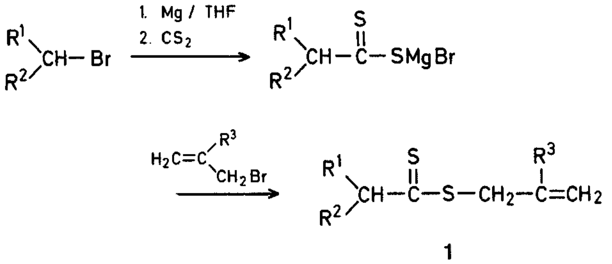
Synthesis of γ,δ-Unsaturated Dithioacids, 1-Alkenyl Alkanedithioates, and γ-Dithiolactones from 2-Alkenyl Alkanedithioates

M. Schoufs, J. Meijer, P. Vermeer, L. Brandsma*

Department of Organic Chemistry of the University, Croesestraat 79, Utrecht, The Netherlands

2-Alkenyl alkanedithioates **1** can be easily obtained by performing the following conversions[1,2].



These dithioesters have been used by us as starting compounds for the synthesis of the new types of sulfur compounds **4**, **6**, and **7**.

Addition of **1** to a slight excess of lithium amide in tetrahydrofuran at −60° led to the formation of the lithium enethiolates **2**, from which the original dithioesters could be recovered by hydrolysis. Compounds **2** have the structure system analogous to that of the ketene-*S*,*S*-acetals **8**, which have been found to undergo a facile thio-Claisen rearrangement[3], and heating of the solutions of **2** could be expected to afford the rearranged products **3**, the salts of the hitherto unknown dithioacids **4**. On the other hand isomerisation of the system $—S—CH_2—C(R^3)=CH_2$ in **2** into the system $—S—CH=C(R^3)CH_3$ in **5** and **6** could be expected to occur by base-catalysis[4].

Table 1. Preparation[1] of 2-Alkenyl Alkanedithioates **1**

R^1	R^2	R^3	Yield[a] [%]	b.p./torr	n_D^{20}
H	H	H	80	92–93°/20	1.5828
H	H	CH_3	85	52–53°/0.1	1.5678
CH_3	H	H	90	96–97°/12	1.5680
CH_3	H	CH_3	92	85–87°/12	1.5555
CH_3	CH_3	H	85	85–86°/12	1.5513
CH_3	CH_3	CH_3	83	65–68°/0.1	1.5460

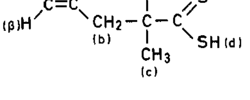
[a] Purity >95 % by ¹H-N.M.R. and G.L.C. analysis.

Table 2. Preparation of γ,δ-Unsaturated Dithioacids **4**

R^1	R^2	R^3	Yield [%]	b.p./torr	n_D^{20}	Molecular formula[a]
H	H	H	90	30–32°/0.5	1.5928	$C_5H_8S_2$ (132.1)
H	H	CH_3	83	35–37°/0.4	1.5810	$C_6H_{10}S_2$ (146.1)
CH_3	H	H	90	32–34°/0.6	1.5682	$C_6H_{10}S_2$ (146.1)
CH_3	H	CH_3	83	38–40°/0.6	1.5603	$C_7H_{12}S_2$ (160.2)
CH_3	CH_3	CH_3	80[b]	38–40°/0.1	1.5572	$C_8H_{14}S_2$ (174.2)
CH_3	CH_3	H	82	34–36°/0.1	1.5598	$C_7H_{12}S_2$ (160.2)

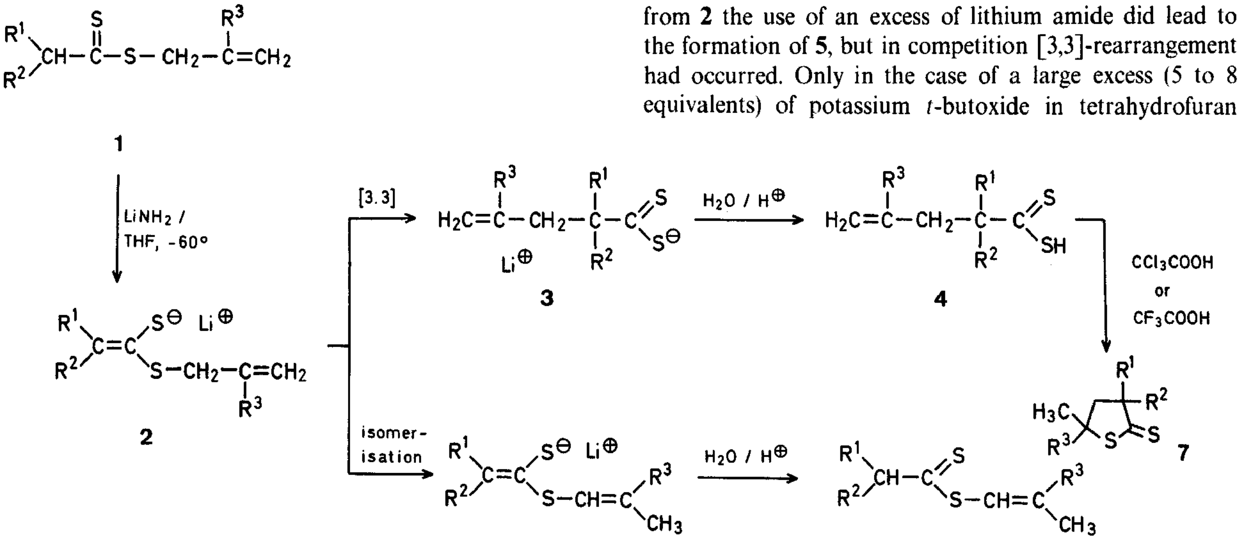
[a] Products of >95 % purity by ¹H-N.M.R.

