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Synthesis and Properties of Alkane-1,2-disulfonate Surfactants

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Synthesis of pure alkane-1,2-disulfonic acids was accomplished by oxidation of the corresponding 1,2-dithiols or cyclic trithiocarbonates. The dithiols were obtained from the epoxides via the thiiranes, or by reacting the corresponding olefin with S_2Cl_2 and subsequent treatment with NaHS. The trithiocarbonates were prepared by reaction of the epoxides with potassium *O*-methyl dithiocarbonate. The disodium salts of the 1,2-disulfonic acids exhibited surfactant properties with critical micelle concentration (CMC) values between 10^{-3} and 10^{-4} M.

Surface-active compounds with more than one hydrophilic group have lately attracted attention.[1] An important group is the disulfonates. Sulfonation of α-olefins with SO_3 or bisulfite yield as major products alkane sulfonates together with a number of other products, e.g., sultones and hydroxy sulfonates.[2] In some cases disulfonates have been reported as well.[3] A recent publication dealing with the SO_3 sulfonation reaction also indicated formation of disulfonates.[4] In a study of the bisulfite sulfonation of α-olefins under free radical conditions formation of alkane-1-sulfonates as well as alkane-1-sulfonate-2-sulfinates was clearly established. These compounds were further oxidized to the corresponding 1,2-disulfonates.[5] We have studied the synthesis and properties of surfactant molecules containing strongly hydrophilic moieties and with the hydrophilic and hydrophobic regions highly separated. Studies of α-sulfonated fatty acid esters have been studied previously.[6]

We report here a study of the selective synthesis of 1,2-disulfonates. As sulfonation of α-olefins may lead to 1,2- as well as 1,3-difunctionalized products, we also confirm by the independent synthesis the structural assignments made by Herke *et al.*[5]

Results and discussion

Synthesis of the 1,2-disulfonates was based on the oxidation of either the 1,2-dithiol compounds or the corresponding cyclic trithiocarbonates. The alkane-1,2-disulfonates, **1**, were prepared from the corresponding 1,2-epoxides by two procedures. Thus, the epoxides **2** were converted into the corresponding thiiranes, **3**. This was best accomplished by the reaction of **2** with thiourea in methanol solution at room temperature. Thiirane formation has been reported to take place upon treatment of epoxides with either thiocyanates[7] or thiourea.[8] Yields were in all cases satisfactory, 90–95%. The thiiranes were next converted into the 1,2-dithiols, **4**, by the reaction with a sodium hydrosulfide–hydrogen sulfide system in methanol or ethanol solution.[9] In order to suppress polymerization reactions, H_2S was used as a proton donor, and a stream of H_2S was passed through the reaction mixture during the course of the ring-opening reaction. In this way the products were obtained in essentially quantitative yields. After distillation the yields of dithiols were moderate only, 37–65% (Fig. 1).

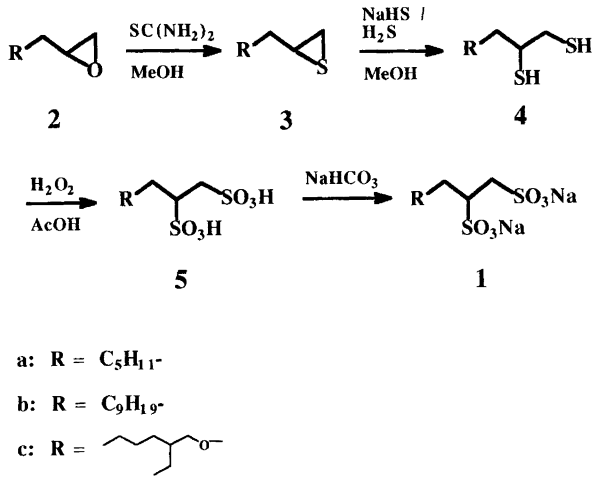

Fig. 1.

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Oxidation of thiols to sulfonic acids can be achieved with a number of oxidizing agents, e.g., nitric acid,[10] sodium hypochlorite,[11] ozone,[12] dinitrogen tetraoxide,[13] potassium peroxymonosulfate (Oxone)[14] or hydrogen peroxide in acetic acid.[15] We investigated a series of these reagents. Thus, oxidation of the dithiol compounds with sodium hypochlorite gave the disulfonates but in low isolated yields only (ca. 15%). Oxidation with ozone yielded as the primary product a peroxosulfate, the structure of which was not further elucidated. We found the most convenient method for conversion of **4** into the disulfonic acids **5** to be oxidation with hydrogen peroxide in glacial acetic acid. With this reagent the 1,2-sulfonic acids, **5**, were isolated in essentially quantitative yields. The products were unstable, however, and darkened upon standing, but the corresponding disodium salts, **1**, were in all cases stable and isolated in quantitative yields as white crystalline powders after adjusting the pH of **5** to 3.0 with sodium bicarbonate in water.

