Tetrahedron Vol. 44, No. 14, pp. 4389 to 4397, 1988
Printed in Great Britain.

0040-4020/88 $3.00+.00
Pergamon Press plc

INTRAMOLECULAR ARYLSULPHOETHERIFICATION AND LACTONIZATION OF UNSATURATED ALCOHOLS AND CARBOXYLIC ACIDS INITIATED BY ANODIC OXIDATION OF DISULPHIDES

SABINE TÖTEBERG-KAULEN and EBERHARD STECKHAN*

Institut für Organische Chemie und Biochemie der Universität Bonn, Gerhard-Domagk-Str. 1, D- 5300 Bonn 1, F.R.G.

(*Received in Germany* 9 *March* 1988)

Abstract: The intramolecular sulphoetherification respectively sulpholactonization of alkenols and alkenoic acids can be initiated by addition of electrochemically generated sulphenyl cations starting from disulphides. The reaction can either be initiated by indirect electrochemical oxidation of diphenyldisulphide using bromide as redox catalyst or preferably by direct anodic oxidation of bis(4-methoxyphenyl)disulphide. 5- and 6-membered thioaryl substituted ethers and lactones thus may be generated starting preferably from mono or disubstituted alkenols and alkenoic acids. The reaction occurs as a trans-addition to the double bond while for endocyclic double bonds the new ring is cis-annelated.

1. INTRODUCTION

Cyclic ethers or lactones may be synthesized from unsaturated alcohols or acids by halolactonization[1] or phenylselonoetherfication[2]. These reactions using bromine, iodine, or phenylselenyl reagents lead to halogen or selenium substituted products.

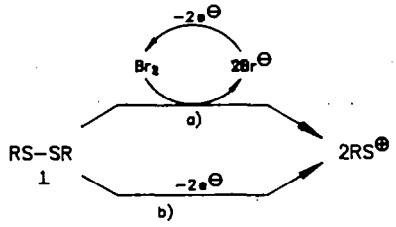
We now want to report upon the intramolecular cyclization of unsaturated alcohols and acids in the presence of electrochemically generated sulphenyl cations leading to arylthio substituted ring systems (Scheme 1).

This new method offers the following advantages compared to the known intramolecular cyclization reactions:

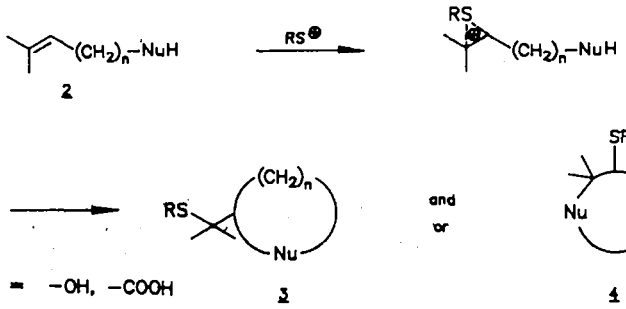
1) The reagent RS^+ is generated in situ from inexpensive and easily available disulphides.
2) The sulphur compounds are less toxic as for example the selenium compounds used in the phenylselenoetherfication.
3) The thio function in the cyclic product is a versatile functional group for further synthetic application. The oxidative or reductive cleavage of the C-S bond offers an entry to both saturated and unsaturated ring systems.

It is well known from the literature that the electrochemical generation of sulphenyl cations from disulphides may be carried out by either direct anodic oxidation[3] (procedure B, Scheme 1, eq. 1b) or by indirect anodic oxidation using bromide ions as redox catalysts[4] (procedure A, Scheme 1, eq. 1a). The bromide mediated electrolysis has the advantage of a low oxidation potential (E_{pox}

Br_2/Br^- = 1.1 V vs. SHE[5]), while direct electrolysis following the proposed reaction sequence is limited to those disulphides with an oxidation potential sufficiently lower than that of the unsaturated substrates.



(1)

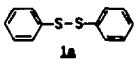
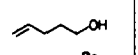
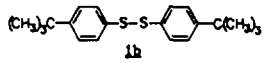
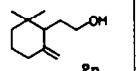
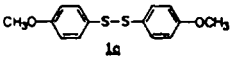
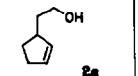
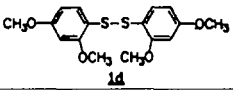
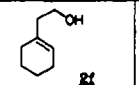
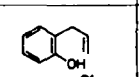


Scheme 1. Principal pathways for the electrochemically initiated arylsulphoetherification and -lactonization

2. ELECTROANALYTICAL STUDIES

The oxidation potentials of different disulphides and unsaturated alcohols were determined by cyclic voltammetry and the results summarized in **Table 1** demonstrate that disulphides **1a - 1d** have sufficiently lower oxidation potentials than alkenes of varying substitution pattern, except for the allylphenol **2**, which is oxidized at the aromatic ring

