Pergamon

Tetrahedron, Vol. 52, No. 48, pp. 15147-15156, 1996

0040-4020/96 $15.00 + 0.00

PII: S0040-4020(96)00972-6

Aggregative Activation and Carbanion Chemistry : Complex Base Deprotonation and Directed Functionalisation of Dithioacetals

Philippe Gros, Philippe Hansen and Paul Caubère*

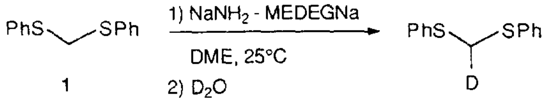
Laboratoire de Chimie Organique I, URA CNRS 457, Faculté des Sciences,
Université Henri-Poincaré, Nancy I, BP 239, F-54506 Vandoeuvre-les-Nancy, France

Abstract: Bis(phenylthio)methane and [1,3]-dithiane were efficiently deprotonated by the $NaNH_2$-$Et(OCH_2CH_2)_2$-ONa complex base. A marked behaviour difference was observed between the sodium carbanion of [1,3]-dithiane and the corresponding lithio-derivative. A "radicaloid" mechanism is proposed to explain the results observed.

Dithioacetals and more particularly [1,3]-dithiane have found wide synthetic uses as precursors of acyl anion equivalents displaying a reactivity umpolung.[1] Their reactions with electrophiles are generally performed via the lithio derivatives.[2] As part of our studies dealing with Aggregative Activation[3] it was of interest to know to what extent the aggregates of the complex bases (CB) $NaNH_2$-RONa would be able to generate sodium carbanion precursors and to replace the currently used lithium reagents.[4] Indeed such complex bases are easily prepared, inexpensive and may be used on a large scale.[5] Of course, the carbanion reactivity is expected to change with the nature of the cationic counter-ion. Thus, going from lithium to sodium should provide interesting application by changing the behaviour of the carbanion during competitive reaction with electrophiles. In the present study we report the results obtained in this area with bis(phenylthio)methane (**1**) and [1,3]-dithiane (**2**).

Generation and condensation of the carbanions of 1 and 2

From our previous exploratory experiments,[6] we knew that the best complex base to generate these carbanions was $NaNH_2$/$Et(OCH_2CH_2)_2$-ONa (usually 2/1 ratio) abbreviated $NaNH_2$-MEDEGNa. However a large excess of base was used. Thus we first optimized this quantity using $(PhS)_2CH_2$ (**1**) as substrate and D_2O as electrophile (Scheme 1 and Table 1).



Scheme 1

Email: caubere@lcol.u-nancy.fr. Fax: (33) 83 40 45 58.

Table 1: Optimisation of the amount of $NaNH_2$-MEDEGNa by deuteration experiments on **1** (1 eq.)

Run	$NaNH_2$ (eq.) / MEDEGNa (eq.)	t (min)	Deuteration yield %[a]
1	4 / 2	30	95
		60	100
2	2 / 1	15	92
		30	100
3	1.5 / 0.75	30	65
		60	76
		120	90
4	2 / 0	60	78
		120	92
5	3 / 0	60	90
		90	100

[a] Determined by ^1H NMR spectroscopy.

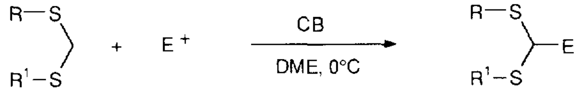
From these data it appears that the carbanion was quantitatively generated in an acceptable reaction time using the ratio substrate (1eq) / $NaNH_2$ (2 eq) / MEDEGNa (1 eq). Control experiments were performed since Arens[7] showed that $NaNH_2$ abstracted the protons of **1** in liquid ammonia. Once more it appeared that $NaNH_2$ was much more reactive in the presence of the activating agent. Thus, without MEDEGNa, $NaNH_2$ (run 4) was unable to quantitatively generate the carbanion. Even in the presence of the total amount of $NaNH_2$ necessary to prepare the complex base (run 5) the reaction time was much longer without any activating agent.

