

## Reactions of 1,3-Dithian-2-ylum Tetrafluoroborate with Organocopper, Organolithium and Organomagnesium Derivatives. A Simple Synthesis of 2-Substituted 1,3-Dithianes

JO KLAVENESS and KJELL UNDHEIM

Department of Chemistry, University of Oslo, Oslo 3, Norway

Recently we reported a simple and efficient method for the synthesis of 1,3-dithiolan-2-ylum and 1,3-dithian-2-ylum tetrafluoroborates; acid chlorides are reacted with 1,2-ethanedithiol or 1,3-propanedithiol in the presence of tetrafluoroboric acid.<sup>1</sup> These salts are potentially important synthetic intermediates, and are the cationic equivalents of the widely used ylide synthons of 1,3-thiolanes and 1,3-dithianes.<sup>2</sup> We herein report on the reactions of 1,3-dithian-2-ylum tetrafluoroborates with organometallic reagents.

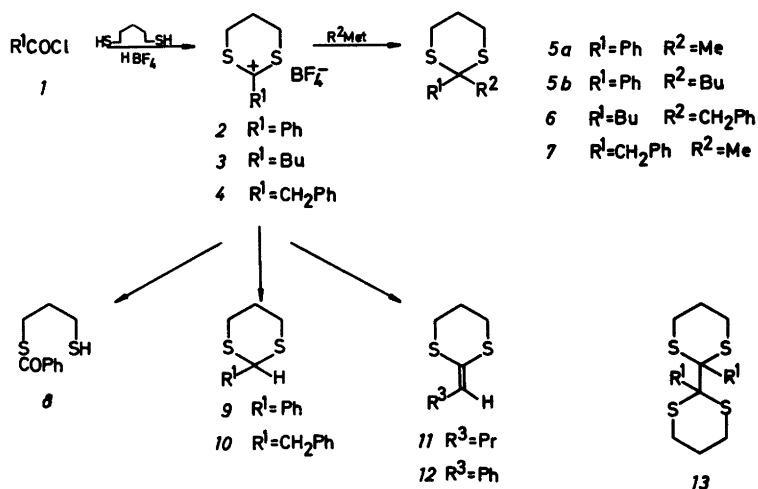
Treatment of the 2-phenyl-1,3-dithian-2-ylum salt **2** with methylmagnesium iodide gave exclusively the desired adduct **5a**. Five equivalents of the organometallic reagent were required for the reaction to go to completion. If less organometallic reagent was used, the thiol ester **8** was part of the product; the latter arises from the unreacted salt **2** during the hydrolytic work-up of the reaction mixture. In related studies of the behaviour of 1,3-benzoxathiolium and 1,3-benzo-

dithiolium salts towards Grignard reagents, it has also been reported that a large excess of the organometallic reagent must be used to effect complete conversion of the salt.<sup>8</sup> Five equivalents of butylmagnesium bromide were also required for complete reaction of the salt **2**; besides **5b** some of the reduced 1,3-dithiane **9** was formed. Such a reduction is not unexpected in moderately slow reactions when the Grignard reagent contains a hydrogen on its  $\beta$ -carbon.<sup>9</sup> The tendency for reduction was more pronounced using butyllithium when the major product was **9**. The reduction, however, was largely overcome by the use of lithium dibutylcuprate (Table 1).

The 2-butyl salt **3** with benzylmagnesium iodide gave the adduct **6**. Despite the basic properties of the Grignard reagent, proton abstraction to the ketene dithioacetal **11** was not important. The latter, however, is readily formed from **3** on treatment with triethylamine.<sup>1</sup> Having achieved alkylation by adduct formation with the Grignard reagents, the use of the other organometallic reagents was not further elaborated. Attention was instead directed towards derivatives which contain at least one hydrogen atom on an activated exocyclic  $\alpha$ -carbon; the 2-benzyl derivative **4** was chosen. With methylmagnesium iodide the main product (64 %) was due to proton elimination (**12**; Table 1), the remaining product was the adduct **7**. The more basic nature of methyllithium was manifested in 90 % yield of the elimination product **12** using this reagent. Elimination, however, is largely overcome by the use of an organocopper reagent which is much less basic than its lithium or magnesium equivalents;<sup>10</sup> the yield of the adduct **7** was 77 %

**Table 1.** Products from the reaction between 1,3-dithian-2-ylum tetrafluoroborates and organometallic reactants. The reactions were run in diethyl ether. The yields were determined by GLC on the crude products after aqueous decomposition of the reaction mixture.