Table 1: Oxidation Potentials E_{pox} of the Disulphides 1a – 1d and Alkenes 2a, 2n, 2e, 2f, 2l

1	$E_{pox}^{a)}$ vs SHE [V]	2	$E_{pox}^{a)}$ vs SHE [V]
 1a	1.75	 2a	>2.4
 1b	1.68	 2n	2.31
 1c	1.54	 2e	2.22
 1d	1.31	 2f	2.09
		 2l	1.66

a) working electrode: Pt, measured against $Ag/AgNO_3$, calculated to SHE
electrolyte: 0.2M $LiClO_4$ / CH_3CN : CH_2Cl_2 = 1:1

3. PREPARATIVE ELECTROLYSES

3.1 Indirect Electrochemical Oxidation of Diphenyldisulphide in Presence of Bromide (Procedure A)

The electrolyses were carried out in a divided cell with platinum electrodes under constant current conditions. Tetrabutylammonium bromide in dichloromethane served as electrolyte and mediator at the same time. Substrates for the cyclization experiments were unsaturated alcohols and carboxylic acids of varying chain length and substitution.

Table 2 demonstrates that the expected cyclization takes place but is limited to the formation of 5- and 6-membered rings. In all other cases various open-chain products are formed which are mainly obtained by the addition of phenylsulphenylbromide or bromine to the double bond. Terminal, monosubstituted double bonds give the best yields of the desired cyclic products, whereas with higher substituted double bonds the addition of bromine is favored. The regiochemistry of the cyclization clearly follows the Markownikow rule except for substrate **2f**. The formation of the anti-Markownikow product **4f** may be explained by a primary cyclization under Markownikow control to the spiro compound with a 4-membered ring **3f**, which subsequently rearranges to the thermodynamically more stable 5-membered ring **4f**[6].

The stereochemical course of the reaction was investigated by NMR studies at the bicyclic product **3m**. By decoupling experiments we found that the rings are cis-fused and the the thio group is arranged trans to the ring ($J_{C1-H/C2-H}$ = 5.2 Hz; $J_{C2-H/C3-H}$ = 3.5 Hz).

As most of the side reactions hindering the cyclization are caused by nucleophilic attack of bromide ions, it is obvious to investigate cyclization reactions initiated by direct oxidation of the disulphides avoiding bromide as mediator.

3.2 Direct Electrochemical Oxidation of Various Disulphides (Procedure B)

Contrary to the electroanalytical predictions direct electrolysis with disulphides **1a** and **1b** showed electrode fouling caused by an oxidative attack at the double bond of the substrate. Only 5-hexenol (**2b**), a compound with a terminal double bond gave small amounts of the desired ring system. Good yields of 5- and 6-membered cyclic ethers and lactones, however, were obtained in the direct electrochemical oxidation of bis(4-methoxyphenyl)disulphide (**1c**), which has a 200 mV lower oxidation potential than **1a** and **1b**. The results are given in **Table 3**.

The stereochemical course of the reaction is identical to the bromide mediated sequence (procedure A). Monosubstituted and 1,1-disubstituted alkenols and alkenoic acids worked especially well, while moderate yields were obtained with 1,2-disubstituted double bonds.

The synthetic applicability is nicely demonstrated in the case of the more complex substrate γ-cyclohomogeraniol (**2m**), which was obtained from 2-methylcyclohexanone in eight steps according to a literature synthesis[7]. The intramolecular cyclization of **2m**, initiated by the direct anodic oxidation of bis(4-

Table 2: Cyclization Reactions Initiated by the Bromide Mediated Anodic Oxidation of Diphenyldisulphide (1a)