On the other hand, the same study undertaken with 1,3-dithiane led, at least in the limits of detection, to no deuterium incorporation. Such a result could indicate that the carbanion was not generated or existed in too low amount to be evidenced with D_2O. Thus we decided to perform some exploratory experiments using the reactive MeI as an electrophile and observed the formation of the expected 2-methyl-[1,3]-dithiane. This point will be examined further. With this result in hand we performed the reactions reported in Table 2.

It clearly appeared that the complex base was very efficient in abstracting the protons from both substrates and that electrophiles condensed easily under our conditions. It is noteworthy that during the reaction performed with **1** we observed the formation of small to appreciable amounts of PhS^- which condensed with the electrophiles. This observation could be explained by the mechanism proposed below.

On the other hand if the results obtained with **1** could be expected, more intriguing were those obtained with **2** which, in fact, led to the best yields. Indeed as mentioned above no deuteration took place when the reaction was quenched with D_2O. This suggests a very low carbanion concentration and it is surprising that the electrophiles, which were not used in large excess, were not destroyed by the complex base and condensed with the small amount of carbanion, if formed. The results obtained support an equilibrium between the starting material and the anionic species evolving when the electrophile was added.

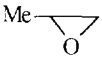
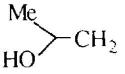
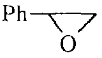
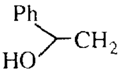
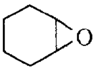
Table 2 : Condensation of dithioacetals **1** and **2** with electrophiles in the presence of CB



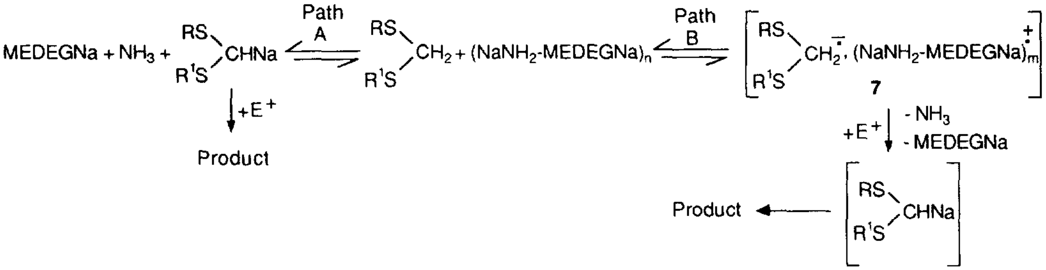
1 : R = R¹ = Ph

2 : R, R¹ = -$(CH_2)_3$-

3-**6**

Substrate	E^+	t (h)	Product No.	Product E	Product Isolated Yields %
1	MeI	0.3	**3a**	Me	91
2		0.2	**4a**		87
1	EtBr	0.3	**3b**	Et	88
2		0.2	**4b**		95
1	EtI	0.25	**3b**	Et	84
2		0.2	**4b**		96
1	Hex-Cl	1	**3c**	Hex	75
2		3	**4c**		78
1	Hex-Br	0.3	**3c**	Hex	90
2		0.2	**4c**		94
1	Hex-I	0.3	**3c**	Hex	90
2		0.2	**4c**		95
1		2	**5a**		64
2		40	**6a**		63
1		2	**5b**		80
2		20	**6b**		90
1		4	**5c**	2-HO-c-C_6H_{10}	52
2		36	**6c**		23
		140			88

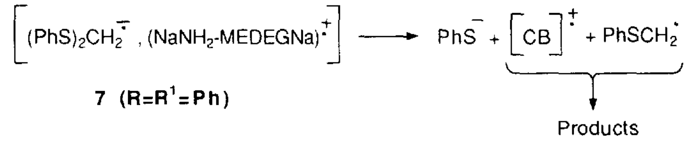
Since the active part of a complex base is NH_2^- such an equilibrium ought to be written according to path A of Scheme 2.



