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ORGANOTIN DERIVATIVES IN THE UMPOLUNG OF 1,3-DITHIAN-2-YLIDES TO 1,3-DITHIAN-2-YLIUM SALTS

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Summary

Lithiated 1,3-dithianes react with trialkyltin or triphenyltin chlorides to form the corresponding 1,3-dithian-2-yltin compounds. The dithiane C(2)–Sn bond in the trialkyltin or triphenyltin compounds is selectively cleaved by iodine, with formation of 1,3-dithian-2-ylium triiodides which can be transformed into the corresponding tetrafluoroborate salts. The ^{1}H and ^{13}C NMR data are consistent with the salt like structures. The ambident nature of β-styryl derivatives is discussed. Preferential cleavage of the C(2)–Sn bond in the stannyl derivatives is evident in the mass spectra.

Introduction

The carbon–tin bond is readily cleaved by electrophiles. A sequence for the ease of cleavage of the organotin bond by halogens has been established with aryl–tin bonds the most reactive and alkyl–tin bonds the least reactive [1]. The cleavage is usually dominated by electrophilic attack at the carbon end of the bond, although the cleavage may be facilitated by nucleophilic attack at the tin [1]. An adjacent sulfur heteroatom would therefore be expected to facilitate the cleavage of the organotin bond, and we show below, that selective cleavage of the C(2)–Sn bond in trialkyl- and triphenyl-1,3-dithian-2-yltin compounds, is the case.

The 1,3-dithiane ring system is of interest to us because of its synthetic potential. 1,3-Dithian-2-ylides are widely used synthons [2]. The 1,3-dithian-2-ylium dithiocarbocation and its 2-substituted derivatives are becoming important cationic formyl or, more generally, acyl equivalent synthons [3]. We have recently described simple and efficient routes for the preparation of such synthons [4]. We describe below a

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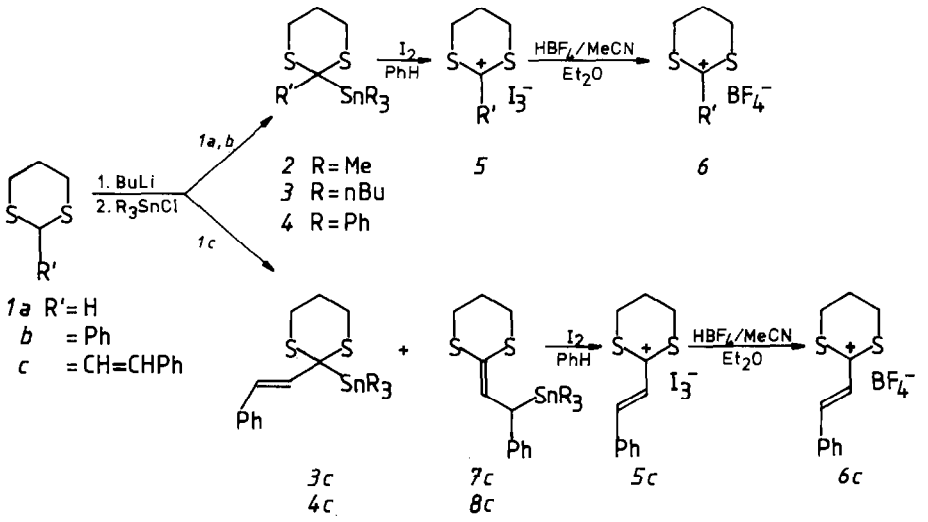
method involving organotin intermediates in the conversion of 1,3-dithian-2-ylides to their corresponding 1,3-dithian-2-ylium salts.



Results and discussion

The 1,3-dithian-2-yltin compounds **2–4** were prepared by treating the ylides of lithiated 1,3-dithianes with trialkyltin or triphenyltin chlorides, initially at −78°C. The synthetic procedures were the same as those used in previous preparations of such compounds [5,6]. In the case of the β-styryl derivative **1c**, the anion has ambident character, and the electrophilic attachment of the tin reagent can occur either at C(2) of the 1,3-dithiane ring or at the β-carbon of the unsaturated side-chain. With tri-n-butyltin chloride the ratio between the C(2) and the C(β) stannylated products **3c** and **7c** was 10/1 (^{1}H NMR) whereas with triphenyltin chloride the corresponding ratio, of **4c** to **8c** was smaller 5/1. In both cases it is the sterically more hindered product which is favoured. In alkylations of this ambident anion it has previously been found that with soft electrophiles and soft leaving groups the major product arises from the attack of the softer nucleophilic center at the exocyclic β-carbon; with hard electrophiles bond formation is exclusively by attack at the harder C(2) nucleophilic center of the ring [7]. The triorganotin chlorides are rather hard electrophiles, and so preferential reaction at C(2) is observed. Furthermore, the tri-n-butyltin is a harder electrophile than the triphenyltin reagent, in agreement with the observed variations in the product ratios. The products from attack at C(2) have *trans* configurations (**3c**, **4c**), which again parallels the results in alkylation of lithiated **1c** [7].

