Synthesis of 12- and 13-Membered Sulfur-Containing Lactones by Homolytic Macrocyclization of Mercaptoacetic Esters with Alkynes

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Received 11 August 1994

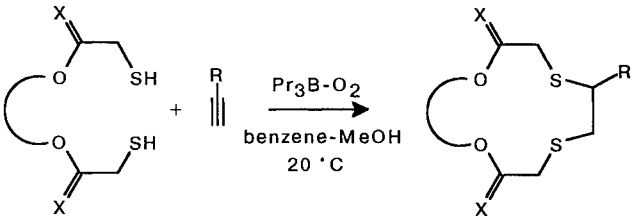
Starting from mercaptoacetic acid esters of 1,2- or 1,3-diols and substituted acetylenes 12- and 13-membered sulfur-containing lactones as 1:1 adducts were synthesised in yields up to 48%. The mechanism of this homolytic reaction, which is initiated by the tripropylborane/oxygen system, includes generation of thiyl radicals and their addition to the triple bond of alkynes.

Condensation of dihalides or ditosylates with glycols or dithiols presents the most common method for the preparation of crown ethers.[1] Especially successful is the template reaction with cesium salts which gives crown thioethers with good yields and selectivity.[2] The reactions of inter- or intramolecular acylation of bifunctional carboxylic acids or their derivatives were also used for the synthesis of macrocycles containing ester or amide groups.[3] Earlier we have suggested the cycloaddition of α,ω-dithiols to alkynes as a method suitable for obtaining sulfur-containing rings of different sizes from 6- and 7-[4] up to 12–21-membered.[5,6] The method employs readily available reagents and an operationally simple experimental procedure.

In the present work we describe the utilization of mercaptoacetic acid esters of 1,2- and 1,3-dithiols as substrates of macrocyclization. We have shown that under radical reaction conditions 1,8- and 1,9-dithiols (products of esterification of 1,2- and 1,3-diols with mercaptoacetic acid), can be attached to alkynes with the formation of 12- and 13-membered sulfur-containing lactones. Thus, the homolytic addition of ethylene glycol diester **1a** to alkynes **2a–d** in the presence of tripropylborane/oxygen system led to 12-membered macrocycles **3a–d** (Scheme 1) in yields up to 48%. Bicyclic product **3e** was obtained from the ester of *trans*-1,2-cyclohexanediol **(1b)**. As it was reported in a preliminary communication,[6] ethers like 3,6-dioxa-1,8-octanedithiol **(1c)** can also be transformed into macrocycles **3f–h**. Substrates **1d–g** derived from 1,3-diols gave the corresponding substituted 13-membered macrocycles **3j–s** including spirolactones **3r,s**. The latter compounds contain two 13-membered rings and were synthesized from pentaerythritol ester in 25 and 42% yield (Table 1).

^1H, ^{13}C NMR and spin-spin coupling constants data for the compounds **3** are presented in Tables 2–6. 12-Membered macrocycles **3a,b**, containing alkyl substituents, and 13-membered **3p–s** are crystalline compounds. The structure of **3a** was proved by X-ray analysis (Figure).[7]

The starting esters **1a–g** were obtained in good yields by acid-catalyzed esterification of glycols with excess of mercaptoacetic acid and were purified by distillation in vacuo. Compounds **1b,g** were purified by chromatography. Formation of 12-membered macrocycles from the simplest alkynes prop-1-yne and hex-1-yne proceeded most smoothly. The reaction was exothermic and after 10–15 minutes the TLC analysis showed the absence of the