Scheme 2

However such a mechanism is highly unlikely since it supposes that NH_3 could interact with the carbanion to give back $NaNH_2$. On the other hand, according to one of the basic concepts of Aggregative Activation[3a] we postulated that the aggregates of a complex base ought to be prone to single electron transfer (SET) and to stabilize a single electron via a cluster effect.[3b] This property was verified with Ph_3CH; the addition of this hydrocarbon to $NaNH_2$-tBuONa led to the corresponding radical anion evidenced by epr spectroscopy .[8a] This observation agrees with the fact that no evolution of NH_3 was observed during the formation of the red intermediate but only when the electrophiles were added.[8b] Finally, during current investigations with new complex bases, SET was also evidenced by epr and trapping.[9]

Thus we propose path B which includes a carbanion precursor 7 constituted by the radical anion of the dithioacetal associated with the aggregates of the complex base which has transferred one electron to the substrate. This highly energetic precursor 7 must react much faster than the complex base with electrophiles allowing the formation of the substituted product. This hypothesis also agrees with the fact that NH_3 evolved only when the electrophiles were added to the reaction medium. Moreover the above mentioned formation of PhS^- from **1**, could be due to the partial destruction of 7 according to Scheme 3.



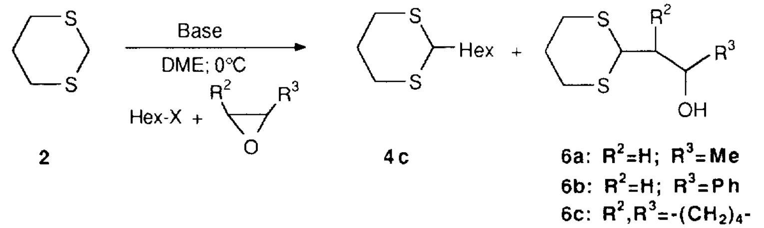
Scheme 3

The reactions observed with **1** could be due to the derived carbanion as well as to **7**. We believe that radicaloid mechanisms are not limited to reactions with complex bases and more likely to occur when the basic reagent is aggregated.

Reactivity comparison of sodium and lithium derivatives of 2

As mentioned in our general considerations a change in the cationic counter-ion nature of a given carbanion should result in a change in the reactivity towards electrophiles. In order to check this hypothesis and to evaluate the usefulness of complex bases in this particular field we chose to compare the behaviour of sodium and lithium derivatives of **2**, generated from $NaNH_2$-MEDEGNa and BuLi respectively. Exploratory competitive experiments were performed with hexyl halides and representative epoxides. Since epoxides are more sensitive to electrophilic assistance than alkyl halides, the lithium reagent was expected to react more readily with epoxide than with alkyl halides. The results obtained are gathered in Table 3.

Table 3 : Competitive condensation between hexyl halides and epoxides for CB and BuLi



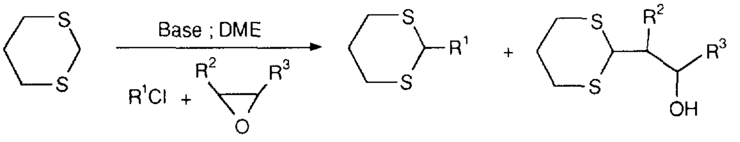
X	R^2	R^3	Base	t (h)	**4c:6**	Isolated yield%
Cl	H	Me	CB	26	52:48	84
			BuLi	1	5:95	87
Br			CB	3	99:1	94
			BuLi	0.25	77:23	99
I			CB	3	100:0	93
			BuLi	0.25	92:8	86
Cl	H	Ph	CB	20	70:30	90
			BuLi	1	11:89	92
Br			CB	2	100:0	93
			BuLi	0.25	89:11	95
I			CB	2	100:0	93
			BuLi	0.25	90:10	92
Cl	$(CH_2)_4$		CB	26	98:2	92
			BuLi	2	20:80	89
Br			CB	2	100:0	92
			BuLi	0.25	99:1	95
I			CB	2	100:0	92
			BuLi	0.25	99:1	91

As far as global yields are concerned, the complex base was as efficient as BuLi in the functionalisation of **2** via carbanion intermediates. It must be underlined that during the experiments performed with lithium reagent, the reaction medium contained a certain amount of hexane coming from the starting solution of BuLi. We verified that the addition of hexane to the solvent used in complex base experiments did not substantially change the reactions observed in pure DME.