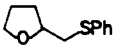
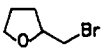
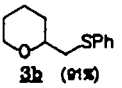
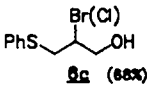
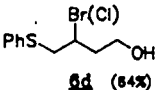
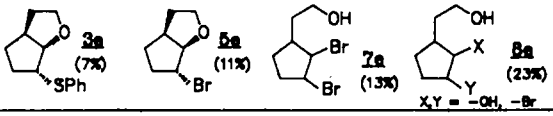
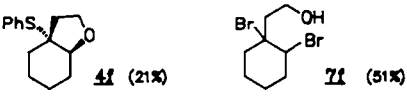
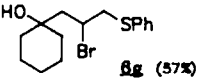
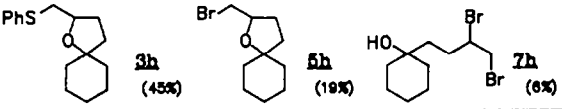
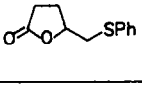
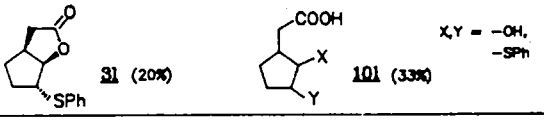
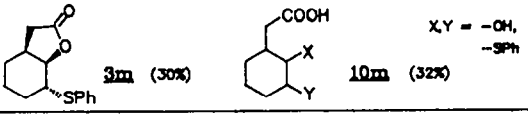
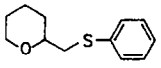
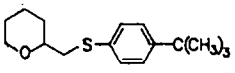
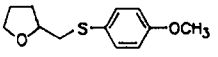
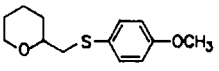
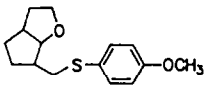
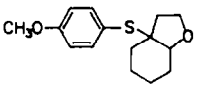
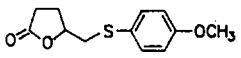
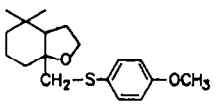
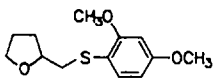
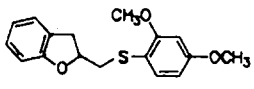
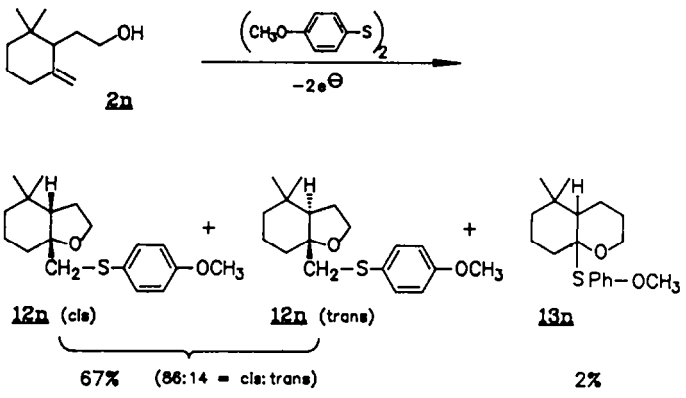
Substrate (mmol)	PhSSPh (mmol)	Products (isolated yields %)
 (7.8) 2a	(3.9)	 3a (72%)  a) 5a (3%)
 (4.2) 2b	(2.5)	 b) 3b (91%)
 (7.4) 2c	(3.7)	 c) 6c (88%)
 (5.8) 2d	(2.9)	 d) 6d (64%)
 (4.5) 2e	(2.3)	 3e (7%) 5e (11%) 7e (13%) 8e (23%) X,Y = -OH, -Br
 (4.0) 2f	(2.0)	 4f (21%) 7f (51%)
 (3.6) 2g	(3.6)	 6g (57%)
 (3.2) 2h	(1.6)	 3h (45%) 5h (19%) 7h (6%)
 (7.7) 2i	(3.9)	 3i (6%) 9i (51%)
 (4.9) 2k	(3.6)	 3k (81%)
 (4.0) 2l	(3.0)	 3l (20%) 10l (33%) X,Y = -OH, -SPh
 (3.6) 2m	(2.0)	 3m (30%) 10m (32%) X,Y = -OH, -SPh

Table 3: Cyclization Reactions Initiated by Direct Anodic Oxidation of the Disulphides **1a** – **1d**

Disulphide 1 (mmol)	Substrate 2 (mmol)	Product (isolated yield %)
1a (2.1)	**2b** (4.2)	 **3b** (36%)
1a (4.4)	**2a** (4.4)	——
1a (4.0)	**2f** (4.0)	——
1b (2.3)	**2b** (4.2)	 **11b** (42%)
1c (2.7)	**2a** (4.9)	 **12a** (64%)
1c (2.3)	**2b** (4.2)	 **12b** (67%)
1c (2.0)	**2e** (3.7)	 **12e** (36%)
1c (2.0)	**2f** (3.5)	 **13f** (24%)
1c (2.7)	**2k** (4.9)	 **12k** (49%)
1c (2.3)	**2i** (3.8)	——
1c (0.814)	**2n** (1.36)	 **12n** (67%)
1d (2.7)	**2a** (4.9)	 **14a** (4%)
1d (2.3)	**2i** (3.8)	 **14i** (21%)

methoxyphenyl)disulphide (1c) gave a 67% yield of the diastereomeric Markownikow products **12n** in a ratio of 86:14 (**Scheme 2**). The crude reaction mixture was contaminated by 2% of the anti-Markownikow product **13n**.