1a-g **2a-f** **3a-s**

	X	1	R	2	3
	O	**1a**	Me	**2a**	**3a**
			Bu	**2b**	**3b**
			CH_2OAc	**2c**	**3c**
			CMe_2OH	**2d**	**3d**
	O	**1b**	Bu	**2b**	**3e**
	H_2	**1c**	Me	**2a**	**3f**[a]
			Bu	**2b**	**3g**[a]
			CH_2OAc	**2c**	**3h**[a]
			CH_2OMe	**2e**	**3i**
	O	**1d**	Me	**2a**	**3j**
			Bu	**2b**	**3k**
			CH_2OAc	**2c**	**3l**
			CH_2OMe	**2e**	**3m**
	O	**1e**	Bu	**2b**	**3n**
			CH_2OH	**2f**	**3o**
	O	**1f**	Me	**2a**	**3p**
			CH_2OMe	**2e**	**3q**
	O	**1g**	Bu	**2b**	**3r**
			CH_2OMe	**2e**	**3s**

[a] Ref. 6

Scheme 1

Table 1. Compounds **3a–s** Prepared

Product[a]	Eluent (R_f)	Yield[b] (%)	mp (°C)	MS (70 eV) *m/z* (%)
3a	benzene/Et_2O (20 : 1) (0.24)	48	102–104	250 (M^+, 55), 151 (40), 119 (73), 118 (83), 87 (63), 86 (100), 83 (80), 75 (53), 74 (43), 73 (41)
3b	pentane/Et_2O (5 : 1) (0.25)	38	77–80	292 (M^+, 67), 162 (57), 142 (41), 133 (68), 119 (65), 118 (77), 115 (100), 101 (37), 86 (66), 82 (45)
3c	heptane/EtOAc (1 : 1) (0.31)	35	oil	308 (M^+, 21), 248 (100), 149 (62), 129 (35), 123 (33), 119 (55), 118 (38), 113 (28), 109 (28), 105 (25), 103 (41)
3d	heptane/EtOAc (1 : 2) (0.29)	15	oil	294 (M^+, 24), 238 (75), 237 (70), 236 (100), 208 (35), 207 (90), 145 (95), 133 (73), 118 (74), 105 (80), 87 (85)
3e	heptane/EtOAc (4 : 1) (0.32)	23	oil	346 (M^+, 66), 173 (72), 172 (76), 161 (39), 140 (48), 115 (93), 83 (41), 81 (100), 55 (44), 41 (44)
3f[c]		30	oil	
3g[c]		28	oil	
3h[c]		21	oil	
3i	benzene/EtOAc (6 : 1) (0.40)	15	oil	252 (M^+, 100), 204 (52), 109 (71), 102 (61), 89 (63), 85 (48), 83 (55), 75 (36), 73 (45), 71 (87)
3j	benzene/Et_2O (6 : 1) (0.33)	32	oil	264 (M^+, 100), 133 (69), 132 (72), 119 (30), 105 (21), 104 (76), 100 (93), 87 (28), 74 (21), 73 (22)
3k	heptane/EtOAc (3 : 1) (0.49)	30	oil	306 (M^+, 24), 161 (30), 133 (49), 132 (41), 115 (100), 101 (42), 100 (66), 83 (43), 82 (47), 73 (26)
3l	heptane/EtOAc (3 : 2) (0.20)	21	oil	322 (M^+, 7), 263 (40), 262 (100), 177 (33), 133 (84), 132 (52), 117 (50), 103 (60), 101 (36), 100 (79), 73 (73)
3m	hexane/EtOAc (3 : 1) (0.31)	20	71–73	294 (M^+, 57), 294 (15), 262 (93), 145 (14), 133 (32), 119 (13), 105 (28), 103 (100), 100 (24), 71 (21)
3n	heptane/EtOAc (6 : 1) (0.36)	24	oil	334 (M^+, 100), 292 (32), 175 (31), 161 (64), 156 (29), 142 (34), 128 (30), 115 (57), 114 (27), 101 (28)
3o	heptane/EtOAc (3 : 2) (0.18)	18	oil	308 (M^+, 32), 290 (100), 179 (36), 161 (81), 160 (66), 135 (64), 131 (42), 128 (70), 105 (46), 103 (56), 87 (58)
3p	heptane/EtOAc (5 : 1) (0.35)	27	85–86	318 (M^+, 100), 168 (67), 133 (77), 132 (39), 128 (56), 119 (53), 114 (57), 95 (71), 87 (54), 81 (64)
3q	heptane/EtOAc (4 : 1) (0.26)	26	88–89	348 (M^+, 62), 316 (100), 163 (33), 154 (43), 150 (95), 103 (76), 102 (38), 85 (52), 83 (98), 81 (57)
3r	0.5% MeOH in CH_2Cl_2 (0.25)	25	130–132	596 (M^+, 69), 349 (64), 197 (49), 163 (47), 162 (48), 161 (100), 157 (46), 156 (83), 129 (56), 115 (79)
3s	1% MeOH in CH_2Cl_2 (0.15)	42	110–113	572 (M^+, 11), 543 (13), 541 (18), 446 (14), 151 (7), 149 (60), 103 (19), 83 (12), 72 (9), 71 (100)