The selectivity trend agrees with our expectations. However the electrophilic assistance of lithium during the condensation of lithium reagent with epoxides is not sufficient to balance the high reactivity of alkyl bromides or iodides and, as a consequence, the behaviours of sodium and lithium reagents become comparable. On the contrary a marked difference was observed during the competitions between alkyl chlorides and epoxides and we decided to continue our investigations on this aspect.

We thus performed a number of representative experiments at two different temperatures which were chosen after a short exploratory study indicating that the selectivity could change with this parameter. The results obtained are given in the Table 4.

Table 4 : Competitive condensation between alkyl chlorides and epoxides for CB and BuLi



2

4d: R^1=Bu

4e: R^1=n-Dec

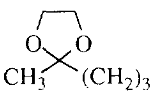
4f: R^1=c-$C_6H_{11}(CH_2)_3$-

4g: R^1= $(CH_3)_2N(CH_2)_3$

4h: R^1=$CH_3C(OCH_2CH_2O)(CH_2)_3$-

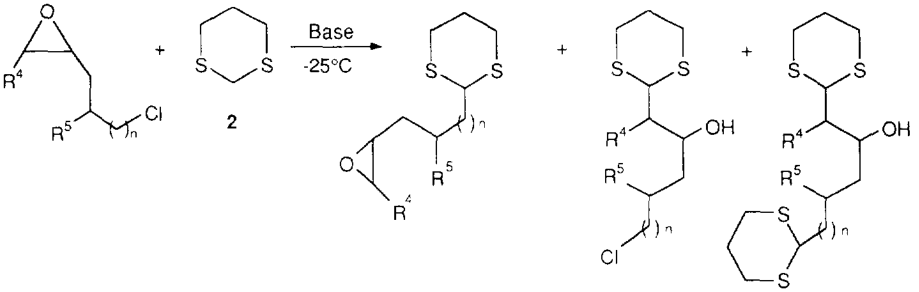
6d: R^2=H; R^3=Bu

6e: R^2,R^3=-$(CH_2)_3$-

				T=0°C			T=-25°C		
R^1	R^2	R^3	Base	t (h)	**4:6**	Isolated yield %	t (h)	**4:6**	Isolated yield %
C_6H_{13}	H	C_6H_5	CB	20	70:30	90	60	84:16	94
			BuLi	2	11:89	92	2	10:90	89
	H	CH_3	CB	20	52:48	84	60	65:35	84
			BuLi	2	6:94	87	2	3:97	85
	H	C_4H_9	CB	20	66:34	91	60	73:27	89
			BuLi	2	6:94	86	2	4:96	83
	$(CH_2)_4$		CB	26	98:2	92	78	98:2	92
			BuLi	2	20:80	89	4	14:86	87
	$(CH_2)_3$		CB	26	96:4	88	78	96:4	88
			BuLi	2	53:47	86	4	40:60	82
C_4H_9	H	C_6H_5	CB	20	73:27	93	60	84:16	92
			BuLi	2	10:90	87	2	10:90	89
$C_{10}H_{21}$	H	C_6H_5	CB	20	72:28	89	60	83:17	90
			BuLi	2	10:90	89	2	7:93	87
c-$C_6H_{11}(CH_2)_3$	H	C_6H_5	CB	20	69:31	90	60	85:15	90
			BuLi	2	9:91	86	2	9:91	88
$(CH_3)_2N(CH_2)_3$	H	C_6H_5	CB	20	71:29	93	60	79:21	88
			BuLi	2	20:80	84	2	3:97	84
	H	C_6H_5	CB	20	70:30	91	60	81:19	90
			BuLi	2	9:91	92	2	9:91	88

Some interesting information emerges from these results. As usual the reaction times with the CB are much longer than with BuLi. Indeed this latter is a stronger base and rapidly reacts with **2** to give the corresponding carbanion while **2** must react with the aggregates of the CB to give a very low concentration of the putative reactive intermediate. The opposed behaviours of lithium and sodium derivatives of **2** are confirmed and seem to be general. Finally, broadly speaking, the lithium reagent appears appreciably less sensitive to the reaction temperature. Such an observation is not unexpected if we admit that aggregates, whose structures vary with temperature, play a much more important role in the reactions performed with the CB.

