

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

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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-annulated.

1. INTRODUCTION

Cyclic ethers or lactones may be synthesized from unsaturated alcohols or acids by halolactonization¹ or phenylselenoetherification². These reactions using bromine, iodine, or phenylselenenyl reagents lead to halogen or selenium substituted products.

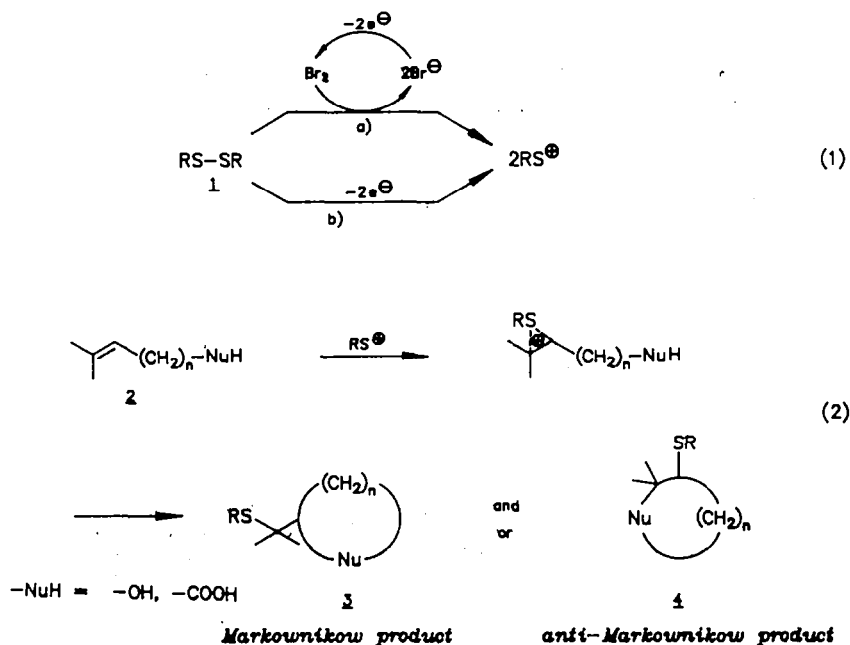
We now want to report upon the intramolecular cyclization of unsaturated alcohols and acids in the presence of electrochemically generated sulphenyl cations leading to arylthio substituted ring systems (Scheme 1).

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 phenylselenoetherification.
- 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 oxidation³ (procedure B, Scheme 1, eq. 1b) or by indirect anodic oxidation using bromide ions as redox catalysts⁴ (procedure A, Scheme 1, eq. 1a). The bromide mediated electrolysis has the advantage of a low oxidation potential (E_{pox}

$\text{Br}^-/\text{Br}_2 = 1.1 \text{ V vs. SHE}^5$), 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.



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_{ox} of the Disulphides **1a** - **1d** and Alkenes **2a**, **2n**, **2e**, **2f**, **2i**

1	$E_{\text{ox}}^{\text{a)}} \text{ vs SHE}$ [V]	2	$E_{\text{ox}}^{\text{a)}} \text{ vs SHE}$ [V]
	1.75		>2.4
	1.68		2.31
	1.54		2.22
	1.31		2.09
			1.66

a) working electrode: Pt, measured against Ag/AgNO_3 , calculated to SHE
electrolyte: $0.2\text{M LiClO}_4 / \text{CH}_3\text{CN} : \text{CH}_2\text{Cl}_2 = 1:1$

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 phenylsulphenyl-bromide 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 4f⁶.

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 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 synthesis⁷. 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**)

