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INFLUENCE OF AN OXIDISING IMPURITY ON PREPARATION OF 2-LITHIO-1,3-DITHIANE : ISOLATION OF BIS[2-(1,3-DITHIANYL)]METHANOL[1]

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Abstract: Bis-dithianylalkanols and dimers are formed in preparation of 2-lithio-1,3-dithianes due to the presence of oxidising impurity in n-BuLi (perhaps n-BuOOLi).

In our ongoing studies[2] directed to stereoselective construction of side chain of the potent plant growth promotor brassinolide[3], we used 2-lithio-1,3-dithiane[4]. In our preparation of 2-lithio-1,3-dithiane we used several times handled, one year old n-BuLi and noticed a formation of an oxidation product. Isolation followed by spectral characterisation revealed that the formed compound is bis-1,3-dithianylmethanol **5**[5]. The alkanol **5** was further characterised as its acetyl and trimethylsilyloxy ether derivatives **6** and **7** respectively. The alkanol **5** was also prepared from the reactions of 2-lithio-1,3-dithiane with formyl dithiane **4**[6] in 65% yield. Similarly with 2-methyl-1,3-dithiane[7](**2**) and 2-phenyl-1,3-dithiane[8](**3**) we observed the formation of the corresponding alkanols **8**[4a,c] and **9** along with dimers **11**[4c,9] and **12**[10] respectively, proving that the central carbon atom in alkanols **5**, **8** and

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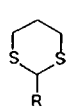
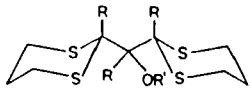
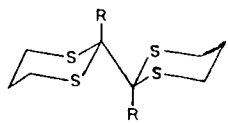


1 R = H
2 R = Me
3 R = Ph
4 R = CHO



5 R = R' = H
6 R = H , R' = $COCH_3$
7 R = H , R' = $Si(CH_3)_3$
8 R = Me , R' = H
9 R = Ph , R' = H



[10 R = H]
11 R = Me
12 R = Ph

9 originates[11] via degradation of the corresponding dithianes **1-3** themselves. We further observed that in the preparation of 2-lithio-1,3-dithianes, use of an excess of n-BuLi (old, 1.5 to 2.0 eqivalents) completely prevents the formation of these alkanols while only the dimers **11** and **12** are formed in case of 2-methyl-1,3-dithiane(**2**) and 2-phenyl-1,3-dithiane(**3**) respectively. To trace the error in our preparation of 2-lithio-1,3-dithianes we checked the authenticity of all our starting materials. Since our n-BuLi was one year old, we feel that alike Grignard reagent[14] it might have undergone oxygenation, in course of time, getting contaminated with oxidising impurity (perhaps n-BuOOLi) as the use of freshly prepared 1.1 equivalents of n-BuLi completely prevented the formation of such type of oxidation products in preparation of 2-lithio-1,3-dithanes.

The formation of alkanol **5** in preparation of 2-lithio-1,3-dithiane was observed earlier in 25% yields (structural assignment by X-ray crystallographic data), although it was claimed[5] to be originating out of reaction between 2-lithio-1,3-dithiane and THF[15].

In summary the formation of bisdithianylalkanols and dimers in preparation of 2-lithio-1,3-dithianes occurs due to presence of oxidising impurity in n-BuLi (perhaps n-BuOOLi).

Experimental

Melting points are uncorrected. Ir spectra were recorded on a Perkin-Elmer spectrophotometer model 599B, using NaCl optics. ^{1}H-Nmr spectra were taken in

$CDCl_3$ on a Bruker WH 90, AC 200 and MSL 300 spectrophotometers with TMS as an internal standard. ^{13}C-Nmr spectra were recorded on a Bruker MSL300 spectrophotometer at 75.47 MHz. ^{13}C-Nmr solutions were 0.2 to 0.3 mmol/mL in $CDCl_3$. Chemical shifts are referred with respect to $CDCl_3$ = 76.9 ppm. Mass spectra were recorded on Finnigan MAT 1020C mass spectrometer at 70 ev. For column chromatography, ACME silica gel 100-200 mesh size was used. Elemental analyses were carried out in the analytical section of the department and were within the usual limits of accuracy (± 0.3%).

Bis[2-(1,3-dithianyl)]methanol(5) : To the stirred solution of 1,3-dithiane (600 mg, 5 mmol) in anhydrous THF (10 ml) at -20 °C (CCl_4-dry ice) under argon atmosphere was added old n-BuLi (320 mg, 5 mmol, 3.30 ml of 1.5N) in hexane in dropwise fashion. The reaction mixture was further allowed to stir for 2 h at -20 °C and then it was quenched with water (5 ml). The reaction mixture was extracted with ether (3 X 25 ml). The etheral extracts were dried (Na_2SO_4) and concentrated to give crude product. Column chromatographic separation over silica gel gave unreacted **1** (310 mg), followed by bisdithianylmethanol **5** (180 mg, 40.3%), colourless prisms (ethyl acetate); mp 131 °C; IR 3400; NMR (δ) 1.85-2.30(m,4H), 2.75(m,4H), 3.07(m,4H), 3.13(t,1H,J=2Hz), 4.29(d,2H,J=2Hz). CMR (ppm) 25.20, 26.98, 27.60, 47.20, 74.60. Mass (m/e) 268, 250, 161, 149, 119, 106, 85, 75, 61. Anal. Calcd. for $C_9H_{16}OS_4$: C, 40.30; H, 5.97; S, 47.76. Found : C, 40.50; H, 6.04; S, 48.00. The aqueous layer was kept open to atmospheric conditions for 24 h. The formed turbid aqueous layer along with some minute particles was extracted with chloroform (3 X 10 ml). The chloroform layer was washed with water, brine and dried over Na_2SO_4. The removal of chloroform on rotary evaporator gave 25 mg of 1,2-dithiolane[12,13] contaminated with some polymeric impurities. The 1,2-dithiolane in $CHCl_3$ or $CDCl_3$ solutions was found to have very high tendency to form polymeric products. **1,2-Dithiolane** : IR 1390, 1460, 1470; NMR (δ) 2.15(quintet,2H,J=7Hz), 2.83(t,4H,J=7Hz); Mass (m/e) 106, 78, 69, 64, 60, 55.