[a] Satisfactory microanalyses obtained: C ± 0.25, H ± 0.22, S ± 0.30.
[b] After column chromatography.
[c] Compounds **3f–h** were obtained earlier. Their analytical and spectral properties are reported in Ref. 6.

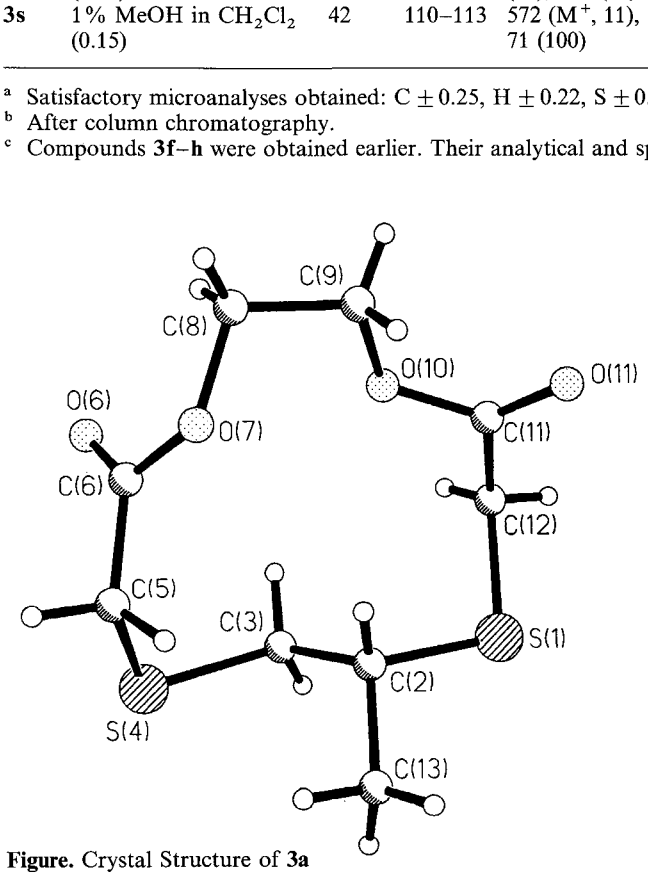


Figure. Crystal Structure of **3a**

starting dithiol **1** in the reaction mixture. In all other cases the starting dithiol and alkyne reacted completely in a period from 30 minutes to 24 hours at room temperature and concentration of about 0.1 mol/L.

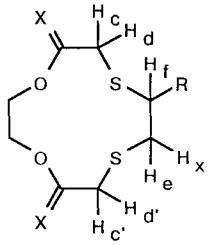
The reaction, which is initiated by the tripropylborane/oxygen system, implies an initial generation of thiyl radicals followed by their addition to the triple bond of alkynes. Besides 1 : 1 adducts **3a–s**, higher cyclooligomers like 2 : 2 adducts **4** were also formed (Scheme 2), which were isolated in some cases. Similar complications were also observed previously in homolytic addition of 1,2- and 1,3-dithiols.[5,8,9] NMR data showed that oligomers **4** were formed as mixtures of positional and stereoisomers. Higher molecular weight telomers were inevitably formed as side products of the described reaction. However, the macrocyclic lactones **3** are easily separated from the mixture by chromatography.