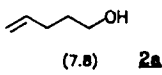
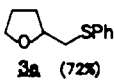
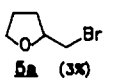
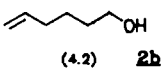
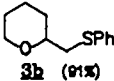
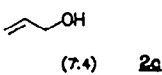
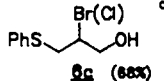
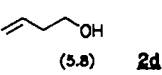
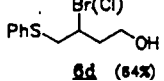
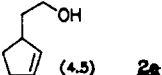
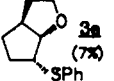
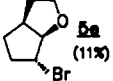
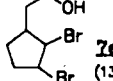
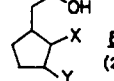
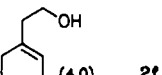
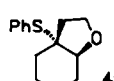
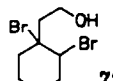
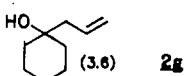
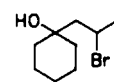
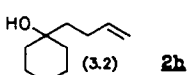
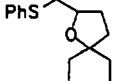
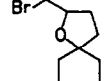
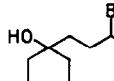
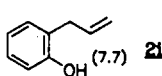
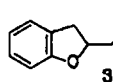
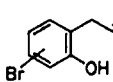
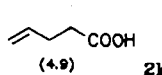
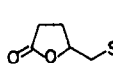
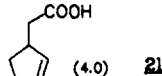
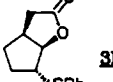
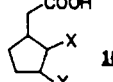
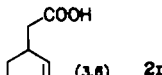
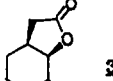
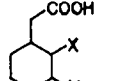
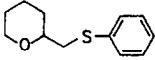
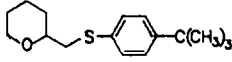
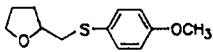
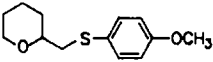
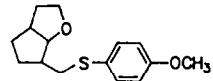
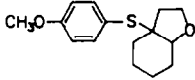
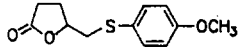
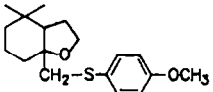
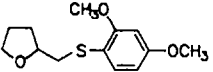
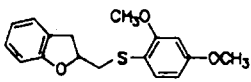
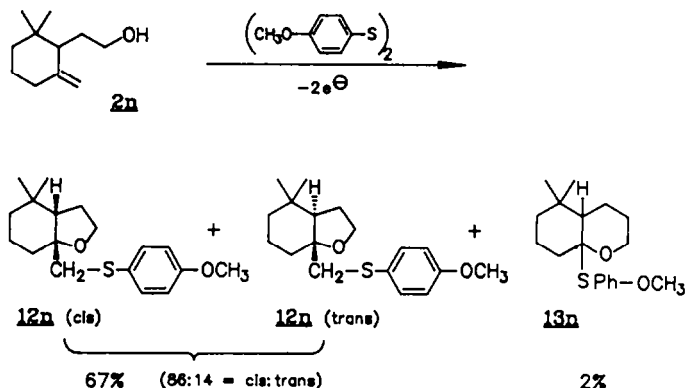
Substrate (mmol)	PhSSPh (mmol)	Products (isolated yields %)
 (7.8) 2a	(3.9)	 3a (72%)  5a (3%) ^{a)}
 (4.2) 2b	(2.5)	 3b (91%) ^{b)}
 (7.4) 2c	(3.7)	 6c (88%) ^{c)}
 (5.8) 2d	(2.9)	 6d (84%) ^{a)}
 (4.5) 2e	(2.3)	 3a (7%)  5a (11%)  7a (13%)  8a (23%) X,Y = -OH, -Br
 (4.0) 2f	(2.0)	 4f (21%)  7f (51%)
 (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 (38%)
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 (84%)
1c (2.3)	2b (4.2)	 12b (87%)
1c (2.0)	2a (3.7)	 12a (36%)
1c (2.0)	2f (3.5)	 13f (24%)
1c (2.7)	2k (4.9)	 12k (40%)
1c (2.3)	2l (3.8)	—
1c (0.814)	2n (1.38)	 12n (87%)
1d (2.7)	2a (4.9)	 14a (4%)
1d (2.3)	2l (3.8)	 14l (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 $\text{CH}_2\text{-S-Ar}$ substituent in the trans-isomer. Consequently the major diastereomer was formed by cis-annellation.

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, 2j, 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 ; $\text{CH}_3\text{CN}/\text{CH}_2\text{Cl}_2=1:1$) via a salt bridge. The cyclic voltammetric data are reported in Table 1.

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 cm²), a Ag/AgNO₃ 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 cm²).

Electrolytes: a) for indirect electrolyses: anolyte = 0.1 M $\text{Bu}_4\text{NBr}/\text{CH}_2\text{Cl}_2$
catholyte = 0.1 M $\text{Bu}_4\text{NBr}/\text{CH}_2\text{Cl}_2$
b) for direct electrolyses: anolyte = 0.1 M $\text{Bu}_4\text{NClO}_4/\text{CH}_2\text{Cl}_2$
catholyte = 1 M $\text{Bu}_4\text{NClO}_4/\text{CH}_2\text{Cl}_2$

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 eluted with ether (250-400 mL) and the ether phase is evaporated to dryness.

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/petroleum ether or dichloromethane).

2-Thiophenylmethyl-tetrahydrofuran (3e). (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 ($C_{arom.}$), 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. C₁₂H₁₆OS requires C, 69.19; H, 7.74). ν (NaCl) 1100 (COC), 1445, 1485, 1590 (C_{arom.}), 2890, 2985 (CH), 3100 (CH_{arom.}) cm⁻¹; δ _H (90 MHz) 1.0-2.1(m, 6H, -CH₂-), 3.0(m, 2H, -CH₂-S-, ABX-System); 3.45(m, 2H, -O-CH₂-), 3.97(m, 1H, -CH-O), 7.2-7.4(m, 5H, *arom.*, CH) ppm; δ _C (200 MHz) 23.30(-CH₂-), 25.86 (-CH₂-), 31.24(-CH₂-), 39.59(-CH₂-S), 68.72(-CH₂-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 (3a). (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 (m, 1H, $-CH-O-$), 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; $\underline{m/z}$ 262(M^+ , 17%), 139(72), 121(100).