1,3-Dithian-2-yltin derivatives can be lithiated in the normal way for 1,3-dithianes, but if the dithiane carries an additional 2-substituent a rapid metal–metal exchange occurs with selective cleavage of the C(2)–Sn bond and formation of the lithiated 1,3-dithiane [5]. Under electrophilic conditions acid chlorides were reported to react with the 1,3-dithian-2-yltin compound (**2a**) mainly to yield products from opening of the dithiane ring, but some of the corresponding 1,3-dithian-2-yl ketone was also formed [8]. We have treated organic solutions of the organotin compounds

2–4 with iodine, and observed selective cleavage of the dithian-2-yl–tin bond. When benzene solutions of the tin derivatives are mixed with a benzene solution of iodine there is immediate precipiation of the iodinated product. For maximum yield two molar equivalents of iodine are required, yields then being 80–90%. Spectroscopic and elemental analyses show that the products are the 1,3-dithian-2-ylium triiodides **5**.

The β-styryl isomer pairs **3c/7c** and **4c/8c** gave the same iodinated product. Spectral data for this were difficult to obtain because of its low solubility in organic solvents, but the structure of the product was verified by its conversion to the tetrafluoroborate salt (see below).

The formation of the triiodide salts **5** can be compared with the formation of 2-substituted-1,3-dithian-2-ylium hydrogen dichlorides when the corresponding 1,3-dithiane is treated with sulfuryl chloride [9].

The triiodide salts **5** can be converted into the tetrafluoroborates **6** by treating a solution of **5** in acetonitrile with ethereal tetrafluoroboric acid and precipitating the borates by addition of ether. The NMR spectra of the triiodides and the tetrafluoroborates are the same, confirming the salt nature of the triiodides. Thus, the chemical shifts for H(2) in **5a** and **6a** are 11.1 ppm (CD_3CN), compared with the chemical shifts for H(2) in 2-chloro-1,3-dithiane of 10.65, 5.76 and 6.2 ppm in liquid sulfur dioxide, benzene, and chloroform respectively, and these figures have been interpreted to mean that 2-chloro-1,3-dithiane is completely dissociated in the first solvent, and covalent in the less polar solvents [10,11]. The ^{13}C NMR shifts for C(2) in **5a** and **6a** are also almost the same, viz. 208.7 and 209.5 ppm (CD_3CN) [4b]; similarly the ^{13}C chemical shifts for **5b** and **6b** are at 222.4 and 223.2 ppm (CD_3CN), respectively [4a].

Low resolution NMR data for the stannyl derivatives **2–4** are presented in the Experimental section. High resolution spectra and conformational analysis of the trimethyltin derivative **2a** and its homologues are available [12]. For the styryl derivative **3c** and **4c** 300 MHz high resolution NMR was used to resolve the very close chemical signals for the pairs of olefinic protons at 6.63 and 6.65 ppm, and 6.67 and 6.69 ppm, respectively.

The mass spectra of **2–4** at 70 eV, and by chemical ionization (isobutane), are characterized by a weak molecular ion, and by a primary fragmentation due to cleavage of the carbon–tin bonds, in accord with previous findings for the fragmentation of tetraalkyltins by electron impact [13]. The base peak in each spectrum is due to cleavage of the 1,3-dithiane C(2)–Sn bond with retention of the positive charge on the dithiane species. This may indicate preferential cleavage of the C(2)–Sn bond by ionization, which would parallel the selectivity observed in the halogenation of **2–4**.

Experimental

The ^1H NMR spectra were recorded at 60 MHz unless otherwise specified. The mass spectra under electron impact conditions were recorded at 70 eV ionizing voltage. Isobutane was used for the chemical ionization (CI) mass spectra.