In summary, the simplicity of the suggested method makes it suitable for construction of 12- and 13-membered macrocyclic sulfur-containing lactones.

Table 2. ^{1}H NMR Data of Compounds **3a–i** ($CDCl_3$/TMS) δ, J (Hz)[a, b]

3	CH_2O	H_c	H_d	$H_{c'}$	$H_{d'}$	H_e	H_f	H_x	R
3a	4.45 (m, 4H)	3.24 d	3.34 d	3.23 s		2.60 dd	3.03 dd	3.11 m	1.37 (d, 3H, J = 7.5)
3b	4.45 (m, 4H)	3.20 d	3.23 d	3.26 d	3.30 d	2.77 dd	3.00 dd	2.95 m	0.93 (t, 3H, J = 7.2), 1.25–1.57 (m, 5H), 1.80 (m, 1H)
3c	4.20–4.40 (m, 4H)	3.19 d	3.41 d	3.25 d	3.27 d	2.82 dd	2.93 dd	3.37 m	2.12 (s, 3H), 4.50–4.75 (m, 2H)
3d	4.17 (m, 2H), 4.83 (m, 2H)	3.19 d	3.26 d	3.22 d	3.46 d	2.70 dd	3.06–3.17 m		1.32 (s, 3H), 1.35 (s, 3H), 3.91 (br s, 1H)
3e	4.70–4.95 (m, 2H)[c]	3.10 d	3.31 d	3.03 d	3.16 d	2.40 dd	2.95 dd	2.75 m	0.81 (t, 3H, J = 7.0), 1.10–1.45 (m, 5H), 1.75–1.89 (m, 1H)[d]
3i	3.42–3.60 (m, 8H)	2.55–2.73 (m, 5H)					3.08 dd	3.42–3.60 m	3.25 (s, 3H), 3.70–3.85 (m, 2H)

[a] **3a–i**.

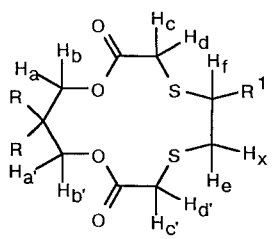


[b] For coupling constants of H_c-H_x, see Table 4.
[c] CHO.
[d] Tetramethylene chain: δ = 1.10–1.45 (m, 4H), 1.58–1.73 (m, 2H), 1.90–2.08 (m, 2H).

Table 3. ^{1}H NMR Data of Compounds **3j–s** ($CDCl_3$/TMS) δ, J (Hz)[a, b]