2-Thiophenylmethyl-2,3-dihydrobenzofuran (31). δ (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, $\text{-CH}_2\text{-S-}$, $\text{-CH}_2\text{-Ph}$), 4.84(m, 1H, -CH-O-), 6.8-7.5(m, 9H, arom.CH) ppm; δ_{C} (200 MHz) 34.9($\text{-CH}_2\text{-Ph}$), 39.0($\text{-CH}_2\text{-S-}$), 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; $m/z = 242(\text{M}^+, 51\%)$, 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 (31). (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, -CH₂-, -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(-CH₂-), 32.1(-CH₂-), 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. C₁₄H₁₆O₂S 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, -CH₂-), 2.28(dd, 1H, -CH₂-CO-), 2.55(dd, 1H, -CH₂-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. C₁₄H₁₈O₂S 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, -CH₂-), 3.67(t, 1H, -CH-O-), 3.85(m, 2H, -CH₂-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. C₁₆H₂₄O₂S 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, -CH₃), 1.3-2.0(m, 6H, -CH₂-), 3.00(m, 2H, -CH₂-S-, ABX-System), 3.48(m, 2H, -CH₂-O-), 4.00(m, 1H, -CH-O-), 7.3(m, 4H, arom. CH); δ_C (200 MHz) 23.3(-CH₂-), 25.9(-CH₂-), 29.5(-CH₂-), 31.2(-CH₂-), 31.3(3 -CH₃), 34.4(-CMe₃), 40.1(-CH₂-), 68.7(-CH₂-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. C₁₂H₁₆O₂S 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, -CH₂-), 2.93(m, 2H, -CH₂-S-, ABX-System), 3.75(s, 3H, -OCH₃), 3.7-4.1(m, 3H, -CH₂-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. C₁₂H₁₈O₂S 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, -CH₂-), 2.95(m, 2H, -CH₂-S-, ABX-System), 3.38(m, 2H, -CH₂-O-), 3.75(s, 3H, -OCH₃), 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[3.3.0]octane (12e). (Found: C, 67.22; H, 7.24. C₁₄H₁₈O₂S 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, -CH₂-), 2.82(m, 1H, -CH-), 3.73(s, 3H, -OCH₃), 3.4-3.8(m, 3H, -CH₂-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. C₁₂H₁₄O₃S 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, -CH₂-), 3.00(m, 2H, -CH₂-S-, ABX-System), 3.73(s, 3H, -OCH₃), 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 (12n). Found: C, 70.69; H, 8.70. C₁₈H₂₆O₂S 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, -CH₃, 12n-trans), 0.91(s, 3H, -CH₃, 12n-cis), 0.93(s, 3H, -CH₃, 12n-trans), 0.95(s, 3H, -CH₃, 12n-cis), 1.0-2.0(m, 8H, -CH₂-), 3.19(s, 2H, -CH₂-S-), 3.76(s, 3H, -OCH₃), 3.65(s, 2H, -CH₂-O-), 6.60(d, 2H, arom. CH), 7.38(d, 2H, arom. CH); δ_C (200 MHz, 12n-cis) 19.65(-CH₂-), 28.74(-CH₃), 29.24(-CH₂-), 30.04(-CH₃), 32.23(-C(CH₃)₂), 32.81(-CH₂-), 34.87(-CH₂-), 46.50(-CH₂-S-), 50.36(-CH-), 55.30(-OCH₃), 64.95(O-CH₂-), 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, 12n-trans) 20.56(-CH₃), 220.96(-CH₂-), 23.47(-CH₂-), 32.65(-CH₃), 33.10(-C(CH₃)₂), 34.74(-CH₂-), 40.02(-CH₂-), 40.88(-CH₂-S-), 55.30(-CH₃), 64.41(-CH₂-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. C₁₅H₂₀O₂S 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, -CH₂-), 3.75(s, 3H, -OCH₃), 3.5-4.0(m, 3H, -CH-O-, -CH₂-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, -CH₂-), 2.95(m, 2H, -CH₂-, ABX-System), 3.73(s, 3H, -OCH₃), 3.80(s, 3H, -OCH₃), 3.6-4.1(m, 3H, -O-CH₂-, -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 (14j). 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, -CH₂-S-, -CH₂-Ph), 3.73(s, 3H, -OCH₃), 3.82(s, 3H, -OCH₃), 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).

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