General procedure for the preparation of the (1,3-dithian-2-yl)trialkyl-(or triaryl)tin compounds 2–4 and 7, 8

A solution of n-butyllithium in hexane (1.6 *M*, 55 mmol) was added dropwise

with stirring under N_2 to a solution of 1,3-dithiane (50 mmol) in dry THF (125 ml) at −78°C. The solution was stirred for 3 h at this temperature, allowed to warm to 0°C during 30 min, then once again cooled to −78°C, and the trimethyltin, tri-n-butyltin, or the triphenyltin chloride (50 mmol) was added gradually. The solution was stirred at −78°C for another 3 h and then at ambient temperature for 12 h. The reaction was quenched by addition of crushed solid carbon dioxide (ca. 10 g) followed by gradual addition of water (200 ml). Most of the THF was then removed by distillation and the remaining aqueous supension extracted with dichloromethane (3 × 200 ml). The dichloromethane solution was shaken with 5% aqueous potassium carbonate (2 × 50 ml) then washed, dried ($MgSO_4$), and evaporated. The residue was purified by distillation, recrystallization, or chromatography.

(1,3-Dithian-2-yl)trimethyltin (**2a**) *[5]*

MS/CI: 285/283/281 (14, 11, 6, $[M + H]^+$), 269/267/265 (18/12/7, $[M - Me]^+$), 165/163/161 (7/5/3, $[M - C_4H_7S_2]^+$), 119 (100, $C_4H_7S_2^+$).

(1,3-Dithian-2-yl)tri-n-butyltin (**3a**) *[5]*

Compound **3a** had b.p. 132°C/0.065 mmHg. ^{13}C NMR ($CDCl_3$): δ 9.4 (CH_2Sn), 13.7 (CH_3), 26.8/27.4/29.0/37.4 (CH_2), 27.0 (CH, C(2')), MS: 410/408/406 (1.1/1.1/0.4, M^+), 291/289/287 (29/21/12, Bu_3Sn^+), 235/233/231 (38/30/17, Bu_2SnH^+), 179/177/175 (56/48/32 $BuSnH_2^+$), 119 (100, $C_4H_7S_2^+$). MS/CI: 411/409/407 (27/25/14, $[M + H]^+$), 119 (100, $C_4H_7S_2^+$).

(2-Phenyl-1,3-dithian-2-yl)tri-n-butyltin (**3b**)

Compound **3b** was obtained from 2-phenyl-1,3-dithiane [14] and tri-n-butyltin chloride in 87% yield, b.p. 168–170°C/0.004 mmHg. (Found: C, 54.31; H, 7.97. $C_{22}H_{38}S_2Sn$ calcd.: C, 54.44; H, 7.89%). ^1H NMR ($CDCl_3$): δ 0.7–3.0 (CH_2 and CH_3), 7.0–7.5 (Ph). ^{13}C NMR ($CDCl_3$): δ 9.7 (CH_2Sn), 13.2 (CH_3), 25.3/26.9/28.3, 29.0 (CH_2), 43.2 (CH, C(2')), 124.0–144.3 (Ph). MS: 486/484/482 (1.1/0.9/0.3, M^+), 291/289/287 (12/9/5, Bu_3Sn^+), 235/233/231 (16/12/7, Bu_2SnH^+), 197 (12), 196 (29), 195 (100, $[M - Bu_3Sn]^+$), 179/177/175 (21/18/11, $BuSnH_2^+$). MS/CI: 487/485/483 (50/41/24, $[M + H]^+$), 429/427/425 (39/29/15, $[M - Bu]^+$), 291/289/287 (23, 17/11), 195 (100, $[M - SnBu_3]^+$].

(2-trans-β-Styryl-1,3-dithian-2-yl)tri-n-butyltin (**3c**)