Scheme 2. Results of the intramolecular cyclization of **2n** initiated by the direct electrochemical oxidation of **1c**

The characterization of the diastereomers was possible by ^1H NMR spectroscopy. One methyl group of the minor diastereomer showed a significant high field shift which was interpreted by interaction of this methyl group with the CH_2-S-Ar substituent in the trans-isomer. Consequently the major diastereomer was formed by cis-annelation.

In spite of a low oxidation potential cyclization experiments initiated by the electrochemical oxidation of bis(2,4-dimethoxyphenyl)disulphide **1d** gave only poor yields of the desired ring systems. One exception is the allyl phenol **2i** which under these conditions can be cyclized in 21% yield.

On the basis of the present results we believe that the intramolecular cyclization of alkenols and alkenoic acids initiated by the electrochemical oxidation of disulphides represents an interesting alternative to known methods.

EXPERIMENTAL

All compounds are identified by microanalysis, ^1H NMR-, IR- and mass spectrometry. M.p.s. were determined with a Reichert hot-stage microscope and are uncorrected. IR spectra were obtained using a Pye Unicam SP-1100 unit, ^1H-NMR spectra were measured with Varian EM-360, Bruker WH-90, AC-200, and WM-400, ^{13}C NMR spectra were recorded on Bruker WH-90 and AC-200 instruments (solutions in deuteriochloroform, tetramethylsilane as internal standard). Mass spectra were obtained at 70 eV using A.E.I. Kratos MS-50 and MS-30 spectrometers and a Varian MAT 111 GC-MS system (Organisch-Chemisches Institut, Univ. Münster). Liquid chromatography was performed on silica gel 63-200 mesh (SiliTech) on glass columns: 1-3 cm (diam.) 30-70 cm. For flash chromatography silica gel Woelm 32-63 was used. All solvents are purified by distillation, dichloromethane is purified by distillation and dried over P_4O_{10}. Substrates **1a**, **2a** - **2d**, **2i**, and **2k** are commercially available. Disulphides **1b** - **1d** are obtained from the corresponding thiophenols by oxidation with bromine or iodine. Substrates **2e** - **2h**, **2l**, and **2m** are obtained by literature syntheses.

Cyclic Voltammetry

A Wenking potentiostat POS 73 is used as current source in combination with a triggerable function generator, Wavetek 133 LF, a Hewlett Packard 7045 A X/Y-recorder, a Metrohm EA 875-20 electrolysis cell equipped with a platinum sheet anode (0.5 cm^2), a platinum wire cathode and a $Ag/AgNO_3$ reference electrode which is in contact with the electrolyte (0.2 M $LiClO_4$; CH_3CN/CH_2Cl_2=1:1) via a salt bridge. The cyclic voltammetric data are reported in **Table 1**.

Preparative Electrolyses (General Procedure)

Apparatus: A stabilized current supply NTN 1400M-350 (F.u.G., Rosenheim) serves as current source and the charge consumption is measured by a digital coulometer. A two-compartment beaker-type glass cell with cooling mantle (150 mL) is equipped with a platinum sheet anode (10 cm^2), a $Ag/AgNO_3$ reference electrode and a magnetic stirrer. The cathode compartment is formed by a glass cylinder closed by a G-3 glass frit and is equipped with a platinum sheet cathode (5 cm^2).

Electrolytes: a) for indirect electrolyses: anolyte = 0.1 M Bu_4NBr/CH_2Cl_2
catholyte = 0.1 M BU_4NBr/CH_2Cl_2
b) for direct electrolyses: anolyte = 0.1 M Bu_4NClO_4/CH_2Cl_2
catholyte = 1 M Bu_4NClO_4/CH_2Cl_2

Procedure: A solution of disulphide 1 (2-4 mmol, 110 mol%) dissolved in one of the anolytes (80 mL) is electrolyzed under argon at a constant current of 0.02-0.03 A (current density = 3 mA/cm^2). After consumption of 10 As substrate 2 (4-8 mmol) is added to the reaction mixture and the electrolysis is continued until total consumption of the substrate is obtained (GC or TLC control).

Work-up: Silica gel (2-3 g, SiliTech 63-200) is added to the reaction mixture and the solvent is removed in vacuo. The residue is eluated with ether (250-400 mL) and the ether phase is evaporated to dryness.
Method A (for unsaturated alcohols): the crude product is purified by column chromatography (SiO_2; ether/petrolether or dichloromethane).
Methode B (for unsaturated carboxylic acids): The crude product is dissolved in ether (100 mL) and the organic phase is dried over $MgSO_4$ and the solvent is evaporated in vacuo. The residue is purified by column chromatography (SiO_2; ether/petrolether or dichloromethane).

