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Synthesis of acylsilanes via oxidative hydrolysis of 2-silyl-1,3-dithianes mediated by *N*-bromosuccinimide

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Abstract

The oxidative method for the hydrolysis of 1,3-dithianes was applied to 2-silyl-1,3-dithianes using *N*-bromosuccinimide providing acylsilanes with good yields under a short reaction period. The oxidation of aroylsilanes to carboxylic acid was prevented by the addition of bases and the lowering of the reaction temperature.

Keywords: Aroylsilanes; Oxidation; 1,3-Dithianes; *N*-Bromosuccinimide

1. Introduction

Acylsilanes are compounds that exhibit unique chemical properties and are frequently applied in several synthetic methodologies such as Reformatsky reactions [1], intermolecular cyclization [2], stereocontrol in nucleophilic addition [3], photo-oxidations [4] and many other general reactions [5]. A variety of methods for the synthesis of acylsilanes are found in the literature and the dithiane route [6] (Scheme 1) appears to be the principal method. In contrast to other synthetic methods, the 1,3-dithiane route enables one to synthesize acylsilanes with a great variety of silyl and R groups such as alkyl, aryl and α,β-unsaturated acylsilanes.

2. Results and discussion

The aldehyde conversion to the corresponding 1,3-dithiane **2** and subsequent silylation to **4** through the masked acyl anion **3**, generally occurs in excellent yields (Table 1). However, the regeneration of the carbonyl group (**4**→**5**) is the crucial step in this method because the C–Si bond in acylsilanes is relatively weak and can be cleaved under the hydrolysis conditions. There are many efficient methods that can be applied for removal of a dithiane moiety [7], but for 2-silyl-1,3-dithianes the mercuric chloride hydrolysis appears to be the most useful. We have extensively prepared acylsilanes through the dithiane route in our work [8] and found problems with the unmasking of the carbonyl. We have noted that the hydrolysis using mercuric chloride needs a long period to complete the reaction and, in some cases, after 12 h at room temperature there was also starting material and the corresponding aldehyde (resulting from the Si–CO cleavage) as a by-product. Moreover, mercuric chloride is poisonous and experiments involving this compound should be handled with extreme caution.

The aim of this work is to search for other methodologies to the carbonyl regeneration on 2-silyl-1,3-dithianes. We found the oxidative hydrolysis with *N*-bromosuccinimide, which is presented in this paper, as a good alternative to obtain acylsilanes in a shorter reaction time. To our knowledge, the excellent method presented by Corey and Erickson [9] for general dithianes was not applicable to 2-silyl-dithianes, possibly due to the oxidative conditions. The oxidation potentials of acylsilanes (1.45 V) are lower than ketones (>2.5 V) [10], therefore acylsilanes are more likely to suffer oxidation to a carboxylic acid mediated by peroxide [11], ozone [12], Fe^{+3}, or nitric acid [13a]. The mechanism proposed for the oxidative hydrolysis with *N*-bromosuccinimide probably occurs through an attack at sulfur by the active bromine (generated in situ)