3	H_a	H_b	$H_{a'}$	$H_{b'}$	H_c	H_d	$H_{c'}$	$H_{d'}$	H_e	H_f	H_x	R	R^1
3j		4.22–4.42 m			3.17 d	3.39 d	3.18 d	3.27 d	2.56 dd	2.98–3.12 m		2.10 (m, 2H)	1.37 (d, 3H, J = 7.6)
3k		4.27–4.43 m			3.16 d	3.39 d	3.20 d	3.27 d	2.67 dd	3.07 dd	2.85–2.96 m	2.09 (m, 2H)	0.92 (t, 3H, J = 6.9), 1.20–1.55 (m, 5H), 1.78–1.98 (m, 1H)
3l		4.16–4.38 m			3.15 d	3.26 d	3.25 s		2.76 dd	2.89 dd	3.16 m	2.04 (m, 2H)	2.07 (s, 3H), 4.16–4.38 (m, 2H)
3m		4.10–4.30 m			3.16 d	3.22 d	3.09 d	3.17 d	2.72 dd	2.83 dd	3.01 m	1.97 (m, 2H)	3.25 (s, 3H), 3.52 (dd, 1H, J = 9.9, 3.9), 3.57 (dd, 1H, J = 9.9, 5.5)
3n	3.89 d	4.02 d	3.93 d	4.01 d	3.15 d	3.28 d	3.16 d	3.22 d	2.65 dd	2.92 dd	2.79 m	1.01 (s, 3H), 1.03 (s, 3H)	0.90 (t, 3H, J = 7.4), 1.22–1.55 (m, 5H), 1.76–1.89 (m, 1H)
3o	3.82 d	4.03 d		3.96 s	3.19 d	3.25 d	3.16 d	3.24 d	2.76–2.84 m		2.88–2.99 m	0.98 (s, 3H), 1.02 (s, 3H)	2.53 (br s, 1H), 3.69–3.82 (m, 2H)
3p	3.99 d	4.09 d		4.06 s	3.16 d	3.32 d	3.19 d	3.25 d	2.55 dd	3.00 dd	2.97 m	1.44–1.56 (m, 4H), 1.60–1.72 (m, 4H)	1.36 (d, 3H, J = 7.3)
3q	3.96 d	4.12 d		4.07 s	3.18 d	3.26 d	3.25 d	3.31 d	2.83–2.89 m		2.98–3.10 m	1.37–1.73 (m, 8H)	3.39 (s, 3H), 3.63 (dd, 1H, J = 11.8, 10.3), 3.65 (dd, 1H, J = 11.8, 9.3)
3r		4.08–4.22 m			3.16 d	3.28 d	3.18 d	3.22 d		2.61–2.89 m		–	0.89 (t, 3H, J = 7.2), 1.22–1.55 (m, 5H), 1.67–1.84 (m, 1H)
3s		4.00–4.30 m				3.10–3.30 m				2.65–2.95 m		–	3.33 (s, 3H), 3.54 (m, 2H)

[a] **3j–s**:

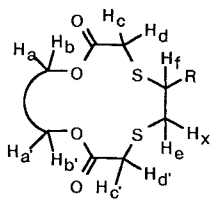


[b] For coupling constants of H_c-H_x, see Table 4.

Table 4. ^{1}H-^{1}H Spin-Spin Coupling Constants for Compounds **3a–r** (Tables 2 and 3) J (Hz)[a,b]

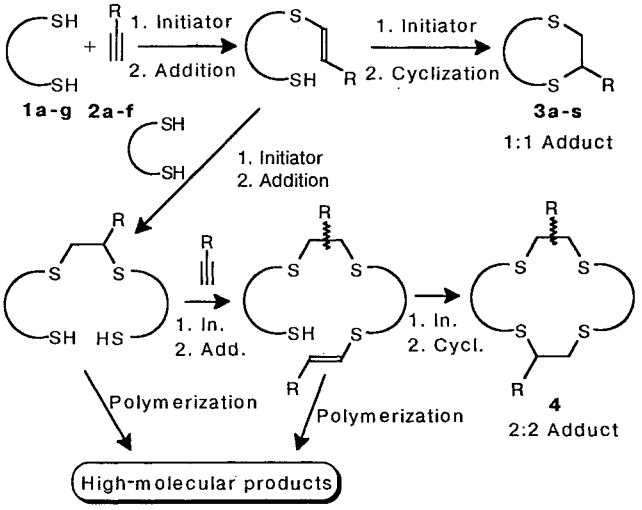
3	J_{cd}	$J_{c'd'}$	J_{ef}	J_{ex}	J_{fx}
3a	14.2	–[c]	12.8	9.2	4.8
3b	13.8	13.8	14.0	10.7	4.9
3c	14.2	14.2	14.2	6.8	8.3
3d	14.0	14.0	15.7	10.7	–[c]
3e	14.0	14.0	13.7	9.5	4.6
3i	–[c]	–[c]	13.5	–[c]	4.8
3j	15.0	15.0	15.0	11.4	–[c]
3k	14.5	14.5	13.6	9.7	3.9
3l	14.4	–[c]	14.4	8.1	6.3
3m	14.3	14.3	14.3	9.4	3.9
3n	14.1	14.1	13.4	8.9	4.5
3o	13.7	13.7	–[c]	–[c]	–[c]
3p	14.1	14.1	14.6	11.4	4.4
3q	14.0	14.0	–[c]	–[c]	–[c]
3r	14.7	15.7	–[c]	–[c]	–[c]

[a]



[b] Determination of J_{ab} and $J_{a'b'}$ usually was complicated. Commonly their calculated values were equal to 11.0–11.4 Hz.