2-Thiophenylmethyl-tetrahydrofuran (3a). (Found: C, 68.00; H, 7.27. $C_{11}H_{14}OS$ requires C, 68.00; H, 7.26). ν(NaCl) 925, 1065 (COC), 1445, 1480, 1590 ($CC_{arom.}$), 3000, 2895 (CH), 3080 ($CH_{arom.}$) cm^{-1}; δ_H (90 MHz) 1.4-2.1(m,4H,-CH_2-), 3.0(m,2H,-CH_2-S-, ABX-System); 3.65-4.10(m,3H,-O-CH_2-,-O-CH-), 7.2-7.4(m,5H,arom. CH) ppm; δ_C (200 MHz) 25.79(-CH_2-), 30.97 (-CH_2-), 38.91(-CH_2-S), 68.36(-CH_2-O), 77.68(-CH-O), 126.04($C_{arom.}$), 128.92(2 $CH_{arom.}$), 129.28(2 $CH_{arom.}$), 136.53($C_{arom.}$-S) ppm; m/z= 194(M^+, 15%), 124(16), 110(3), 109(50), 84(8), 71(100), 43(44), 41(20).

2-Thiophenylmethyl-tetrahydropyran (3b). (Found: C, 69.13; H, 7.88. $C_{12}H_{16}OS$ requires C, 69.19; H, 7.74). ν(NaCl) 1100 (COC), 1445, 1485, 1590 ($CC_{arom.}$), 2890, 2985 (CH), 3100 ($CH_{arom.}$) cm^{-1}; δ_H (90 MHz) 1.0-2.1(m,6H,-CH_2-), 3.0(m,2H,-CH_2-S-, ABX-System); 3.45(m,2H,-O-CH_2-), 3.97(m,1H,-CH-O), 7.2-7.4(m,5H,arom. CH) ppm; δ_C (200 MHz) 23.30(-CH_2-), 25.86 (-CH_2-), 31.24(-CH_2-),39.59(-CH_2-S), 68.72(-CH_2-O), 76.42(-CH-O), 125.85($CH_{arom.}$), 128.89(2 $CH_{arom.}$), 129.05(2 $CH_{arom.}$), 136.95-($C_{arom.}$-S) ppm; m/z= 208(M^+, 24%), 176(4), 141(13), 124(22),110(10), 109(5), 85(100), 77(38).

2-Oxa-8-thiophenyl-bicyclo[3,3,0]octane (3e). (Found: C, 71.2; H, 7.5. $C_{13}H_{16}OS$ requires C, 70.86; H, 7.32). ν(NaCl) 1050, 1080 (COC), 1445,1485, 1590 (arom.CC), 2900, 2980 (CH), 3100 (arom.CH) cm^{-1}; δ_H (90 MHz) 1.3-2.3(m,6H,-CH_2-), 2.85(m,1H, -CH-), 3.6-3.8(m,3H,-CH-S-,-CH_2-O-), 4.23(m1H,-CH-O-), 7.2-7.4(m,5H,arom.CH) ppm; m/z= 220(M^+, 42%), 110(100), 109(17), 82(29), 67(18), 55(28), 41(22).

1-Oxa-2-thiophenylmethyl-spiro[4.5]decane (3h). (Found: C, 73.24; H, 8.46. $C_{16}H_{22}OS$ requires C, 73.23; H, 8.45). ν(NaCl) 1035, 1070 (COC), 1445, 1485, 1590 (arom.CC), 2890, 2980 (CH), 3100 (arom.CH) cm^{-1}; δ_H (90 MHz) 1.2-2.2(m,14H,-CH_2-), 3.0(m,2H,-CH_2-S-, ABX-System); 4.15(m,1H,-O-CH-), 7.2-7.4(m,5H,arom.CH) ppm; m/z= 262(M^+, 17%), 139(72), 121(100).

2-Thiophenylmethyl-2,3-dihydrobenzofuran (3i). ν (NaCl) 1235, (COC), 1445,1485, 1590, 1605, 1620 (arom.CC), 2880, 2970 (CH), 3040 (arom.CH) cm^{-1}; δ_H (90 MHz) 2.9-3.5(m,4H,-CH_2-S-, -CH_2-Ph), 4.84(m,1H,-CH-O-), 6.8-7.5(m,9H,arom.CH) ppm; δ_C (200 MHz) 34.9(-CH_2-Ph), 39.0(-CH_2-S), 81.1(-CH-O-), 109.6(C-8), 120.7(C-6), 125.1(arom.CH), 126.1(C-4), 126.7(arom.CH), 128.1(2 arom.CH), 129.1(2 arom.CH), 129.9(arom.CH), 135.6(arom.C-S-), 159.2(C-9) ppm; m/z= 242(M^+, 51%), 133(48), 132(48), 131(50), 124(56), 119(89), 118(21), 110(35), 109(43), 105(33), 91(100), 77(50).

