

Franco Bellesia, Monica Boni, Franco Ghelfi* and Ugo M. Pagnoni

Dipartimento di Chimica dell' Università,
Via Campi 183, I-41100, Modena, Italy
Received November 10, 1993

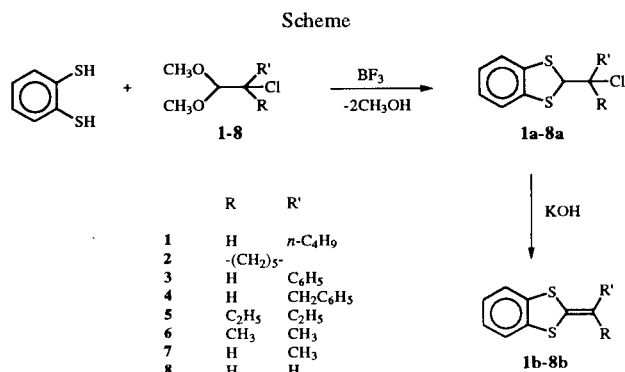
Boron trifluoride promoted transdithioacetalization of α -chloroacetals with 1,2-benzodithiol affords good yields of 2-(1-chloroalkyl)-1,3-benzodithioles, which dehydrochlorinates very satisfactorily to the corresponding 2-alkylidene-1,3-benzodithioles.

J. Heterocyclic Chem., **31**, 1721 (1994).

2-Alkylidene-1,3-benzodithioles are suggested as intermediates in the reaction of 2-alkyl-1,3-benzodithiolylium salts with a number of carbon electrophiles [1a-g] in the synthesis of dyes and photochromic adducts. As far as we know, these ketene dithioacetals have been prepared by reaction of aromatic nitriles with 1,2-benzodithiol [1c], or by a Horner-Emmons reaction of 2-(*O,O*-dimethylphosphonyl)-1,3-benzodithiole with carbonyl compounds [2a-b].

In a recent study of the stabilization effect of sulphur on an adjacent carbanion [3], we developed a synthesis of ketene thioacetals by dehydrochlorination [5] of α -chloromercaptals [4] obtained from α -chloroaldehyde dimethyl acetals. Now we report that this non-connective procedure can be usefully applied to the preparation of a number of 2-alkylidene-1,3-benzodithioles (Scheme).

The preparation of benzo-1,4-dithiadene [6] is the only reported reaction between an aryldithiol (dithiocatechol) and an α -haloacetal.



The use of cobalt(II) chloride-trimethylchlorosilane in acetonitrile, which was successful in the case of aliphatic dithiols [4], failed to give transdithioacetalisation of α -chlorohexanal dimethyl acetal with the 1,2-benzodithiol, even under long heating at 80°.

Table 1
Physical and Spectroscopical Data of 2-(1-Chloroalkyl)-1,3-benzodithioles 1a-8a.

	Reaction time (h)	Yield (%)	Bp °C (mm Hg)	Formula M ⁺ (m/z)	Elemental analysis (Calcd./Found)			¹ H NMR, δ , CDCl ₃
					C	H	S	
1a	0.5	85	145-150 (0.01)	C ₁₂ H ₁₅ ClS ₂ 258	55.69	5.84	24.77	0.87 (3H, t), 1.19-1.81 (4H, m), 1.95 (2H, m), 3.97 (1H, dt), 5.01 (1H, d), 6.94-7.29 (4H, m)
					55.55	5.79	24.86	
2a	1	94	94-96 [a]	C ₁₃ H ₁₅ ClS ₂ 270	57.65	5.58	23.67	0.95-2.06 (10H, m), 5.16 (1H, s), 6.90-7.32 (4H, m)
					57.68	5.57	23.50	
3a	2	46	171-176 (0.02)	C ₁₄ H ₁₁ ClS ₂ 278	60.31	3.98	23.00	4.90 (1H, d), 5.32 (1H, d), 6.88-7.46 (9H, m)
					60.41	3.94	23.03	
4a	1	75	186-190 (0.01)	C ₁₅ H ₁₃ ClS ₂ 292	61.52	4.47	21.90	2.80-3.60 (2H, m), 4.10-4.38 (1H, m), 5.06 (1H, d), 6.97-7.37 (4H, m)
					61.49	4.61	21.93	
5a	0.5	72	139-143 (0.05)	C ₁₂ H ₁₅ ClS ₂ 259	55.69	5.84	24.77	0.97 (6H, t), 1.96 (4H, dq), 5.36 (1H, s), 6.97-7.20 (4H, m)
					55.55	5.98	24.68	
6a	1	65	50-52 [a]	C ₁₀ H ₁₁ ClS ₂ 230	52.05	4.80	27.79	1.66 (6H, s), 5.11 (1H, s), 6.88-7.26 (4H, m)
					51.96	4.87	27.99	
7a	1	82	122-126 (0.05)	C ₉ H ₉ ClS ₂ 216	49.87	4.19	29.58	1.57 (3H, d), 4.11 (1H, dq), 4.97 (1H, d), 6.92-7.30 (4H, m)
					49.72	4.04	29.49	
8a	1	84	136-140 (0.2)	C ₈ H ₇ ClS ₂ 202	47.40	3.48	31.63	3.70 (2H, d), 4.81 (1H, t), 6.93-7.33 (4H, m)
					47.46	3.58	31.80	