Finally, we performed the reactions reported in Scheme 4 dealing with intramolecular competitions.



$R^4 = R^5 = H$, n = 6	CB	56 (**8a**)	8 (**9a**)	12 (**10a**)
	BuLi	3	82	3
$R^4, R^5 = (CH_2)_2$, n = 2	CB	83 (**8b**)	-	-
	BuLi	6	47 (**9b**)	22 (**10b**)

Scheme 4

These results complete our investigations and show how they may be used in synthesis in order to functionalise chloro-epoxides step by step.

EXPERIMENTAL

^1H and ^{13}C NMR spectra were recorded on a Bruker spectrometer at 400 MHz and 100 MHz respectively with TMS as an internal standard.IR spectra (NaCl plates or KBr pellets) were recorded on a Perkin-Elmer 841 apparatus. GC/MS measurements (IE and IC) were performed on HP5971A spectrometers. Elemental analysis were performed by the Service Central d'Analyse du CNRS at Vernaison (France).

Materials

Sodium amide powder and BuLi solutions were obtained commercially from Merck and Aldrich respectively. MEDEG was distilled before use. 1,2-dimethoxyethane (DME) was distilled from sodium and stored under sodium until used. Commercially available starting materials were used as such. [1,3]dithiane was prepared as described by Corey and Seebach. [1]

Typical procedures

Preparation of the complex base (CB): To a suspension of $NaNH_2$ (1.17 g; 30 mmol) in 5 ml of DME was added dropwise under nitrogen, a solution of MEDEG (1.34 g; 10 mmol) in 10 ml of DME. After addition, the reaction mixture was stirred at 40-45°C for 2h and brought to the desired reaction temperature.

a) Condensation of sodium carbanion of bis(phenylthio)methane **1** *with electrophiles*

A solution of **1** (2.32 g; 10 mmol) in 10 ml of DME was added dropwise at 25°C to the complex base prepared above.The mixture was stirred at this temperature for 1 h. The temperature was adjusted at 0°C and a solution of the electrophile (12 mmol) was added dropwise, the reaction was then monitored by GC. After completion, the reaction mixture was poured into ice, extracted with ether and the organic layer dried over $MgSO_4$. After solvents evaporation the crude product was purified by flash chromatography (ether/hexane or ethyl acetate/hexane eluents).

b) Condensation of sodium carbanion of [1,3]-dithiane **2** *with electrophiles*

A solution containing **2** (1.2 g; 10 mmol) and the electrophile (12 mmol) (12 mmol of each electrophile in case of competition reactions) in 15 ml of DME was added at room temperature to the suspension of complex base (CB) prepared above.The temperature was adjusted to the desired value (see tables) and the reaction was monitored by GC. After completion the reaction mixture was submitted to the usual work-up.

c) Condensation of lithium carbanion of [1,3]-dithiane **2** *with electrophiles*

To a solution of **2** (1.2 g; 10 mmol) in 7 ml of DME cooled at -50°C was added BuLi (12 mmol; 7.5 ml of a 1.6M solution in hexane). The temperature was kept at -50°C for 1h and the solution of 2-lithio-[1,3]dithiane was transferred via a cannula to a nitrogen flushed dropping funnel and added slowly (5 min) to a precooled solution of 12 mmol of each electrophile in 15 ml of DME. After completion, the reaction mixture was submitted to the usual work-up.

Products

1,1-bis(phenylthio)ethane (**3a**)[2]; 1,1-bis(phenylthio)propane (**3b**)[11]; 1,1-bis(phenylthio)heptane (**3c**)[12]; 4,4-bis(phenylthio)-2-butanol (**5a**)[2]; 3,3-bis(phenylthio)-1-phenyl-1-propanol (**5b**)[2]; 2-bis(phenylthio)methyl-1-cyclohexanol (**5c**)[2]; 2-methyl-[1,3]-dithiane (**4a**)[13]; 2-ethyl-[1,3]-dithiane (**4b**)[13]; 2-hexyl-[1,3]-dithiane (**4c**)[14]; 2-butyl-[1,3]-dithiane (**4d**)[15]; 2-decyl-[1,3]-dithiane (**4e**)[16]; 1-[(1,3-dithian)-2-yl]-2-propanol (**6a**)[17]; 2-[(1,3]-dithian)-2-yl]-1-phenyl-1-ethanol (**6b**)[17]; 2-[(1,3-dithian)-2-yl]-1-cyclohexanol (**6c**)[17]; 1-[(1,3-dithian)-2-yl]-2-hexanol (**6d**)[18] were found identical to authentic samples.