R <sup>2</sup> Met	Substrate	Product yields					
		Comp.	%	Comp.	%	Comp.	%
MeMgI	2	5a	76				
BuMgBr	2	5b	85	9	9		
BuLi	2	5b	26	9	49		
Bu <sub>2</sub> CuLi	2	5b	48				
PhCH <sub>2</sub> MgBr	3	6	73				
BuMgBr	4	6	26	10	12	12	58
BuLi	4	6	9	10	15	12	74
Bu <sub>2</sub> CuLi	4	6	75	10	7	12	8
MeMgI	4	7	30			12	64
MeLi	4	7	6			12	90
Me <sub>2</sub> CuLi	4	7	77			12	13



Scheme 1.

using lithium dimethylcuprate (Table 1). Also with butylmagnesium bromide proton elimination from 4 to form 12 is favoured, whereas the corresponding organocopper reagent gives mainly the adduct 6. In the reactions with butylmagnesium bromide, reduction of the dithianium salt 4 to form 10 also occurs to some extent (7–15 %).

In the above reaction, varying but small amounts of a dimeric product 13 was also observed. This is formed by reductive dimerization of the salts 2–4; the reductive dimerization is more easily effected using zinc in acetonitrile.<sup>11</sup>

**Experimental.** All the reactions were carried out under an atmosphere of dry argon. Diethyl ether was dried by distillation from lithium aluminium hydride. The concentration of the butyl- and methyl lithium solutions was ascertained by titrations.<sup>12</sup> The copper iodide was purified as described.<sup>13</sup>

GLC was used for analysis of the crude product (Table 1; before purification); the analyses were run on columns of 3 or 10 % SR 2100 Chrom WAV-DMCS 80/100 in the range 100–250 °C at 16 °C/min. Mass spectra were recorded at 70 eV.

The 1,3-dithian-2-ylidene tetrafluoroborates were prepared as previously described.<sup>1</sup> When salts had been stored for some time they were washed with diethyl ether before the reaction was started.

The reaction products have previously been prepared by other routes. References to compounds in Table 1 which are not discussed below are: 9,<sup>14</sup> 10,<sup>6</sup> 12.<sup>7</sup>

**General procedure for Grignard reactions.** The

1,3-dithian-2-ylidene tetrafluoroborate (0.01 mol) was added with vigorous stirring at 0 °C to the Grignard reagent (0.05 mol) in ether (70 ml). The cooling bath was removed once the addition was completed, the mixture stirred at room temperature for 30 min and then heated under reflux for 15 min, the cold mixture carefully hydrolyzed with 0.5 M HCl, the organic layer separated, the aqueous layer extracted with ether (3×50 ml), the combined ether solutions washed with saturated aqueous NaHCO<sub>3</sub> and a little water and the dried (MgSO<sub>4</sub>) solution evaporated. The residual material was subjected to GLC analysis; the results are given in Table 1. In preparative runs the crude product was distilled.

*2-Methyl-2-phenyl-1,3-dithiane*,<sup>3a</sup> 5a, was thus obtained from 2 in 72 % yield, b.p. 90–91 °C/0.05 mmHg.