Compound **3c** was obtained from 2-*trans*-β-styryl-1,3-dithiane [7] and tri-n-butyltin chloride. The crude oily product, was a mixture of **3c** and its isomer [2-(1,3-dithian-2-ylidine)-1-phenylethyl]tri-n-butyltin (**8c**) in a 10/1 ratio (^1H NMR); the yield of crude product was 82%. Chromatographic separations of the isomers was difficult, but **3c** was isolated from the mixture by chromatography on silica gel using 2/1 light petroleum/chloroform as eluant; yield 28% of a yellow oil. (Found: C, 55.76; H, 7.81. $C_{24}H_{40}S_2Sn$ calcd.: C, 56.36; H, 7.88%). ^1H NMR (300 MHz; $CDCl_3$): δ 0.89 (CH_3), 1.1/1.3/1.55 (CH_2 in Bu), 1.95–2.35 (CH_2, H(4',6'), 3.1 (CH_2, H(5')), 6.63 and 6.65 (HC=CH, AB J_{trans}, 15.3 Hz), 7.2–7.5 (Ph). ^{13}C NMR ($CDCl_3$): δ 10.3 (CH_2Sn), 13.6 (CH_3), 25.6–29.0 (CH_2), 41.8 (CH, C(2')), 126.0–137.8 (Ph, C=C), MS/CI: 513/511/509 (12/10/6, $[M + H]^+$), 221 (100, $[M - SnBu_3]^+$). ^1H NMR (300 MHz; $CDCl_3$) of **3c**/**4c** mixture showed characteristic signals for **4c** at δ 4.15 (C*H*–C*H*=, d, *J* 10 Hz) and 6.70 (CH–C*H*=, d, *J* 10 Hz).

(1,3-Dithian-2-yl)triphenyltin (**4a**) *[6]*

Compound **4a** was obtained from 1,3-dithiane and triphenyltin in 52% yield, m.p. 148°C (chloroform/light petroleum). ^{1}H NMR ($CDCl_3$): δ 1.9–2.4 (CH_2, H(5′)), 2.5–3.2 (CH_2, H(4′,6′)), 4.63 (CH, H(2′)), 7.1–7.8 (Ph). ^{13}C NMR ($CDCl_3$): 26.3 (C(5′)), 29.8 (C(2′)), 32.5 (C(4′,6′)), 126.8–138.6 (Ph). MS: 351/349/347 (100/70/41, Ph_3Sn^+), 197/195/193 (26/20/11, $SnPh^+$), 119 (95, $C_4H_7S_2^+$). MS/CI: 471/469/467 (1.4/1.1/0.6 $[M + H]^+$), 119 (100, $C_4H_7S_2^+$).

(2-Phenyl-1,3-dithian-2-yl)triphenyltin (**4b**) *[6]*

Compound **4b** was prepared from 2-phenyl-1,3-dithiane [14] and triphenyltin chloride in 77% yield. ^{1}H NMR ($CDCl_3$): δ 1.7–2.5 (CH_2, H(4′,6′), 2.6–3.1 (CH_2, H(5′)), 7.0–8.0 (Ph). ^{13}C NMR ($CDCl_3$): δ 25.5 (C(5′)), 25.8 (C(4′,6′)), 47.0 (C(2′)), 125.0–137.0 (Ph). MS: 546/544/542 (0.8/0.6/0.2, M^+), 351/349/347 (11/9/4, Ph_3Sn^+), 197 (15), 196 (18), 195 (100, $[M - Ph_3Sn]^+$).

(2-trans-β-Styryl-1,3-dithian-2-yl)triphenyltin (**4c**) *and [2-(1,3-dithian-2-ylidine)-1-phenylethyl]triphenyltin* (**8c**)

A mixture of these compounds in 5/1 ratio (^{1}H NMR) was obtained from 2-*trans*-β-styryl-1,3-dithiane [7] and triphenyltin chloride, after chromatography on silica gel with 2/1 light petroleum/chloroform as eluant; yield 32%. Attempts to separate the isomers failed, they crystallized together from light petroleum/benzene and the mixture melted at ca. 142°C. Anal. Found: C, 63.93; H, 5.14. $C_{30}H_{28}S_2Sn$ calcd.: C, 63.08; H, 4.98%.

Physical data for **4c**: ^{1}H NMR (300 MHz; $CDCl_3$): δ 6.67 and 6.69 (CH=CH, AB, J_{trans} 15.6 Hz). Physical data for **8c**: ^{1}H NMR (300 MHz, $CDCl_3$): 4.66 (H(1), d, *J* 10.8 Hz), 6.76 (H(2), d, *J* 10.8 Hz).

General procedure for the cleavage of the carbon–tin bond

A solution of iodine (10 mmol) in dry benzene (15 ml) was added dropwise with stirring to a solution af the tin derivative **3** or **4**, or the mixtures **3c**/**7c** and **4c**/**8c** (5 mmol) in dry benzene (30 ml) at 10°C. A coloured solid separated immediately. The mixture was stirred at ambient temperature for 5 min and the product was filtered off and washed with dry benzene in a dry atmosphere.

