tolyl)-1,3-dithiolane 14a. A solution of thiophenol (0.39 g, 3.55 mmol) and triethylamine (0.40 g, 4 mmol) in acetonitrile (2 ml) was added to a stirred solution of 2-(4-tolyl)-1,3-dithiolan-2-ylium tetrafluoroborate[1] (1.00 g, 3.55 mmol) in acetonitrile (10 ml) at 0 °C. The colourless mixture was allowed to reach room temperature before it was poured into water (40 ml). The resultant mixture was extracted with ether (3×100 ml) and the ether solution washed with water and dried ($MgSO_4$). The ether was then distilled off and the residue crystallized from dilute aqueous methanol; yield 0.60 g (56 %), m.p. 94–96 °C. Anal. $C_{16}H_{16}S_3$: C, H. ^{1}H NMR: δ 2.30 (Me), 3.50 (2 CH_2-4,5), 6.9–7.5 (2 Ph). ^{13}C NMR: δ 21.0 (Me), 39.5 (2 CH_2-4,5), 82.9 (C-2), 127.4–139.0 (2 Ph). MS: 196 (15), 195 (100, M-SPh), 135 (67). MSCI: 305 (15, M+H).

2-Methoxy-2-(4-tolyl)-1,3-dithiolane 15a. A solution of methanol (2 ml) and diisopropylamine (0.57 g, 40 mmol) in acetonitrile (3 ml) was added dropwise at room temperature to a stirred solution of 2-(4-tolyl)-1,3-dithiolan-2-ylium tetrafluoroborate[1] (1.00 g, 3.6 mmol) in acetonitrile (10 ml). The colourless solution was stirred for 10 min after the addition was completed and was then poured into water (40 ml). The aqueous mixture was extracted with ether (3×50 ml) and the dried ($MgSO_4$) ether solution evaporated; semicrystalline material in 88 % yield (0.71 g). Anal. $C_{11}H_{14}OS_2$: C, H. ^{1}H NMR: δ 2.30 (Me), 3.40 (OMe), 3.50 (2 CH_2-4,5) 7.0–7.3 and 7.5–7.7 (Ph). ^{13}C NMR: 21.0 (Me), 40.9 (2 C-4,5), 52.4 (OMe), 111.2 (C-2). MS: 226 (13, M). 195 (93), 166 (22), 135 (100).

2-Methoxy-2-phenyl-1,3-dithiane 16b. Methanol (20 ml), followed by sodium bicarbonate (2.57 g, 30.0 mmol), was added to a stirred solution of 2-phenyl-1,3-dithian-2-ylium tetrafluoroborate[1] (2.82 g, 10.0 mmol) in acetonitrile (30 ml), at 0 °C, and the stirring continued for 10 min at this temperature before the mixture was poured into water (100 ml). The aqueous mixture was extracted with ether (3×30 ml), the dried ($MgSO_4$) solution evaporated and the residue distilled; yield 1.67 g (74 %), b.p. 118 °C/0.015 mmHg. The oil solidified on cooling, m.p. 68–70 °C. Anal. $C_{11}H_{14}OS_2$: C, H. ^{1}H NMR: δ 2.0–2.3 (CH_2-5), 2.6–3.5 (2 CH_2-4,6), 3.30 (OMe), 7.2–7.7)Ph). ^{13}C NMR: δ 24.4 (C-5), 27.9 (2 C-4,6), 52.8 (OMe), 91.9 (C-2), 126–140 (Ph). MS: 226 (27, M), 152 (100), 121 (59), 105 (89).

2-Ethoxy-2-phenyl-1,3-dithiane 17b. This compound was prepared as above in 69 % yield using ethanol instead of methanol; yellow oil b.p. 138–139 °C/0.05 mmHg. ^{1}H NMR: δ 1.30 and 2.65 (OEt), 1.9–2.3 (CH_2-5), 3.1–3.6 (2 CH_2-4,6), 7.1–7.7 (Ph). MS: 240 (100, M), 211 (10), 195 (90), 166 (80). High resolution MS: M 240.065. Calc. for $C_{12}H_{16}OS_2$: 240.064.