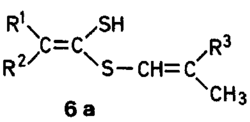
[b]



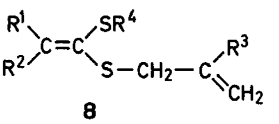
¹H-N.M.R. (CCl_4, TMS $\delta=0$ ppm): $\delta=1.42$ [H(c)]; 1.75 [H(a)]; 2.54 [H(b)]; 4.71 [H(β)]; 4.81 [H(α)]; 6.07 ppm [H(d)].

When the tetrahydrofuran solutions of **2** were heated for 1 h at 50°, complete rearrangement into **3** had occurred in all cases, as became clear after acid hydrolysis giving the dithioacids **4** in good yields. In order to effect a clean isomerisation of **2** into **5**, and thus avoid any [3,3]-rearrangement, the base-catalysis had to be very efficient. Starting from **2** the use of an excess of lithium amide did lead to the formation of **5**, but in competition [3,3]-rearrangement had occurred. Only in the case of a large excess (5 to 8 equivalents) of potassium *t*-butoxide in tetrahydrofuran could a clean formation of **5** be effected. In some cases hydrolysis of **5** with dilute mineralic acids gave the enethiols **6a** in addition to **6**, but treatment of the mixtures with trifluoroacetic acid converted them completely into **6**.





6a



8

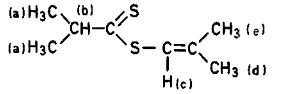
0039–7881/78/0632–0439 $ 03.00

Table 3. Preparation of 1-Alkenyl Alkanedithioates **6**

R^1	R^2	R^3	Yield [%]	b.p./torr	*E*/*Z* ratio	Reaction time	n_D^{20}	Molecular formula[a]
H	H	H	85	68–70°/17	25/75	6 min	1.6065	$C_5H_8S_2$ (132.1)
H	H	CH_3	83	82–84°/17	—	6 min	1.5986	$C_6H_{10}S_2$ (146.1)
H	CH_3	H	83	81–83°/17	27/73	10 min	1.5913	$C_6H_{10}S_2$ (146.1)
H	CH_3	CH_3	87	95–97°/17	—	10 min	1.5877	$C_7H_{12}S_2$ (160.2)
CH_3	CH_3	H	71	87–89°/17	36–64	10 min	1.5735	$C_7H_{12}S_2$ (160.2)
CH_3	CH_3	CH_3	61[b]	100–102°/17	—	30 min	1.5706	$C_8H_{14}S_2$ (174.2)

[a] Products of ≥95% purity by ^{1}H-N.M.R. and G.L.C. analysis showing parent ion peaks in the mass spectra.

[b]



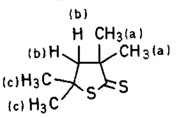
^{1}H-N.M.R. (CCl_4, TMS $\delta=0$ ppm): $\delta=1.28$ [H(a)]; 1.78 [H(e)]; 1.92 [H(d)]; 3.32 [H(b)]; 6.50 ppm [H(c)].

Table 4. Preparation of γ-Dithiolactones **7** from Dithioacids **4**

R^1	R^2	R^3	Yield [%]	b.p./torr	m.p.	n_D^{20}	Molecular formula[a]
H	H	H	66	56–58°/0.15	—	1.6205	$C_5H_8S_2$ (132.1)
H	H	CH_3	81	57–59°/0.15	—	1.5910	$C_6H_{10}S_2$ (146.1)
H	CH_3	H	89	61–62°/0.15	—	1.5937	$C_6H_{10}S_2$ (146.1)
H	CH_3	CH_3	90	61–62°/0.20	40–41°	—[c]	$C_7H_{12}S_2$ (160.2)
CH_3	CH_3	H	80	65–67°/0.15	—	1.5686	$C_7H_{12}S_2$ (160.2)
CH_3	CH_3	CH_3	88[b]	69–71°/0.20	51–52°	—[d]	$C_8H_{14}S_2$ (174.2)

[a] Products of ≥98% purity by ^{1}H-N.M.R. and G.L.C. analysis showing parent ion peaks in the mass spectra.