4-Thiophenylmethylbutyrolactone (3k). (Found: C, 63.52; H, 5.84. $C_{11}H_{12}O_2S$ requires C, 63.43; H, 5.84). m.p.: 45°C; ν (KBr) 1425, 1445, 1485, 1580, 1590 (arom.CC), 1780 (CO), 2970, 2990 (CH), 3100 (arom.CH) cm^{-1}; δ_H (90 MHz) 1.7-2.6(m,4H,-CH_2-,-CH_2-CO-), 3.10(m,2H,-CH_2-S-,ABX-System) ppm; m/z = 208(M^+, 30%), 123(61), 85(100), 45(37).

2-Oxa-3-oxo-8-thiophenyl-bicyclo[3.3.0]octane (3l). (Found: C, 66.53; H, 5.99. $C_{13}H_{14}O_2S$ requires C, 66.63; H, 6.02), m.p.: 50°C; ν (KBr) 1445, 1485, 1590 (arom.CC), 1790 (CO), 2900, 3000 (CH) cm^{-1}; δ_H (200 MHz) 1.5-1.9(m,2H,-CH_2-), 2.1-

2.4(m,3H,-CH_2-,-CH-CO), 2.82(dd,1H,-CH-CO), 3.11(m,1H,-CH-), 3.87(m,1H,-CH-S), 4.82(d,1H,-CH-O-, J = 6 Hz), 7.2-7.4(m,5H,arom.CH) ppm; δ_C (200 MHz) 29.9(-CH_2-), 32.1(-CH_2-), 37.4 (-CH-), 51.2(-CH-S-), 89.9(-CH-O-), 127.0(arom.CH), 129.2(2 arom.CH), 130.3(2 arom.CH), 134.5(arom.C-S), 176.8(-C=O) ppm; m/z = 234(M^+, 100%), 149(28), 124(13), 110(93).

7-Oxa-8-oxo-5-thiophenylbicyclo[4.3.0]nonane (3m). (Found: C, 67.22; H, 6.64. $C_{14}H_{16}O_2S$ requires C, 67.71; H, 6.49). ν(NaCl) 1445, 1485, 1590 (arom.CC), 1790 (CO), 2890, 2980 (CH), 3100 (arom.CH) cm^{-1}; δ_H (200 MHz) 1.1-2.1(m,6H,-CH_2-), 2.28(dd,1H,-CH_2-CO-), 2.55(dd,1H,-CH_2-CO-), 3.62(dt,1H,-CH-S-, J=3.5 Hz), 4.40(dd-,1H,-CH-O, J=5.2, 3.5 Hz), 7.2-7.4(m,5H,arom.CH) ppm; m/z = 248(M^+, 63%), 139(33), 138(30), 110(100), 109(18), 95(31), 79(449), 67(60), 55(53), 41(75).

7-Oxa-1-thiophenyl-bicyclo[4.3.0]nonane (4f). (Found: C, 71.83; H, 7.86. $C_{14}H_{18}OS$ requires C, 71.75; H, 7.74). ν(NaCl) 1030, 990 (COC), 1440, 1480, 1590 (arom.CC), 2900, 2980 (CH), 3095 (arom.CH) cm^{-1}; δ_H (90 MHz) 1.1-2.2(m,10H,-CH_2-), 3.67(t,-1H,-CH-O-), 3.85(m,2H,-CH_2-O-), 7.2-7.4(m,5H,arom.CH); m/z = 234(M^+, 6%), 201(3), 125(92), 110(17), 109(12), 81(31), 55(100), 41(42).

2-(4-tert-Butylphenylthiomethyl)tetrahydropyran (11b). (Found: C, 72.74; H, 9.19. $C_{16}H_{24}OS$ requires C, 72.68; H, 9.15). ν(NaCl) 1100(COC), 1445, 1470, 1505 (arom.CC), 2890, 2985, 2995(CH), 3110(arom.CH) cm^{-1}; δ_H (90 MHz) 1.33(s,9H,-CH_3), 1.3-2.0(m,6H,-CH_2-), 3.00(m,2H,-CH_2-S-,ABX-System), 3.48(m,2H,-CH_2-O-), 4.00(m,-1H,-CH-O-), 7.3(m,4H,arom.CH); δ_C (200 MHz) 23.3(-CH_2-), 25.9(-CH_2-), 29.5(-CH_2-), 31.2(-CH_2-), 31.3(3 -CH_3), 34.4(-CMe_3), 40.1(-CH_2-), 68.7(-CH_2-O), 76.5(-CH-O-), 126.0(2 arom.CH), 129.3(2 arom.CH), 133.3(arom.C), 149.3(arom.C-S-); m/z = 264(M^+, 22%), 180(19), 165(7), 85(100).