[c] Full analysis was not performed due to the very complex character of the spectrum.



Scheme 2

carried out on a Chrom-5 instrument equipped with a 3 m × 5 mm glass column with 5% SE-superphase on Inerton-N-AW 0.12 × 0.20 mm. Melting points were determined on a Kofler block and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on Bruker WM-250 spectrometer in $CDCl_3$ with TMS as an internal standard. Mass spectra were obtained using a Varian MAT CH-6 spectrometer at 70 eV.

Esterification of 1,2- and 1,3-Diols With Mercaptoacetic Acid; General Procedure:

A mixture containing diol (92 mmol) and mercaptoacetic acid (2.49 g, 27 mmol) was boiled with TsOH (0.5 g, 2.6 mmol) in toluene

Table 5. ^{13}C NMR Data of Compounds **3a–i**, δ

3	C=X	C=X	CH_2O	CH_2O	CHS	SCH_2CH	CH_2SCH	CH_2SCH_2	R
3a	169.93	169.83	61.80	61.69	39.32	38.81	33.29	32.52	19.54 (CH_3)
3b	170.29	170.13	62.01		45.95	37.90	33.33		13.68 (CH_3), 22.44, 28.42, 33.71 (3CH_2)
3c	169.66	169.50	62.17	61.66	44.31	35.28	34.50	32.75	20.49 (CH_3), 64.84 (CH_2), 170.24 (C=O)
3d	170.86	170.16	62.72	61.48	58.78	36.92	36.04	35.38	26.15, 26.91 (2CH_3), 74.31 (C)
3e	170.33, 169.03[a]	170.11, 168.87[a]	74.82[b]	74.50	47.58, 41.34[a]	34.08, 33.60, 31.97, 31.70, 31.49, 30.29[a]			13.61 (CH_3), 22.17, 28.07, 34.84 (3CH_2)[c]
3i	74.33	74.12	70.55	70.29	46.13	35.35	32.12	31.47	59.01 (CH_3), 73.51 (CH_2)

[a] Mixture of stereoisomers.

[b] CHO.

[c] For tetramethylene chain, δ = 23.41 (2CH_2), 30.07 (2CH_2).

The solvents of reagent quality for the reaction and chromatography were dried and distilled under argon. Commercially available chemicals were of reagent grade, and used without further purification. *trans*-1,2-Cyclohexanediol was obtained by oxidation of cyclohexene using H_2O_2 in HCO_2H; mp 103°C (70%). 2,2-Dimethylpropane-1,3-diol was prepared by $LiAlH_4$ reduction of dimethylmalonic acid in Et_2O; mp 123–126°C (75%). 1,1-Bis(hydroxymethyl)cyclopentane was prepared by $LiAlH_4$ reduction of corresponding ester in Et_2O; mp 88–91°C (80%). 3,6-Dioxaoctane-1,8-dithiol (**1c**) was obtained from triethylene glycol by treatment with thiourea in conc. HCl; bp 83°C/0.1 Torr (55%). Tripropylborane was prepared by the interaction of $BF_3 \cdot E_2O$ with PrMgBr;[10] bp 53°C/10 Torr (85%). To prepare a 1 M solution of Pr_3B in hexane, Pr_3B (11.2 g, 15.5 mL) was dissolved in hexane (64.5 mL) under Ar.