*2-(4-*N,N-*Dimethylanilino)-2-phenyl-1,3-dithiane* 18b. 2-Phenyl-1,3-dithian-2-ylium tetrafluoroborate[1] (1.27 g, 4.5 mmol) was added to a stirred solution of *N,N*-dimethylaniline (0.61 g, 5.0 mmol) and pyridine (0.40 g, 5.0 mmol) in acetic acid (40 ml) at 20 °C. The mixture was heated at 80 °C for 2 h. The product was precipitated when the reaction mixture was poured into water (70 ml); yield 0.90 g (64 %), m.p. 110 °C (2-PrOH). Anal. $C_{18}H_{21}NS_2$: C, H. ^{1}H NMR: δ 1.7–2.2 (CH_2-5), 2.6–3.0 (2 CH_2-4,6), 2.9 (NMe_2), 6.65 and 7.35

(4H; aniline, dd, *J* 8 Hz), 7.1–7.8 (Ph). ^{13}C NMR: δ 24.7 (C-5), 29.6 (2 C-4,6), 40.4 (NMe_2), 62.7 (C-2), 112.1–149.7 (Ph). MS: 315 (16, M), 241 (100), 210 (20), 209 (63), 208 (66).

2-(1-Imidazolo)-2-phenyl-1,3-dithiane 19b. A solution of 2-phenyl-1,3-dithian-2-ylium tetrafluoroborate[1] (1.41 g, 5.0 mmol) in acetonitrile (20 ml) was added dropwise at room temperature to a stirred solution of imidazole (1.36 g, 10.0 mmol) in acetonitrile (20 ml). The mixture was stirred for another 10 min and the reaction stopped by the addition of water (80 ml). The precipitate was collected and recrystallized from acetonitrile – water; yield 1.22 g (92 %), m.p. 150–152 °C. Anal. $C_{13}H_{14}N_2S_2$: C, H. ^{1}H NMR: δ 1.8–2.2 (CH_2-5), 2.6–3.0 (2 CH_2-4,6), 6.8–7.3 (Ph, 1 H-imid.), 7.32 and 8.18 (2 H-imid.). ^{13}C NMR: δ 23.0 (C-5), 29.1 (2 C-4,6), 72.9 (C-2), 120.8–141.8 (Ph, 3 C-imid.). MS 262 (0.3, M), 195 (100), 121 (78). MSCI: 263 (10, M+H).

2-(1-Imidazolo)-2-(4-tolyl)-1,3-dithiane 20b was obtained from *13b* as above in 87 % yield, m.p. 137–139 °C (MeOH). Anal. $C_{14}H_{16}N_2S_2$: C, H. ^{1}H NMR: δ 1.8–2.1 (CH_2-5), 2.6–3.0 (2 CH_2-4,6), 6.77 and 7.00 (4 H-Tol, dd, *J* 8 Hz), 7.10, 7.42 and 8.10 (3 H-imid.). ^{13}C NMR: δ 21.0 (Me), 23.0 (C-5), 29.2 (2 C-4,6), 72.8 (C-2), 120.3–139.4 (Tol, 3 C-imid.). MS 276 (0.1, M), 109 (100), 135 (67). MSCI-MeH: 277 (2, M+H).

2,2'-Di(4-tolyl)-2,2-bis-(1,3-dithiolane) 21a. Zinc dust (0.39 g, 0.005 g atom) was added to a solution of 2-(4-tolyl)-1,3-dithiolan-2-ylium tetrafluoroborate[1] (1.41 g, 5.0 mmol) in acetonitrile (10 ml) and the mixture stirred for 10 min. The mixture was then poured into water and the resultant mixture extracted with chloroform (3×50 ml). The dried ($MgSO_4$) was evaporated and the residual material recrystallized from acetone: yield 0.40 g (41 %), m.p. 182–184 °C. Anal. $C_{20}H_{22}S_4$: C, H. ^{1}H NMR: δ 2.30 (Me), 3.30 (2 CH_2-4,5), 6.7–7.5 (Ph). ^{13}C NMR: δ 22.0 (Me), 40.7 (2 C-4,5), 87.3 (C-2), 126.8–140.2 (Tol.). MS: 195 (20, M), 119 (100). MSCI: 391 (3, M+H).