[b]



^{1}H-N.M.R. (CCl_4, TMS $\delta=0$ ppm): $\delta=1.35$ [H(a)]; 1.63 [H(c)]; 2.39 ppm [H(b)].

[c] $C_7H_{12}S_2$ (160.2)	calc.	C 52.44	H 7.54	S 40.00
	found	52.27	7.53	39.69
[d] $C_8H_{14}S_2$ (174.2)	calc.	C 55.11	H 8.09	S 36.79
	found	54.80	8.03	36.34

In analogy with γ,δ-unsaturated acids the dithio-compounds could be cyclised to the hitherto unknown γ-dithiolactones **7**. Trichloro- and trifluoroacetic acid appeared to be the most effective catalysts.

Preparation of γ,δ-Unsaturated Dithioacids 4:

To a suspension of lithium amide [0.055 mol; prepared from a 1.5 molar solution of butyllithium in hexane (36.6 ml, 0.055 mol) and a slight excess of liquid ammonia (1 ml) at −60°] in tetrahydrofuran (300 ml) is added at once a solution of the dithioester **1** (0.05 mol; for physical constants and yields of **1** see Table 1) in tetrahydrofuran (30 ml) at −60°. Subsequently the temperature of the mixture is raised to 50°. After heating at this temperature for 1 h the solution is poured into a 10% (by weight) aqueous solution of sulfuric acid (300 ml), cooled at −10°. The organic products are extracted with pentane. The combined extracts are well washed with water, dried with magnesium sulfate, and then concentrated in vacuo. For physical constants and yields see Table 2.

Preparation of 1-Alkenyl Alkanedithioates 6:

The dithioester **1** (0.03 mol) is added with vigorous stirring to a solution of potassium *t*-butoxide (0.12 mol for $R^1=H$ or CH_3 and $R^2=CH_3$ or 0.24 mol for $R^1=R^2=H$) in tetrahydrofuran (250 ml) at 25–30°. After 6–30 min of stirring (compare Table 3) at this temperature the reaction mixture is poured into ice/water (200 ml). The aqueous layer is extracted with pentane in order to remove some impurities. Subsequently, the enethiols **6a** ($R^1=H$ or CH_3, $R^2=CH_3$) or the dithioesters **6** ($R^1=R^2=H$) can be isolated by extraction with pentane after acidification of the aqueous layer with sulfuric acid to pH 1 at 0°. Distillation of the enethiols **6a** causes partial isomerisation into the corresponding dithioesters **6**. A complete conversion is effected by treating **6a** ($R^1=H$ or CH_3, $R^2=CH_3$, $R^3=H$ or CH_3) with trifluoroacetic acid (0.2 equiv) in benzene (20 ml) at 20° during 15 min. Physical constants of the isolated compounds **6** are recorded in Table 3.

Formation of γ-Dithiolactones 7 from the γ,δ-Unsaturated Dithioacids 4:

The dithioacid **4** ($R^3=CH_3$; 0.05 mol) is treated with trichloroacetic acid (10 equiv) in benzene (100 ml) during 1 h at 0°. Subsequently the reaction mixture is poured into water (200 ml) and the γ-dithiolactone **7** ($R^3=CH_3$) is extracted with pentane. After repeated washing with water and drying the extracts with magnesium sulfate, the solvent is removed in vacuo, and the residue distilled in a high vacuum. In the case of $R^3=H$ the dithioacid **4** is dissolved in trifluoroacetic acid (40 ml) and cooled at 0°. After 2 h standing at room temperature the solvent is removed in vacuo. The residue is distilled at low pressure. Physical constants and yields of the γ-dithiolactones **7** obtained in this way are collected in Table 4.

Received: February 7, 1978

---

[1] J. Meijer, P. Vermeer, L. Brandsma, *Recl. Trav. Chim. Pays-Bas* **92**, 601 (1973).

[2] J. M. Beiner, A. Thuiller, *C. R. Acad. Sci. Ser. C* **274**, 642 (1972).

[3] P. J. W. Schuijl, L. Brandsma, *Recl. Trav. Chim. Pays-Bas* **87**, 929 (1968).

[4] C. C. Price, W. H. Snyder, *J. Am. Chem. Soc.* **83**, 1773 (1968).