[a] Melting point.

Table II
Physical and Spectroscopic Data of 2-Alkylidene-1,3-benzodithioles **1b-8b**

	Reaction time (h)	Yield (%)	Bp °C (mm Hg)	Formula M ⁺ (m/z)	Elemental analysis (Calcd./Found)			¹ H NMR, δ, CDCl ₃
					C	H	S	
1b	1	93	118-23 (0.01)	C ₁₂ H ₁₄ S ₂ 222	64.82	6.35	28.84	0.83 (3H, bt), 1.03-1.37 (4H, m), 1.78-2.11 (2H, m), 5.39 (1H, t), 6.53-6.87 (4H, m) [c]
					64.71	6.22	28.87	
2b	1	96	92-4 [a]	C ₁₃ H ₁₄ S ₂ 234	66.62	6.02	27.36	1.37 (6H, m), 2.08 (4H, m), 6.56-6.94 (4H, m) [c]
					66.50	5.94	27.46	
3b	1	62	131-3 [a]	C ₁₄ H ₁₀ S ₂ 242	69.38	4.16	26.46	6.58 (1H, s), 6.96-7.42 (9H, m) [d]
					69.39	4.02	26.63	
4b	1	94	55-7 [a]	C ₁₅ H ₁₂ S ₂ 256	70.27	4.72	25.01	3.48 (2H, d), 5.70 (1H, t), 6.96-7.46 (9H, m) [d]
					70.17	4.61	25.14	
5b	4	98	96-9 [a]	C ₁₂ H ₁₄ S ₂ 222	64.82	6.35	28.84	1.04 (6H, t), 2.17 (4H, q), 6.93-7.29 (4H, m) [d]
					64.93	6.30	28.66	
6b	1	91	n.d. [b]	C ₁₀ H ₁₀ S ₂ 194				1.55 (6H, s), 6.58-6.92 (4H, m) [c]
7b	0.5	88	n.d. [b]	C ₉ H ₈ S ₂ 180				1.48 (3H, d), 5.18 (1H, q), 6.51-6.92 (4H, m) [c]
8b	0.5	77	n.d. [b]	C ₈ H ₆ S ₂ 166				4.92 (2H, s), 6.64 (4H, s) [c]

[a] Melting point. [b] Not determined owing to extended decomposition during the solvent evaporation. [c] ¹H nmr spectra in deuterobenzene. [d] ¹H nmr spectra in deuteriochloroform.

However, using an harder acid such as boron trifluoride ethyl etherate in boiling acetonitrile, 2-(1-chloropentyl)-1,3-benzodithiole was obtained in good yield, on replacing the acetonitrile with chloroform the yields further improved.

As can be seen from Table 1, this procedure gave excellent yields on a number of α-haloacetals. Only the reaction of α-chlorophenylacetaldehyde dimethyl acetal was poor, likely owing to the high mobility of the benzylic halogen 3-phenylbenzo-1,4-dithiadene was isolated as the main side product (10%). Unlike the transdithioacetalization with ethanedithiol or propanedithiol [4], even α-bromohexanal dimethyl acetal was efficiently transformed into the 2-(1-bromopentyl)-1,3-benzodithiole.

By dehalogenation of 2-(1-chloroalkyl)-1,3-benzodithioles with potassium hydroxide in boiling benzene, the corresponding 2-alkylidene-1,3-benzodithioles (Table II) were easily obtained in high yields.

EXPERIMENTAL

The ¹H nmr spectra were recorded on a Bruker WP80 or a Varian XL200 spectrometer. Mass spectra were obtained on a HP 5989 mass spectrometer. The elemental analyses were performed on a Fisons CHNOS Model 1108 instrument. Reagents and solvents were standard grade commercial products, and were used without further purification. α-Chloroacetals were prepared by chlorination of aldehyde dimethyl acetals with manganese(IV) oxide-trimethylchlorosilane [7].