*2-Benzyl-2-butyl-1,3-dithiane*,<sup>5</sup> 6, was thus obtained from 4 in 46 % yield after chromatography on a silica gel column using toluene–light petroleum 1:1 with subsequent distillation: b.p. 140 °C/0.001 mmHg. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 0.95(Me), 1.1–2.1 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub> and CH<sub>2</sub>-5), 2.7–3.0 (CH<sub>2</sub>-4,6), 3.25 (CH<sub>2</sub>Ph), 7.3 (Ph). MS [*m/z* (% rel.int.)]: 266(1,M), 209(2), 177(7), 176(7), 175(100), 135(2), 117(5), 91(11).

**General procedure for alkyllithium reactions.** The alkyllithium solution (16 mmol) was added dropwise with vigorous stirring at –78 °C to a suspension of the 1,3-dithian-2-ylidene tetrafluoroborate (10 mmol) in ether (70 ml). The cooling bath was removed when the addition was completed, the mixture allowed to reach room temperature and worked up and analyzed (Table

1) as above.

*General procedure for lithium dialkylcuprate reactions.* The alkyllithium solution (20 mmol) was added dropwise with vigorous stirring at 0 °C to a suspension of copper iodide (10 mmol) in ether (40 ml). The resultant mixture was stirred for 10 min before the 1,3-dithian-2-ylidene tetrafluoroborate (2 mmol) was added. After stirring for an additional 6 h at 0 °C the mixture was poured into 1 M HCl and worked up and analyzed (Table 1) as above.

*2-Butyl-2-phenyl-1,3-dithiane*, <sup>3b</sup> *5b*, was thus obtained in 17 % yield, b.p. 125 °C/0.05 mmHg. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 0.95(Me), 1.1–2.1 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub> and CH<sub>2</sub>-5), 2.75–3.0 (CH<sub>2</sub>-C4,6), 7.1–7.9 (Ph). MS [*m/z* (% rel.int.)]: 252(29,M), 205(9), 195(71), 178(31), 163(46), 136(100), 121(34).

*2-Benzyl-2-methyl-1,3-dithiane*, <sup>4</sup> *7*, was isolated from the reaction between *4* and lithium dimethylcuprate in 64 % yield after chromatographic separation on a silica gel column using benzene–light petroleum 1:1; the other product, 2-benzylidene-1,3-dithiane, <sup>7</sup> *12*, was isolated in 7 % yield.

1. Klaveness, J. and Undheim, K. *Acta Chem. Scand. B* 37 (1983) *In press*.
2. Gröbel, B.-T. and Seebach, D. *Synthesis* (1977) 357.
3. a. Kalff, H. T. and Havinga, E. *Recl. Trav. Chim. Pays-Bas* 85 (1966) 467; b. Seebach, D. and Wilka, E.-M. *Synthesis* (1976) 476.
4. Seebach, D. and Corey, E. J. *J. Org. Chem.* 40 (1975) 231.
5. Carlson, R. M. and Helquist, P. M. *Tetrahedron Lett.* (1969) 173.
6. Corey, E. J. and Erickson, B. W. *J. Org. Chem.* 36 (1971) 3553.
7. Seebach, D., Kolb, M. and Gröbel, B. T. *Chem. Ber.* 106 (1973) 2277.
8. Degani, I. and Fochi, R. *J. Chem. Soc. Perkin Trans. 1* (1976) 1886.
9. Nützel, K. *Methoden der Organischen Chemie (Houben-Weyl)*, 4th Ed., Thieme, Stuttgart 1973, Vol. XIII/2a, p. 297.
10. Posner, G. H. *Org. React.* 22 (1975) 253.
11. Klaveness, J. and Undheim, K. *Unpublished work*.
12. a. Watson, S. C. and Eastham, J. F. *J. Organomet. Chem.* 9 (1967) 165; b. Gilman, H. and Cartledge, F. K. *J. Organomet. Chem.* 2 (1964) 447.
13. Posner, G. H., Whitten, C. E. and Sterling, J. J. *J. Am. Chem. Soc.* 95 (1973) 7788.
14. Seebach, D., Erickson, W. W. and Singh, G. *J. Org. Chem.* 31 (1966) 4303.