1,3-Dithian-2-ylium triiodide (**5a**)

Compound **5a** was obtained from (1,3-dithian-2-yl)trimethyltin (**2a**) in 84% yield; from (1,3-dithiane-2-yl)tri-n-butyltin (**3a**) in 80% yield; and from (1,3-dithian-2-yl)triphenyltin (**4a**) in 83% yield. It was very dark violet; m.p. 77°C. (Found: C, 9.66; H, 1.39, I, 75.71. $C_4H_7S_2I_3$ calcd.: C, 9.61; H, 1.41; I, 76.15%). ^{1}H NMR (CD_3CN): δ 2.3–2.7 (CH_2, H(5′)), 3.4–3.8 (CH_2, H(4′,6′)), 11.1 (CH, br.s., H(2′)). ^{13}C NMR (CD_3CN): δ 17.6 (C(5′)), 32.0 (C(4′,6′)), 208.7 (C(2′)). MS/CI: 247 (57, $[MI + H]^+$), 121 (97), 120 (49), 119 (100, M^+), 107 (30).

2-Phenyl-1,3-dithian-2-ylium triiodide (**5b**)

Compound **5b** was obtained from (2-phenyl-1,3-dithian-2-yl)tri-n-butyltin (**3b**) in 89% yield, and from (2-phenyl-1,3-dithian-2-yl)triphenyltin (**4b**) in 84% yield. The product from **3b** was brown, m.p. 116°C, whereas that from **4b** was dark green, m.p. 85°C. Recrystallization of each from acetonitrile/diethyl ether gave brown products

with the same crystalline form, m.p. 118°C. (Found: C, 20.92; H, 1.74; I, 68.95. $C_{10}H_{11}I_3S_2$ calcd.: C, 20.85; H, 1.92; I, 66.09%). ^{1}H NMR (CD_3CN): δ 2.4–2.7 (CH_2, H(4',6')), 3.7–3.8 (CH_2, H(5')), 7.6–8.0 (Ph). ^{13}C NMR (CD_3CN): δ 18.3 (C(5')), 34.6 (C(4',6')), 222.4 (C(2')). MS/CI: 323 (31, $[MI + H]^+$), 197 (26), 196 (18), 195 (100, M^+).

2-trans-β-Styryl-1,3-dithian-2-ylium triiodide (**5c**)

Compound **5c** was obtained from a mixture of (2-*trans*-β-styryl-1,3-dithian-2-yl)tri-n-butyltin (**3c**) and its isomer **7c** in 29% yield, and from a mixture of (2-*trans*-β-styryl-1,3-dithian-2-yl)triphenyltin (**4c**) and its isomer **8c** in 83% yield. It was a dark purple solid m.p. 147°C. (Found: C, 24.44, H, 2.18; I, 63.30. $C_{12}H_{13}I_3S_2$ calcd.: C, 23.94; H, 2.18; I, 63.23%). Low solubility in organic solvents stopped collection of NMR data.

1,3-Dithian-2-ylium tetrafluoroborate (**6a**) *[3a]*

Ethereal tetrafluoroboric acid (54%; 2.5 ml) was added dropwise with stirring to a solution of 1,3-dithian-2-ylium triiodide (0.94 g, 2.0 mmol) in dry acetonitrile (20 ml) at 35–40°C. The heating bath was removed and the mixture stirred at ambient temperature for 5 min. then the mixture was added to dry ether (100 ml) at 0°C. The pale yellow solid which separated was filtered off under a dry atmosphere; yield 0.22 g (54%) m.p. 180°C. The physical data agreed with those in the literature.

2-Phenyl-1,3-dithian-2-ylium tetrafluoroborate (**6b**) *[4a]*

Compound **6b** was obtained as above from 2-phenyl-1,3-dithian-2-ylium triiodide in 85% yield as yellow flakes, m.p. 192°C. The physical data agree with those previously reported.

2-trans-β-Styryl-1,3-dithian-2-ylium tetrafluoroborate (**6c**) *[4a]*

Compound **6c** was obtained as above from 2-*trans*-β-styryl-1,3-dithian-2-ylium triiodide as yellow crystals in 75% yield, m.p. 132°C. The physical data agree with those previously reported.

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