1-cyclohexyl-3-[(1,3-dithian)-2-yl]-2-propane (4f)

^1H NMR ($CDCl_3$): δ ppm: 0.8-0.9 (m; 2H); 1.14-1.24 (m; 6H); 1.49-1.75 (9H); 1.81-2.16 (m; 2H); 2.79-2.92 (m; 4H); 4.05 (t; 1H). ^{13}C NMR ($CDCl_3$); δ ppm: 23.7; 25.9; 26.2; 26.5; 30.3; 33.1; 35.5; 36.8; 37.2; 47.5. GC/MS (IE): m/e: 244 (M^+); 211; 169; 136; 119; 106; 87; 67; 55. Anal.Calcd. for $C_{13}H_{24}S_2$: C, 63.87; H, 9.90; S, 26.23. Found: C,63.61; H, 10.11; S, 26.28.

*1-(N,N-dimethylamino)-3-[(1,3-dithian)-2-yl]-propane (**4 g**)*

^{1}H NMR ($CDCl_3$); δ ppm: 1.68 (q; 2H); 1.77 (q; 2H); 1.78-2.15 (m; 2H); 2.21 (s; 6H); 2.27 (t; 2H); 2.75-2.95 (m; 4H); 4.06 (t; 1H). ^{13}CNMR ($CDCl_3$); δ ppm: 24.7; 25.9; 30.3; 33.2; 45.3; 47.4; 59.1. GC/MS (IE): m/e: 205(M^+); 172; 132; 119; 85; 71; 58. Anal.Calcd. for $C_9H_{19}NS_2$: C, 52.69; H, 9.26; N, 6.83; S, 31.22. Found: C, 52.63; H, 9.32; N, 6.82; S, 31.32.

*1-[(1,3-dithian)-2-yl]-3-[2-methyl-[1,3]-dioxol-2-yl]-propane (**4 h**)*

^{1}H NMR ($CDCl_3$); δ ppm: 1.3 (s; 3H); 1.6-1.7 (m; 4H); 1.77 (q; 2H); 1.8-2.16 (m; 2H); 2.80-2.92 (m; 4H); 3.94 (s; 4H); 4.04 (t; 1H).^{13}C NMR ($CDCl_3$); δ ppm: 21.2; 23.8; 26; 30.3; 35.4; 38.5; 47.39; 64.5; 109.7. GC/MS (IC): m/z: 249 (M+1); 187; 175; 149; 141; 115; 87; 73; 59; Anal.Calcd. for $C_{11}H_{20}O_2S_2$: C, 53.19; H, 8.12; S, 25.81. Found: C, 53.35; H, 8.12; S, 25.62.

*2-[(1,3-dithian)-2-yl]-1-cyclopentanol (**6 e**)*

^{1}H NMR ($CDCl_3$); δ ppm: 1.5-1.8 (m; 4H); 1.9-2-11 (m; 4H); 2.20 (sextuplet; 1H); 2.35 (s; 1H); 2.80-2.96 (m; 4H); 4.04 (d; 1H); 4.19 (q; 1H). ^{13}C NMR ($CDCl_3$); δ ppm: 21.7; 25.6; 28.2; 29.4; 29.6; 34.4; 50.6; 51.8; 76.13. GC/MS (IE): m/e: 204 (M^+); 186; 119; 107; 97; 81; 57.Anal.Calcd. for $C_9H_{16}OS_2$: C, 52.90; H, 7.89; S, 31.38. Found: C, 52.61; H, 7.90; S, 31.65.