TLC analysis was performed on Silufol plates. The spots were detected by plunging into a $KMnO_4$ solution. For flash chromatography silica gel L 40 × 100 was used. Gas chromatography was

(100 mL) until the evolution of H_2O was over. The solution was cooled, washed with H_2O (100 mL), sat. aq solution of $NaHCO_3$ (3 × 100 mL), H_2O (50 mL) and dried ($MgSO_4$). The solvent was evaporated and then **1a,d–f** were distilled in vacuo. **1a:** bp 126–30°C/0.15 Torr (70%); **1d:** bp 142–6°C/0.3 Torr (75%); **1e:** bp 120–30°C/0.1 Torr (56%); **1f:** bp 120–5°C/0.08 Torr (60%). **1b** (90%) and **1g** (52%) were used without further purification. All the starting compounds were pure according to TLC and GC data.

Macrocyclization of Dithiols 1 With Alkynes 2; General Procedure:

To a solution of dithiol **1** (4 mmol), alkyne **2** (4 mmol) and MeOH (0.65 mL, 12 mmol) in benzene (40 mL) in an Ar atmosphere was added a 1 M solution of Pr_3B in hexane (4 mmol, 4 mL). The reaction was monitored by TLC and GC until the dithiol was completely converted. The solvent was evaporated in vacuo, and the reaction products **3a–r** were isolated by column chromatography. Solvents for chromatography are listed in Table 1. Besides compounds **3a,p,q**, the corresponding 2:2 adducts **4a,p,q** were also isolated.[11]

Table 6. ^{13}C NMR Data of Compounds **3j–s**, δ

3	C=O	C=O	CH_2O	CH_2O	CHS	SCH_2CH	CH_2SCH	CH_2SCH_2	CR_2	R	R^1
3j	170.65			64.19	40.53	40.00	34.19	33.30	27.32	–	19.45 (CH_3)
3k	170.65	170.55		63.92	46.40	39.62	34.14	32.65	27.22	–	13.7 (CH_3), 22.27, 28.42, 33.38 (3 CH_2)
3l	170.30			63.44	45.25	34.93	34.06	33.45	26.92	–	20.55 (CH_3), 64.77 (CH_2), 170.56 (C=O)
3m	170.78			63.81	46.08	34.92	34.16	33.60	27.06	–	59.11 (CH_3), 77.35 (CH_2)
3n	171.01	170.85		71.08	47.10	38.75	34.40	33.42	33.97	22.41 (2 CH_3)	13.92 (CH_3), 22.47, 28.50, 33.67 (3 CH_2)
3o	171.01	170.71		70.77	49.52	35.05	34.55	33.53	33.85	22.36 (2 CH_3)	63.54 (CH_2)
3p	171.07			70.00	40.81	39.74	34.18	33.25	44.92	24.82 (2 CH_2), 33.17 (2 CH_2)	19.81 (CH_3)
3q	170.99		69.68	69.59	46.63	35.22	34.60	33.77	44.86	24.79 (2 CH_2), 33.09 (2 CH_2)	59.13 (CH_3), 73.87 (CH_2)
3r	170.61	170.40		63.08	47.55	38.85	34.38	33.59	41.25	–	13.97 (CH_3), 22.51, 28.62, 33.90 (3 CH_2)
3s	169.63	168.16		62.91	46.92	35.44	34.63	33.65	41.29	–	59.17 (CH_3), 74.49 (CH_2)

The authors are grateful to the Russian Foundation of Fundamental Studies for financial support (Project 93-03-18110).