2,2'-Diphenyl-2,2'-bis-(1,3-dithiane) 22b.[17] This compound was prepared as above in 82 % yield from *12b* and zinc dust; m.p. 203–205 °C. (Lit.[17a] 204 °C). ^{13}C NMR: δ 24.6 (C-5), 28.9 (2 C-4,6), 70.8 (C-2), 127.1–135.4 (Ph). MS: 390 (91, M), 195 (57), 185 (57), 121 (100).

Reaction between cycloheptatriene and 2-(4-tolyl)-1,3-dithiolan-2-ylium tetrafluoroborate. Cycloheptatriene (1.10 g, 12 mmol) was added to a solution of 2-(4-tolyl)-1,3-dithiolan-2-ylium tetrafluoroborate[1] (2.82 g, 10.0 mmol) in acetonitrile (30 ml) and the resultant solution heated under reflux for 15 min. Tropylium tetrafluoroborate was precipitated on the addition of ether to the cold reaction mixture; yield 1.39 g (78 %). The filtrate and the ether washings were combined, shaken with water, the dried ($MgSO_4$) solution evaporated and the residual material recrystallized from methanol; yield 1.16 g (59 %) of 2-(4-tolyl)-1,3-dithiolane[18] *23a.*

Reaction between cycloheptatriene and 2-phenyl-1,3-dithian-2-ylium tetrafluoborate. When this reaction was carried out as above, 82 % of tropylium tetrafluoroborate and 48 % of 2-phenyl-1,3-dithiane[19] *24b* were isolated; *24b,* m.p. 67–70 °C (MeOH).

References

1. Klaveness, J. and Undheim, K. *Acta Chem. Scand. B37* (1983) 687.
2. Gröbel, B.-T. and Seebach, D. *Synthesis* (1977) 357.
3. Wilson, S. R., Georgiadis, G. M., Khatri, H. N. and Bartmess, J. E. *J. Am. Chem. Soc. 102* (1980) 3577.
4. Seebach, D. and Corey, E. J. *J. Org. Chem. 40* (1975) 231.
5. Yamashita, M. and Suemitsu, R. *Chem. Commun.* (1977) 691.
6. Klaveness, J. and Undheim, K. *Acta Chem. Scand. B37* (1983) 258.
7. Murphy, W. S. and Wattanasin, S. *J. Chem. Soc. Perkin Trans I* (1980) 2678.
8. (a) Ho, T.-L. *Hard and Soft Acids and Bases Principle in Organic Chemistry,* Academic Press, New York, 1977. p. 35; (b) Ho, T.-L. *J. Chem. Educ. 55* (1978) 355.
9. Okuyama, T., Fujiwara, W. and Fueno, T. *J. Am. Chem. Soc. 106* (1984) 657.
10. Okuyama, T. *Tetrahedon Lett. 23* (1982) 2665.
11. Kruse, C. G., Wijsman, A. and van der Gen, A. *J. Org. Chem. 44* (1979) 1847.
12. Arai, K. and Oki, M. *Bull. Chem. Soc. Jpn. 49* (1976) 553.

13. Corey, E. J. and Walinsky, S. W. *J. Am. Chem. Soc. 94* (1972) 8932.
14. Andersen, N. H., Yamamoto, Y. and Denniston, A. D. *Tetrahedron Lett.* (1975) 4547.
15. Seebach, D., Kolb, M. and Gröbel, B.-T. *Chem. Ber. 106* (1973) 2277.
16. (a) Jo, S., Shigeo, T., Oida, T. and Masaya, O. *Bull. Chem. Soc. Jpn. 54* (1981): 1434; (b) Dedieu, M., Pascal, Y.-L., Diazabo, P. and Basselier, J.-J. *Org. Mass Spectrom. 12* (1977) 159.
17. (a) Baarschers, W. H. and Loh, T. L. *Tetrahedron Lett* (1971) 3483; (b) Russell, G. A., Jawdosiuk, M. and Makosza, M. *J. Am. Chem. Soc. 101* (1979) 2355.
18. Indictor, N., Horodniak, J. W., Jaffe, H. and Miller, D. *J. Chem. Eng. Data, 14* (1969) 76.
19. Seebach, D., Erickson, B. W. and Singh, G. *J. Org. Chem. 31* (1966) 4303.

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