2-(4-Methoxyphenylthiomethyl)tetrahydrofuran) (12a). (Found: C, 64.36; H, 7.12. $C_{12}H_{16}O_2S$ requires C, 64.25; H, 7.19). b.p.: 150°C/0.3 Torr; ν(NaCl) 1045, 1080, 1250, 1290 (COC), 1445, 1470, 1500, 1580, 1600 (arom.CC), 2980, 2990 (CH) cm^{-1}; δ_H (90 MHz) 1.5-2.2(m,4H,-CH_2-), 2.93(m,2H,-CH_2-S-,ABX-System), 3.75(s,3H,-OCH_3), 3.7-4.1(m,3H,-CH_2-O-),-CH-O), 6.83(d,2H,arom.CH), 7.33(d,2H,arom.CH); m/z = 224 (M^+, 47%), 154(12), 140(22), 139(14), 85(10), 71(100), 43(26).

2-(4-Methoxyphenylthiomethyl)tetrahydropyran (12b). (Found: C, 65.69; H, 7.62. $C_{12}H_{18}O_2S$ requires C, 65.51; H, 7.61). b.p.: 130°C/0.1 Torr; ν (NaCl) 1040, 1100, 1190, 1240, 1285 (COC), 1445, 1470, 1500, 1580, 1600 (arom.CC), 2880, 2985 (CH) cm^{-1}; δ_H (90 MHz) 1.1-2.0(m,6H,-CH_2-), 2.95(m,2H,-CH_2-S-,ABX-System), 3.38(m,2H,-CH_2-O-), 3.75(s,3H,-OCH_3), 4.00(m,1H,-CH-O-),6.83(d,2H,arom.CH), 7.33(d,2H,arom.-CH); m/z = 238 (M^+, 30%), 154(18), 140(5), 139(12), 85(100), 67(13), 57(19), 43(19).

2-Oxa-8-(4-methoxyphenylthio)bicyclo[5.3.0]octane (12g). (Found: C, 67.22; H, 7.24. $C_{14}H_{18}O_2S$ requires C, 67.17; H, 7.25). ν(NaCl) 1050, 1080, 1195, 1250, 1290 (COC), 1445, 1470, 1500, 1580, 1600 (arom.CC), 2900, 2990 (CH) cm^{-1}; δ_H (90 MHz) 1.3-2.3(m,6H,-CH_2-), 2.82(m,1H,-CH-), 3.73(s,3H,-OCH_3), 3.4-3.8(m,3H,-CH_2-O-),-CH-S-), 4.21(d,1H,-CH-O-), 6.83(d,2H,arom.CH), 7.36(d,2H,arom.CH); m/z = 250 (M^+, 67%), 140(100), 139(29), 110(61), 93(26), 67(33), 55(48), 41(34).

4-(4-Methoxyphenylthio)butyrolactone (12k). (Found: C, 60.62; H, 6.03. $C_{12}H_{14}O_3S$ requires C, 60.48; H, 5.92). ν(NaCl) 1185, 1250, 1290(COC), 1470, 1500, 1580, 1600 (arom.CC), 1780 (CO), 2880, 2980 (CH) cm^{-1}; δ_H (90 MHz) 1.65-2.6(m,4H,-CH_2-), 3.00(m,2H,-CH_2-S-,ABX-System), 3.73(s,3H,-OCH_3), 4.45(m,1H,-CH-O-CO-), 6.80(d,2H,-arom.CH), 7.33(d,2H,arom.CH); m/z = 238(M^+, 100%), 153(100), 140(12), 139(30), 109(18), 85(44).

2,2-Dimethyl-6-(4-methoxyphenylthiomethyl)-7-oxa-bicyclo[4.3.0]nonane (12m). Found: C, 70.69; H, 8.70. $C_{18}H_{26}O_2S$ requires C, 70.55; H, 8.55). ν(NaCl) 1050, 1070, 1210, 1250, 1290,(COC), 1445, 1470, 1500, 1580, 1600(arom.CC), 2900, 2980 (CH) cm^{-1}; δ_H (400 MHz) 0.81(s,3H,-CH_3,12m-trans), 0.91(s,3H,-CH_3,12m-cis), 0.93(s,3H,-CH_3,12m-trans), 0.95(s,3H,-CH_3,12m-cis), 1.0-2.0(m,8H,-CH_2-), 3.19(s,-2H,-CH_2-S-), 3.76(s,3H,-OCH_3), 3.65(s,2H,-CH_2-O-), 6.60(d,2H,arom.CH), 7.38(d,2H,-arom.CH); δ_C (200 MHz, 12m-cis) 19.65(-CH_2-), 28.74(-CH_3), 29.24(-CH_2-), 30.04(-CH_3), 32.23(-$C(CH_3)_2$), 32.81(-CH_2-), 34.87(-CH_2-), 46.50(-CH_2-S-), 50.36(-CH-), 55.30(-OCH_3), 64.95(O-CH_2-), 85.56(-C-O-), 114.47(2 arom.CH), 128.35(arom.C-S-), 133.03(2 arom.CH), 158.64(arom.C-OMe); δ_C (200 MHz, 12m-trans) 20.56(-CH_3), 220.96(-CH_2-), 23.47(-CH_2-), 32.65(-CH_3), 33.10(-$C(CH_3)_2$), 34.74(-CH_2-), 40.02(-CH_2-), 40.88(-CH_2-S-), 55.30(-CH_3), 64.41(-CH_2-O-), 57.71(-CH-), 81.38(-C-O-), 114.47(2 arom.CH), 128.35(arom.C-S-), 133.03(2 arom.CH), 158.64(arom.C-OMe); m/z = 306 (M^+, 12%), 154(18), 153(100), 140(6), 139(4), 95(22), 85(13), 69(33).