*1-[(1,3-dithian)-2-yl]-8-(2-oxiryl)-octane (**8 a**)*

^{1}H NMR ($CDCl_3$); δ ppm: 1.25-1.55 (m; 14H); 1.74 (q; 2H); 1.81-2.15 (m; 2H); 2.46 (dd; 1H); 2.75 (t; 1H); 2.80-2.95 (m; 5H); 4.04 (t; 1H). ^{13}C NMR ($CDCl_3$); δ ppm: 25.9; 26.0; 26.5; 29.3; 30.4; 32.3; 35.3; 47.0; 47.4; 52.2. GC/MS (IC): m/z: 275 (M+1); 257; 241; 215; 201; 167; 149; 121; 107; 95; 71; 55. Anal.Calcd. for $C_{14}H_{26}OS_2$: C, 61.26; H, 9.55; S, 23.36. Found: C, 52.63; H, 9.32; S, 23.44.

*1-[(1,3-dithian)-2-yl]-2-perhydrobenzo[b]oxiren-3-yl-ethane (**8 b**)*

^{1}H NMR ($CDCl_3$); δ ppm: 1.25-1.45 (m; 10H); 1.74 (q; 2H); 1.81-2.15 (m; 2H); 2.80-2.95 (m; 5H); 3.25 (m; 2H); 4.04 (t; 1H). ^{13}C NMR ($CDCl_3$); δ ppm:.23; 23.9; 24.8; 25.6; 26.5; 28.9; 30.0; 31.9; 32.2; 33.2; 47.2; 51.2; 52.0. GC/MS (IC): m/z: 245 (M+1); 227; 211; 185; 137; 119; 107; 89; 75; 57. Anal.Calcd. for $C_{12}H_{20}OS_2$: C, 59.02; H, 8.20; S, 13.12. Found: C, 59.15; H, 8.05; S, 13.32.

*10-chloro-1-[(1,3-dithian)-2-yl]-2-decanol (**9 a**)*

^{1}H NMR ($CDCl_3$); δ ppm: 1.20-1.50 (m; 12H); 1.75 (q; 2H); 1.81-2.15 (m; 4H); 2.80-2.95 (m; 4H); 3.53 (t; 2H); 3.89-3.94 (m; 1H); 4.26 (t; 1H). ^{13}C NMR ($CDCl_3$); δ ppm: 25.4; 26.0; 26.7; 28.7; 29.3; 29.9; 30.20; 32.5; 37.3; 42.6; 44.1; 45.0; 68.2. Anal.Calcd. for $C_{14}H_{26}ClOS_2$: C, 54.28; H, 8.41; S, 20.68; Cl, 11.48. Found: C, 54.08; H, 8.61; S, 20.62; Cl, 11.55.

*4-(2-chloroethyl)-2-[(1,3-dithian)-2-yl]-1-cyclohexanol (**9 b**)*

^{1}H NMR ($CDCl_3$); δ ppm: 1.20-1.90 (m; 9H); 2.10-2.15 (m; 1H); 2.19 (m; 1H); 2.85-3.05 (m; 5H); 3.56 (t; 2H); 3.73-3.80 (m; 1H); 4.49 (d; 1H). ^{13}C NMR ($CDCl_3$); δ ppm: 26.1; 27.0; 29.3; 29.9; 30.7; 30.8; 34.5; 43.2; 44.8; 50.4; 69.7. Anal.Calcd. for $C_{12}H_{21}ClOS_2$: C, 51.33; H, 7.54; S, 22.83; Cl, 12.62. Found: C, 51.44; H, 7.72; S, 22.71; Cl, 12.55.

*1,10-di[(1,3-dithian)-2-yl]-2-decanol (**10a**)*

^{1}H NMR ($CDCl_3$); δ ppm: 1.20-1.60 (m; 14H); 1.75 (q; 2H); 1.80-1.95 (m; 4H); 2.05-2.15 (m; 2H); 2.75-2.95 (m; 8H); 3.91 (m; 1H); 4.04 (t; 1H); 4.26 (t; 1H). ^{13}C NMR ($CDCl_3$); δ ppm: 25.4; 26.0; 26.5; 29.6; 30.0; 30.30; 35.3; 37.5; 42.6; 44.3; 47.6; 68.6. Anal.Calcd. for $C_{18}H_{36}OS_4$: C, 54.50; H, 9.15; S, 32.32; Cl, 11.48. Found: C, 54.79; H,8.98; S, 32.47.