General Procedure for the Preparation of 2-(1-Chloroalkyl)-1,3-benzodithioles.

In a 2-neck round-bottom flask (25 ml), α-chlorodimethyl acetal (1.0 mmole), benzene-1,2-dithiol [8a-d] (1.1 mmoles) and boron trifluoride ethyl etherate (1.0 mmole) were dissolved in chloroform (3 ml) at room temperature. The solution was then heated at reflux and monitored by tlc using ethyl ether/*n*-hexane (0.5:9.5) as the eluant. After the time reported in Table 1 the mixture was washed with 5% aqueous sodium bicarbonate (5 ml) and the aqueous phase further extracted with chloroform (2 x 2 ml). The collected extracts were dried over sodium sulfate and evaporated. The crude products were purified by preparative tlc or by bulb to bulb distillation in an air bath thermostat [9]. Yields are on isolated products. 2-(1-Chloroalkyl)-1,3-benzodithioles are quite stable and can be indefinitely stored at -25°.

General Procedure for the Preparation of 2-Alkylidene-1,3-benzodithioles.

In a 2-neck round-bottom flask (25 ml) fitted with a condenser, 2-(1-chloroalkyl)-1,3-benzodithiole (1.0 mmole) was dissolved in benzene (2 ml). Finely ground potassium hydroxide (337 mg, 6.0 mmoles) was added to the stirred solution and the resulting mixture was heated at reflux and monitored by tlc using ethyl ether/*n*-hexane (0.5:9.5) as the eluant. When conversion was complete, the reaction mixture was filtered on a celite-sodium sulfate bed. After solvent evaporation at reduced pressure, an almost pure product was obtained; adducts **6b**, **7b** and **8b**, however, at this step degraded at a great extent, and needed to be left in solution for storage. Products **1b-5b** were purified by preparative tlc, using ethyl ether/*n*-hexane (1:9) as the eluant, or by bulb to bulb distillation in an air bath thermostat [9]. The 2-alkylidene-1,3-benzodithioles are unstable and slowly deteriorate even at -25°.

Acknowledgements.

We thank the C.N.R. (Rome) and the Ministero della Università e della Ricerca Scientifica e Tecnologica (MURST) for financial assistance.

REFERENCES AND NOTES

- [1] [a] H. Prinzbach and E. Futterer, *Adv. Heterocyclic Chem.*, **7**, 132 (1966); [b] N. Lozac'h and M. Stavaux, *Adv. Heterocyclic Chem.*, **27**, 229 (1980); [c] L. Soder and R. Wizinger, *Helv. Chim. Acta*, **42**, 1733 (1959); [d] L. Soder and R. Wizinger, *Helv. Chim. Acta*, **42**, 1779 (1959); [e] D. Leaver and W. A. H. Robertson, *Proc. Chem. Soc.*, 252 (1960); [f] R. Wizinger and D. Dürr, *Helv. Chim. Acta*, **46**, 2167 (1963); [g] P. Appriou and R. Guglielmetti, *Bull. Soc. Chim. France*, 510 (1973).
- [2a] K. Ishikawa, K. Akiba and N. Inamoto, *Tetrahedron Letters*, 3695 (1976); [b] M. Ceruti, I. Degani and R. Fochi, *Synthesis*, 79 (1987).
- [3] F. Bernardi, I. G. Csizmadia, A. Mangini, H. B. Schlegel, M. H. Whangbo and S. Wolfe, *J. Am. Chem. Soc.*, **97**, 2209 (1975).
- [4] F. Bellesia, M. Boni, F. Ghelfi and U. M. Pagnoni, *Tetrahedron*, **49**, 199 (1993).
- [5] F. Bellesia, M. Boni, F. Ghelfi and U. M. Pagnoni, *Synth. Commun.*, 3179 (1993).
- [6] W. E. Parham, T. M. Roder and W. R. Hasek, *J. Am. Chem. Soc.*, **75**, 1647 (1953).
- [7] F. Bellesia, M. Boni, F. Ghelfi, R. Grandi, U. M. Pagnoni and A. Pinetti, *Tetrahedron*, **48**, 4579 (1992).
- [8] For preparations of 1,2-benzenedithiol see: [a] D. M. Giolando and K. Kirschbaum, *Synthesis*, 451 (1992); [b] I. Degani and R. Fochi, *Synthesis*, 471 (1976); [c] S. Hünig and E. Fleckestein, *Liebigs Ann. Chem.*, **738**, 192 (1970); [d] W. R. H. Hurlley and S. Smiles, *J. Chem. Soc.*, 1821 (1926).
- [9] Since the boiling points have been determined by this procedure, the values reported are uncorrected.