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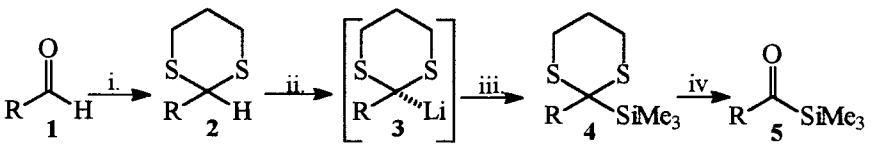
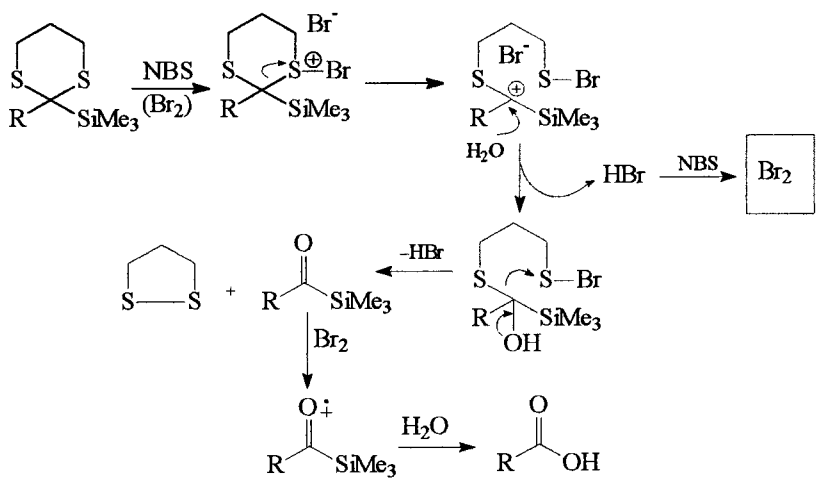
to afford halo-sulfides [14] and the subsequent formation of disulfide derivatives [7]. Thus, when the product is an acylsilane (properly aroylsilanes) a subsequent reaction of oxidation to the corresponding carboxylic acid may take place (Scheme 2). We observed in our laboratory, that the bromine (in excess) promotes this undesirable acylsilane oxidation [13b].

Although alkanoylsilanes could be obtained without problem due to their resistance to oxidation (entries 1 and 2, Table 2), some 2-aryl-2-silyl-dithianes lead to a great amount of the corresponding carboxylic acid. In the latter case, when electron-withdrawing groups are attached to the aromatic ring, the carboxylic acid was obtained rather than acylsilanes (entries 10 and 12). In some cases, we have partially circumvented this problem by the addition of base to stop the formation of excess of bromine through HBr neutralisation. The lowering of the reaction temperature either inhibits the oxidation of the aroylsilanes allowing for better yields of compounds **5g–h** at −23°C using acetonitrile in-



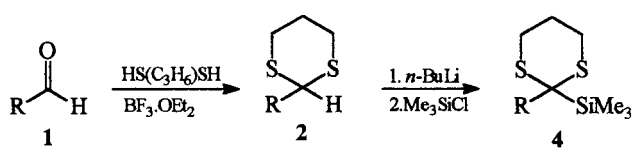
i. 1,3-propanedithiol, $BF_3.OEt_2$, CH_2Cl_2; ii. *n*-BuLi, THF; iii. Me_3SiCl; iv. hydrolysis

Scheme 1.



Scheme 2.

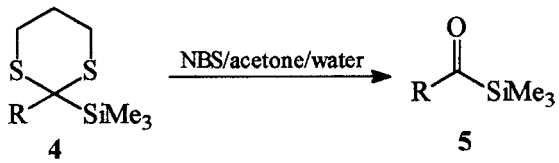
Table 1
Yields obtained in preparation of 1,3-dithianes and 2-silyl-1,3-dithianes



Entry	Aldehyde **1**	1,3-Dithiane (**2**) (%) [a]	2-Silyl-1,3-dithiane (**4**) (%) [a]
1	**1a** ($R = PhCH_2$)	80	69
2	**1b** ($R = Ph_2CH$)	96	76
3	**1c** ($R = Ph$)	94	82
4	**1d** ($R = 2\text{-}MeOC_6H_4$)	93	90
5	**1e** ($R = 3,4\text{-}(MeO)_2C_6H_3$)	90	85
6	**1f** ($R = 3,4\text{-}(OCH_2O)C_6H_3$)	89	82
7	**1g** ($R = 4\text{-}ClC_6H_4$)	95	85
8	**1h** ($R = 3\text{-}CF_3C_6H_4$)	88	92

[a] Purified by crystallization from hexane, except for **4h** (soluble).