7-Oxa-1-(4-methoxyphenylthio)bicyclo[4.3.0]nonane (13f). Found: C, 68.22; H, 7.65. $C_{15}H_{20}O_2S$ requires C, 68.14; H, 7.62). ν(NaCl) 1240, 1290 (COC), 1445, 1485, 1500, 1570, 1600, 1670(arom.CC), 2900, 2980 (CH) cm^{-1}; δ_H (90 MHz) 1.0-2.3(m,10H,-CH_2-), 3.75(s,3H,-OCH_3), 3.5-4.0(m,3H,-CH-O-,-CH_2-O-), 6.83(d,2H,arom.CH),

7.43(d,2H,arom.CH); m/z = 264 (M^+, 13%), 140(43), 125(100), 81(21), 55(60).

2-(2,4-Dimethoxyphenylthiomethyl)tetrahydrofuran (14a). ν(NaCl) 1180, 1230, 1310 (COC), 1415, 1445, 1470, 1495, 1585, 1605 (arom.CC), 2900, 2980, 3000 (CH) cm^{-1}; δ_H (90 MHz) 1.6-2.2(m,4H,-CH_2-), 2.95(m,2H,-CH_2-,ABX-System), 3.73(s,3H,-OCH_3), 3.80(s,3H,-OCH_3), 3.6-4.1(m,3H,-O-CH_2-,-O-CH-), 6.53(m,2H,arom.CH), 7.38(m,1H,-arom.CH); m/z = 254 (M^+, 62%), 184(29), 183(16), 170(30), 139(27), 71(100).

2-(2,4-Dimethoxyphenylthiomethyl)-2,3-dihydrobenzofuran (14i). ν(NaCl) 1045, 1090, 1180, 1230 (COC), 1415, 1445, 1470, 1490, 1580, 1605 (arom.CC), 2880, 2980 (CH), 3020 (arom.CH) cm^{-1}; δ_H (90 MHz) 2.8-3.5(m,4H,-CH_2-S-,-CH_2-Ph), 3.73(s,3H,-OCH_3), 3.82(s,3H,-OCH_3), 5.78(m,1H,-CH-O-), 6.45(m,2H,arom.CH), 6.70-7.50(m,5H,-arom.CH); m/z = 302 (M^+, 83%), 184(20), 170(100), 138(55), 133(339.

Acknowledgements: Financial support by the Deutsche Forschungsgemeinschaft (Ste 227/13-2), the Fonds der Chemischen Industrie, and the BASF Aktiengesellschaft is gratefully acknowledged.

REFERENCES

1 E.J. Corey, N.M. Weinshenker, T.K. Schaaf, and W. Huber, J.Am.Chem.Soc. 91 (1969) 5675.

2 K.C. Nicolaou, Tetrahedron 37 (1981) 4097.

3 J.M. Mellor, D.E. Coe, A. Bewick, and D.J. Walton, J.Chem.Soc., Chem.Commun. 1980, 51.

4 S. Torii, K. Uneyama, and M. Ono, Tetrahedron Lett. 21 (1980) 2653.

5 N.L. Weinberg, Techniques of Chemistry (A. Weissberger, Ed.), Vol. 5, Technique of Electroorganic Synthesis (N.L. Weinberg, Ed.), Part II, p. 2, John Wiley and Sons, New York 1975.

6 K.C. Nicolaou, S. Seitz, W.J. Sipio, and J.F. Blount, J.Am.Chem.Soc. 101 (1979) 3884.

7 P. Seifert and H. Schinz, Helv.Chim.Acta 34 (1951) 727; S. Julia, M. Julia, H. Linares, and J.C. Blondel, Bull.Soc.Chim.Fr. 1962, 1952.