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(7) Crystals of **3a** are monoclinic, $a = 14.12(3)$, $b = 5.513(7)$, $c = 14.95(4)$ Å, $\beta = 97.44(2)°$, space group $P2_1/c$, $Z = 4$ ($C_9H_{14}O_4S_2$), $d_c = 1.440$ g/cm^3, μ(MoKα) = 4.53 cm^{-1}. Unit cell parameters and intensities of 2258 independent reflections were measured with an automatic four-circle Siemens P3/PC diffractometer at r.t. (λMoKα, graphite monochromator, $\theta/2\theta$-scan, $2\theta_{max} = 50°$). The structure was solved by the direct method and refined by the full-matrix least-squares procedure in the anisotropic approximation for non-hydrogen atoms. Hydrogen atoms were located in the different Fourier synthesis and refined isotropically. The final discrepancy factors were: $R = 0.075$, $R_w = 0.102$, GOF = 1.34 for 1315 observed ($I > 2.5\sigma(I)$) reflections and 192 refined parameters. All calculations were carried out with an IBM-PC/AT computer using SHELXTL PLUS program package (Robinson W., Sheldrick G.M. SHELX In: *Crystallographic Computing-Techniques and New Technologies*, Isaacs N.W.; Taylor M.R. (Eds.); Oxford Univ. Press; Oxford, 1988, 366). Selected Bond Lengths (Å): S(1)-C(2), 1.836(8), C(2)-C(3), 1.539(11), C(3)-S(4), 1.834(8), S(4)-C(5), 1.811(9), C(5)-C(6), 1.498(11), C(6)-O(7), 1.359(8), O(7)-C(8), 1.438(9), C(8)-C(9), 1.484(11), C(9)-O(10), 1.443(10), O(10)-C(11), 1.348(9), C(11)-C(12), 1.495(11), S(1)-C(12), 1.815(9), C(2)-C(13), 1.523(11); Selected Bond Angles (°): C(2)-S(1)-C(12), 104.8(4), S(1)-C(12)-C(11), 111.7(5), S(1)-C(2)-C(13), 106.7(6), S(1)-C(2)-C(3), 110.0(5), C(3)-C(2)-C(13), 113.9(6), C(2)-C(3)-S(4), 114.6(5), C(3)-S(4)-C(5), 101.6(4), S(4)-C(5)-C(6), 113.1(5), C(5)-C(6)-O(6), 126.1(6), C(5)-C(6)-O(7), 109.6(6), O(6)-C(6)-O(7), 124.3(6), C(6)-O(7)-C(8), 117.6(5), O(7)-C(8)-C(9), 108.5(6), C(8)-C(9)-O(10), 106.5(6), C(9)-O(10)-C(11), 117.6(5), O(10)-C(11)-O(11), 123.5(6), O(10)-C(11)-C(12), 110.2(6), O(11)-C(11)-C(12), 126.2(7); torsion angles (τ,°), S(1)-C(2)-C(3)-S(4), 171.8(4), C(12)-S(1)-C(2)-C(13), −174.3(6).

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(11) **4a** (9%): ^1H NMR ($CDCl_3$/TMS): $\delta = 1.37$ (d, 6H, $J = 6.9$ Hz), 2.67 (m, 2H), 2.98–3.08 (m, 2H), 3.08–3.20 (m, 2H), 3.20–3.45 (m, 8H), 4.36 (m, 8H); MS: m/z (%) = 83 (100), 105 (90), 91 (80), 97 (64), 135 (60), 119 (58), 500 (44, M^+), 147 (34), 284 (33), 62 (30). **4p** (8%): ^1H NMR ($CDCl_3$/TMS): $\delta = 1.35$ (d, 6H, $J = 6.9$ Hz), 1.45–1.55 (m, 8H), 1.55–1.70 (m, 8H), 2.59–2.75 (m, 2H), 3.00–3.43 (m, 12H), 3.95–4.02 (m, 8H); MS: m/z (%) = 318 (100), 133 (75), 95 (71), 67 (66), 272 (64), 81 (63), 115 (62), 114 (61), 113 (58), 119 (57), 636 (53, M^+). **4q** (3%): ^1H NMR ($CDCl_3$/TMS): $\delta = 1.45$–1.70 (m, 16H), 2.94 (m, 4H), 3.20 (m, 2H), 3.27–3.40 (m, 8H), 3.35 (s, 6H), 3.53–3.67 (m, 4H), 4.02 (s, 8H); MS: m/z (%) = 95 (100), 71 (96), 103 (86), 131 (64), 81 (59), 149 (55), 387 (48), 154 (46), 118 (44), 665 (43), 696 (14, M^+).