Table 2
Hydrolysis of 2-silyl-1,3-dithianes



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Entry	2-Silyl-1,3-dithianes (**4**)	Acylsilanes **5**			
		NBS			$HgCl_2$
		Base	Reaction time (min)	Yield (%) [c]	Yield (%) [e]
1	**4a** (R = $PhCH_2$)	–	40	88 [a]	
2	**4b** (R = Ph_2CH)	–	40	80 [a]	
3	**4c** (R = Ph)	–	40	74 [b]	70
4	**4d** (R = 2–$OMeC_6H_4$)	–	40	77 [a]	65
5		Et_3N	40	90 [a]	
6	**4e** (R = 3,4-$(OMe)_2C_6H_3$	–	30	90 [a]	75
7		Et_3N	30	95 [a]	
8		$Ba(OH)_2$	30	96 [a]	
9	**4f** (R = 3,4-$(OCH_2O)C_6H_3$)	Imidazole	40	70 [a]	76
10	**4g** (R = 4-ClC_6H_4)	–	30	27 [b]	25
11		$Ba(OH)_2$	30	40 [b,d]	
12	**4h** (R = 3-$CF_3C_6H_4$)	–	30	7 [a], 20 [b]	30
13		$Ba(OH)_2$	30	44 [b,d]	

[a] Reaction temperature at 0°C.
[b] Reaction temperature at −23°C.
[c] Total dithiane conversion.
[d] Acetonitrile was used as solvent.
[e] 8–12 h at r.t.

stead of acetone as the solvent. Table 2 shows the hydrolysis yields using mercuric chloride and NBS. It is evident that besides the shorter reaction time, the hydrolysis of 2-aryl-2-silyl-dithianes using NBS increases, in some cases, the reaction yields in comparison with the hydrolysis using mercuric chloride.

3. Experimental

Melting points were measured on a Microquimica MQAFP-301 apparatus and are uncorrected. IR spectra were recorded on a Perkin–Elmer 1600 FT or Bomen MB series spectrophotometer. NMR spectra were recorded on a Bruker AC 300P, Varian Gemini 300 or Inova-500 spectrometer, with $CDCl_3$ as solvent and $CHCl_3$ as internal standard. Elemental analyses were measured on a Perkin–Elmer 2400 CHN. Chromatography columns were performed with Silica gel-60. Mass spectra were obtained on a Shimadzu CG/MS-QP5000. Commercially available chemicals and solvents were used without further purification. The 1,3-dithianes **2c–g**, 2-silyl-1,3-dithianes **4c–g** and acylsilanes **5c–g** were described previously (Ref. [8] and references cited therein). Also, the dithiane **2a** and the acylsilane **5a** were described in Refs. [5c] and [9], respectively.

*3.1. General procedure for the preparation of 1,3-dithianes **2** [6]*

$BF_3{\cdot}OEt_2$ (80.0 mmol) was added slowly to a stirred solution of aldehyde (20.0 mmol), 1,3-propanedithiol (20.5 mmol) in CH_2Cl_2 (50.0 ml) and molecular sieves (4 Å) (12–15 g) at 0°C. The solution was stirred for 2 h at 0°C and warmed to room temperature and was stirred for another 15 h. After that, aqueous sodium bicarbonate was added, the product was extracted with $CHCl_3$ (3×40 ml), the organic phase dried with $MgSO_4$ and the solvent was evaporated under reduced pressure. The product was purified by crystallization in hexane.

*3.2. General procedure for the preparation of 2-trimethylsilyl-1,3-dithianes **4** [6]*

Under Ar atmosphere, *n*-BuLi (21.0 mmol in hexane solution) was added cautiously to a stirred solution of 2-aryl-1,3-dithiane (20.0 mmol) in THF (50 ml) at −23°C. After 1 h, the solution was warmed to 0°C and then trimethylchlorosilane (25.0 mmol) was added. The reaction mixture was stirred for another 1 h at 0°C. After that water was added and then the product was

extracted with $CHCl_3$ (3×40 ml). The organic phase was dried, the solvent evaporated under reduced pressure and the product purified by crystallization in hexane.