*2-[(1,3-dithian)-2-yl]-4-[2-[(1,3-dithian)-2-yl]-ethyl]-1-cyclohexanol (**10b**)*

^{1}H NMR ($CDCl_3$); δ ppm: 1.40-1.90 (m; 13H); 2.10-2.20 (m; 3H); 2.85-3.00 (m; 9H); 3.74 (m; 1H); 4.03 (t; 1H); 4.49 (m; 1H). ^{13}C NMR ($CDCl_3$); δ ppm: 26.0; 27.2; 27.9; 28.3; 29.2; 29.9; 30.5; 30.7; 32.2; 33.0; 37.7; 44.4; 47.1; 49.1; 50.4; 69.5. GC/MS (IC): m/z: 365 (M+1); 347; 257; 239; 165; 119; 107; 75; 57. Anal.Calcd. for $C_{16}H_{28}OS_4$: C, 52.70; H, 7.74; S, 35.17. Found: C, 52.44; H, 7.77; S, 35.48.

Acknowledgements: The authors thank the referees for helpful comments.

REFERENCES

1. (a) Seebach, D., *Synthesis*, **1969**, 17-36; (b) Bulman Page, P.; Van Niel, M.; Prodger, J., *Tetrahedron*, **1989**, *45*, 7643-7677 and refs cited therein.
2. Corey, E.J.; Seebach, D., *J. Org. Chem.*, **1966**, *31*, 4097-4099.
3. (a) Caubère, P. *Chem. Rev.*, **1993**, *93*, 2317-2334 and refs cited therein; (b) Caubère, P. *Rev. Heteroatom Chem.* **1991**, *4*, 78-138 and refs cited therein.
4. (a) Wakefield, B.J., *The Chemistry of Organolithium Compounds* Pergamon, Oxford, **1974**; (b) Seebach, D.; Corey, E.J., *J. Org. Chem.*, **1975**, *40*, 231-237.
5. Bouisset, M.; Chignac, M.; Pigerol, C., Sanofi French Patent 7,930,039, **1979**, EP 80870053.8, **1980**, *Chem. Abstr.* **1980**, *95*, 168579f.
6. Carré, M.C.; Ndebeka, G.; Riondel, A.; Bourgasser, P.; Caubère, P., *Tetrahedron Lett.*, **1984**, *25(15)*, 1551-1554.
7. Fröling, A.; Arens, J.F., *Rec. Trav. Chim. Pays Bas* , **1962**, *82*, 1009-1011.
8. (a) Perdicakis, M.; Bessière, J., *C. R. Acad. Sc. Paris*, **1982**, Série II, 879-881; (b) Caubère, P.; Loubinoux, B., *Bull. Soc. Chim. Fr.*, **1968**, *9*, 3857-3861.
9. Gros, Ph.; Fort, Y.; Caubère, P., To be published.
10. Corey, E.J.; Seebach, D., *Org.Synth.*, **1970**, *50*, 72.
11. Durman, J.; Elliott, J.; McElroy, A.; Warren, S., *Tetrahedron Lett.*, **1983**, *34*, 3927-3930.
12. Mukayiama, T.; Narasaka, K.; Furusato, M., *J. Am. Chem. Soc.*, **1972**, *94*, 8641-8642.
13. Corey, E.J.; Seebach, D., *Angew. Chem.*, **1965**, *77*, 1134-1135.
14. Vedejs, E.; Fuchs, P.L., *J. Org. Chem.*, **1971**, *36*, 366-367.
15. Carlson, R.M; Helquist, P., *Tetrahedron Lett.*, **1969**, *3*, 173-174.
16. Smith, R.G.; Daves, G.D., *J. Org. Chem.*, **1975**, *40*, 1593-1594.
17. Seebach, D., Jones, N.R., Corey, E.J., *J. Org. Chem.*, **1968**, *33*, 300-301.
18. Stossel, D.; Chan, T.H., *J. Org. Chem.*, **1988**, *53*, 4901-4908.

(*Received in Belgium* 8 *July* 1996; *accepted* 22 *October* 1996)