The reaction of 2-lithio-1,3-dithiane (2.5 mmol) in THF (10 ml) with formyl dithiane **4** (2 mmol) also furnished **5** in 60-65% yield (-20°C, 2h., aq. workup).

Bis[2-(1,3-dithianyl)]methyl acetate(6) : To the solution of bisdithianylmethanol **5** (100 mg, 0.37 mmol) in pyridine (5 ml) was added acetic anhydride (3 ml, 32 mmol) and the reaction mixture was kept in dark for 24 h. Aqueous work-up furnished the acetyl derivative of bisdithianylmethanol **6** (110 mg, 95%), colourless crystals (ethyl acetate); mp 125 °C; IR 1750; NMR (δ) 1.85-2.24(m,4H), 2.16(s,3H), 2.44-3.16(m,8H), 4.33(d,2H,J=6Hz), 5.69(t,1H,J=6Hz); Mass (m/e) 310, 250, 191, 176, 129, 119, 97, 85, 55. Anal. Calcd. for $C_{11}H_{18}O_2S_4$: C, 42.58; H, 5.80; S, 41.29. Found : C, 42.80; H, 5.92; S, 41.06. Similarly the acetyl derivative **6** can also be obtained by treatment of **5** with acetic anhydride and potassium acetate (25 °C, 24 h, aqueous work-up) in quantitative yields.

Trimethylsilyloxybis[2-(1,3-dithianyl)]methane(7) : To the stirred solution of bisdithianylmethanol **5** (100 mg, 0.37 mmol) in pyridine (3 ml) was added chlorotrimethylsilane (218 mg, 2 mmol) in a dropwise fashion at 0 °C. The reaction mixture was further kept at room temperature for 1 h. Aqueous work-up followed by ether extraction (3 X 20 ml) yielded the silyloxyderivative **7** (115 mg, 91%), colourless crystals (ethyl acetate-hexane); mp 98-99 °C; IR 1470, 1255; NMR (δ) 0.28(s,9H), 2.02(m,4H), 2.90(m,8H), 4.04(t,1H,J=6Hz), 4.50(d,2H,J=6Hz); Mass (m/e) 340, 325, 250, 233, 222, 179, 147, 129, 119, 103, 91, 85, 73.

Similarly the reactions of methyl dithiane and phenyl dithiane with old n-BuLi gave corresponding dimers and alkanols.

1,1-Bis[2-(2-methyl-1,3-dithianyl)]ethanol[4a,c](8) : Yield (11.2%), colourless crystals (ethyl acetate-pet ether); mp 103-105 °C (lit[4c], mp 99.5-100 °C); IR 3500; NMR (δ) 1.80(s,3H), 2.04(s,6H), 1.80-2.18(m,4H), 2.78-3.11(m,8H), 3.42(s,1H); Mass (m/e) 310, 177, 133, 119, 105, 75, 59. Anal. Calcd. for $C_{12}H_{22}OS_4$; C, 46.45; H, 7.09; S, 41.29. Found : C, 46.32; H, 7.37; S, 41.17.

2,2'-Bi-1,3-dithiane, 2,2'-dimethyl[13](11) : Yield (3.2%), colourless crystals (ethyl acetate-pet ether); mp 185-187°C (lit[4c], mp 184-186°C); NMR (δ) 1.75-2.15(m,4H), 2.18(s,6H), 2.65-3.20(m,8H); Mass 266, 191, 159, 147, 133, 119, 107, 91, 85, 73, 59. Anal. Calcd. for $C_{10}H_{18}S_4$: C, 45.11; H, 6.76; S, 48.12. Found : C, 45.09; H, 6.92; S, 48.27.

Bis[2-(2-phenyl-1,3-dithianyl)]phenylmethanol(9) : Yield (24.2%), thick oil; IR 3455; NMR (δ) 1.65-2.25(m,4H), 2.45-2.65(m,4H), 2.70-2.85(m,2H), 3.25-3.45(m,2H), 5.55(s,1H), 7.25-8.05(m,15H). Mass (m/e) 301, 211, 195, 167, 152, 121, 105, 77.Anal. Calcd. for $C_{27}H_{28}OS_4$: C, 65.32; H, 5.65; S, 25.81. Found : C, 65.53; H, 5.60; S, 25.77.

2,2'-Bi-1,3-dithiane, 2,2'-diphenyl[14](12) : Yield (8.5%), colourless crystals (ethyl acetate-pet ether); mp 216-218 °C; NMR (δ) 1.75-2.22(m,4H), 2.50-2.80(m,8H), 7.20-7.70(m,10H); Mass (m/e) 390, 284, 255, 240, 210, 195, 178, 121, 106, 77. Anal. Calcd. for $C_{20}H_{22}S_4$: C, 61.54; H, 5.64; S, 32.82. Found : C, 61.29; H, 5.55; S, 32.73

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