3.3. General procedure for hydrolysis of 2-silyldithianes **4**

The 2-silyldithiane **4** was slowly added to a stirred mixture of *N*-bromosuccinimide (4–6 molar equivalents) in an 80% aqueous acetone or acetonitrile (~ 25 ml) at 0°C or -23°C (see Table 2). During the addition of the dithiane, the pH was maintained nearly to neutral by simultaneous addition of base (4–6 molar equivalents of organic base or 2–3 molar equivalents of barium hydroxide). After the total addition of dithiane, the stirring of reaction mixture was maintained for an additional 20–30 min at 0°C. The cold bath was removed and sodium sulfide solution (~ 25 ml) was rapidly added and after that the product was extracted with ethyl acetate (3×25 ml). The combined organic layers were washed with water (40 ml), dried with $MgSO_4$ and the solvent evaporated under reduced pressure. The product was purified by filtration in a short column (SiO_2, 9:1 hexane–ethyl acetate).

3.4. 2-(Diphenylmethyl)-1,3-dithiane (**2b**)

Obtained as a crystalline solid, m.p. 114.0–116.5°C, ν_{max} (KBr, cm^{-1}) 1599, 1480, 1440 and 1279. δ_H (300 MHz, $CDCl_3$) 1.70–2.10 (m, 2H), 2.85–2.95 (4H, m), 4.15 (1H, d, *J* 10.2 Hz), 4.82 (1H, d, *J* 10.2 Hz) and 7.18–7.50 (10H, m). δ_c (75 MHz, $CDCl_3$) 25.4, 30.7, 51.1, 56.9, 127.2, 128.3, 128.5 and 140.9. *m*/*z* 286 [$M^{+\bullet}$ 2%], 178 (36), 165 (60), and 119 (100). (Found: C, 70.7; H, 5.8%. $C_{17}H_{18}S_2$: Anal Calc.: C, 71.3; H, 6.3%.)

3.5. 2-(3-Trifluoromethylphenyl)-1,3-dithiane (**2h**)

Obtained as crystalline solid, m.p. 72.0–72.5°C. ν_{max} (KBr, cm^{-1}) 1489, 1425 and 1331. δ_H (500 MHz, $CDCl_3$) 1.90–2.24 (2H, m), 2.94 (2H-eq, ddd, *J* 14.0, 4.7 and 3.4 Hz), 2.82 (2H-ax, ddd, *J* 14.0, 11.3 and 3.0 Hz); 4.60 (s, 1H), 7.48 (1H, dd, *J* 4.7, 4.7 Hz), 7.57 (1H, d, *J* 4.7 Hz), 7.68 (1H, d, *J* 4.7 Hz) and 7,75 (1H, broad s). δ_c (125 MHz, $CDCl_3$) 24.8, 31.9, 31.9, 123.8 (q, *J* -271.5, *C*F_3), 124.8, 125.2, 129.2, 131.1 (q, *J* -32.0 Hz, *C*CF_3), 131.2 and 140.0. *m*/*z* 264 [$M^{+\bullet}$ 20%] 190 (12), 189 (31), 145 (8), 74 (100). (Found: C, 49.6; H, 4.2. $C_{11}H_{11}F_3S_2$: Anal Calc.: C, 50.0; H, 4.2%).

3.6. 2-Benzyl-2-trimethylsilyl-1,3-dithiane (**4a**)

Obtained as a crystalline solid, m.p. 93.0–95.0°C. ν_{max} (KBr, cm^{-1}) 1599, 1495, 1422, 1276 and 847. δ_H (300 MHz, $CDCl_3$) 0.10 (9H, s), 1.70–2.00 (2H, m), 2.38 (2H-eq, ddd, *J* 15.3, 4.1 and 3.3 Hz), 2.71 (2H-ax, ddd, *J* 15.3, 11.1 and 3.3 Hz), 3.45 (s, 2H), 7.30–7.50 (3H, m) and 7.55 (2Har-*ortho*, dd, *J* 1.8 and 7.3 Hz). δ_c (75 MHz, $CDCl_3$) -3.0, 24.0, 24.1, 37.9, 45.0, 127.0, 128.2, 131.3 and 139.0. *m*/*z* 282 [$M^{+\bullet}$, 2%], 209 (20), 191 (84), 91 (38), and 73 (100). (Found C, 59.3; H, 7.3. Anal Calc. $C_{14}H_{22}S_2Si$: C, 59.6; H, 7.8%.)

3.7. 2-(Diphenylmethyl)-2-trimethylsilyl-1,3-dithiane (**4b**)

Obtained as a crystalline solid, m.p. 126.0–128.0°C. ν_{max} (KBr, cm^{-1}) 1490, 1424, 1233 and 836. δ_H (300 MHz, $CDCl_3$) 0.01 (9H, s), 1.50–1.78 (2H, m), 2.05 (2H-ax, ddd, *J* 13.9, 11.1 and 3.3 Hz), 2.22 (2H-eq, ddd, *J* 13.9, 4.5 and 3.6 Hz), 4.43 (1H, s), 7.20–7.38 (3H, m) and 7.94 (2Har-*ortho*, d, *J* 7.4 Hz). δ_c (75 MHz, $CDCl_3$), -1.8, 23.0, 25.4, 39.4, 63.5, 126.9, 128.1, 130.7 and 142.8. *m*/*z* 358 [$M^{+\bullet}$ none found], 167 (100), 165 (44) and 152 (30). (Found C, 66.6; H, 7.9. Anal Calc. $C_{20}H_{26}S_2Si$: C, 67.0; H, 7.3%.)

3.8. 2-(3-Trifluoromethylphenyl)-2-trimethylsilyl-1,3-dithiane (**4h**)

Obtained as a yellow solid, m.p. 59–60°C. ν_{max} (KBr, cm^{-1}) 1478, 1424, 1251 and 1324. δ_H (500 MHz, $CDCl_3$), 0.07 (9H, s), 1.90–2.09 (m, 2H), 2,46 (2H-eq, ddd, *J* 15.0, 4,0 and 2.6 Hz), 2.72 (2H-ax, ddd, *J* 15.0, 12.1 and 2.7), 7.44–7.52 (2H, m), 8.12 (1H, d, *J* 8.3 Hz) and 8.21 (1H, broad s). δ_c (125 MHz, $CDCl_3$), -4.1, 24.9, 25.1, 47.2, 122.1, 124.4 (q, *J* -271.5 Hz, *C*F_3), 126.3, 128.8, 130.8 (q, *J* -32.2 Hz, *C*CF_3), 132.9 and 142.3. *m*/*z* 336 [$M^{+\bullet}$, 2%], 263 (8), 244 (39), 189 (28), 170 (19) and 73 (100). (Found C, 50.4; H, 5.5. Anal Calc. $C_{14}H_{19}F_3S_2Si$: C, 50.0; H, 5.7%.)

3.9. 2,2-Diphenylethanoyltrimethylsilane (**5b**)

Obtained as a yellow solid, m.p. 58–60°C. ν_{max} (KBr, cm^{-1}) 1640, 1588, 1233 and 846. δ_H (300 MHz, $CDCl_3$), 0.07 (9H, s), 5.42 (1H, s) and 7.20–7.40 (10H, m). δ_c (75 MHz, $CDCl_3$), -2.3, 69.0, 127.4, 129.0, 130.0, 137.4 and 242.4. *m*/*z* 268 [$M^{+\bullet}$ 1%], 253 (2), 167 (8), 101 (10) and 73 (100). (Found C, 75.5 and H, 6.9. Anal Calc. $C_{17}H_{20}OSi$: C, 76.1; H, 7.5%.)

3.10. 3-Trifluoromethylbenzoyltrimethylsilane (**5h**)

Obtained as yellow oil. ν_{max} (KCl, film, cm^{-1}) 1423, 1250, 1126 and 844. δ_H (500 MHz, $CDCl_3$) 0.40 (9H, s) and 7.60–8.20 (4H, m). δ_c (125 MHz, $CDCl_3$), -2.0, 123.8 (q, *J* -271.5 Hz, *C*F_3), 124.2, 129.2, 129.6, 130.9, 31.5 (q, *J* -32.0 Hz, *C*CF_3), 140.2 and 235.3.

m/*z* 246 [$M^{+\bullet}$ 2%], 231 (2), 154 (4), 145 (8), 126 (20) and 73 (100). (Found C, 53.3; H, 6.0. Anal Calc. $C_{11}H_{13}F_3OSi$: C, 53.7; H, 5.3%.)

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