An alternative route for the preparation of the dithiol compound, **4**, was also investigated (Fig. 2). A modification of an earlier reported reaction[16] was used. According to this, dodec-1-ene, **6**, was reacted with disulfur dichloride and subsequently treated with sodium hydrosulfide–hydrogen sulfide yielding dodecane-1,2-dithiol, **4b**, in moderate yield after distillation. Based on the spectroscopic properties observed a number of by-products, e.g., disulfides, were formed as well. Oxidation of the product with hydrogen peroxide in acetic acid gave the desired product together with a number of unidentified by-products.

Compounds **1** were also prepared via oxidation of the cyclic thiocarbonates, **7**, which were readily available from the epoxides **2** by treatment with an excess of potassium *O*-methyl dithiocarbonate, **8**, Fig. 3. The trithiocarbonates were subsequently oxidized with hydrogen peroxide in acetic acid to give the desired 1,2-disulfonic acids, **5**, in high yields.

The spectroscopic properties of all synthetic intermediates and products were in full agreement with those for the expected structures. The ^{13}C NMR data for compounds **1a** and **1b** were in agreement with those previously reported by Herke *et al.*[5] For the ^{13}C experiments with the 1,2-disulfonates in water, however, very poor signal/noise (S/N) ratios were observed. Changes of NMR parameters or addition of paramagnetic relaxation agents, e.g., [$Cr(acac)_3$] only partly alleviated this problem. The reason for the low S/N-ratio may be ascribed to slow relaxation of the ^{13}C nuclei in the surfactant aggregates.

Table 1. CMC values and surface tension values at CMC for the synthetic disulfonates.

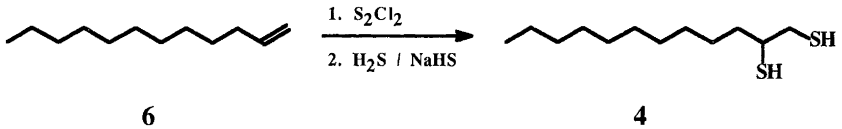
Surfactant	CMC in distilled water/ molality	γ_{cmc}/mN m^{-1}
1b	4.63×10^{-4}	32.4
1c	1.48×10^{-3}	34.5

The critical micellar concentrations, (CMC), were determined from the plots of the measured surface tensions vs. the log of the surfactant concentrations, *c*. The CMC values measured for the surfactants **1b** and **1c** as well as their ability to lower surface tension, γ_{cmc}, are summarized in Table 1. The plot of γ vs. log *c* did not give very well defined CMC values, indicating increased aggregation with increasing concentrations. These observations were in agreement with the ^{13}C NMR measurements mentioned above. The materials for these measurements were obtained exclusively by the trithiocarbonate route, which gave products of high purity. From a CMC point of view, products **1b** and **1c** were moderately active surfactants.

In conclusion, the best method for large-scale synthesis of the pure 1,2-disulfonates involved the oxidation of the thiocarbonates **7** with hydrogen peroxide in acetic acid. This method involved few reaction steps, the overall yields were high and the use of hydrogen sulfide was avoided.

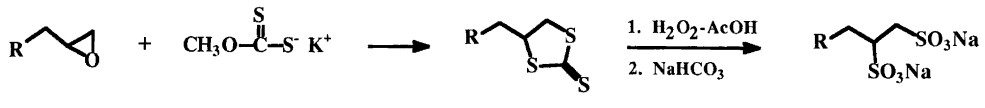
Experimental

Materials. 1,2-Epoxydodecane and 1,2-epoxyoctane were commercial products obtained from Lancaster Synthesis.



6 4

Fig. 2.



2 8 7 1

Fig. 3.

2-Ethylhexyl glycidyl ether, sodium hydrosulfide, hydrogen sulfide and carbon disulfide were all purchased from Aldrich.

Methods. The critical micelle concentration (CMC) was determined on a Lauda tensiometer by measuring the surface tension change vs. the log of the surfactant concentration. The surface tension measurements were performed at 25°C by the Wilhelmy vertical plate technique,[17] using a 199 × 100 mm platina blade. Before the measurements the blade was cleaned by successive washing with distilled water, acetone and ethanol and subsequent heating in a propane flame to evaporate traces of solvents. Measurements were taken until the change in surface tension was less than 0.2 mN m^{-1}. The CMC values were determined as the point of intersect between the two linear segments of the γ vs. log c curve. The γ_{cmc} value is the surface tension at the CMC.

^1H and ^{13}C NMR spectra including HH- and HC-COSY spectra were recorded on a JEOL JNM-EX400 FT NMR instrument in $CDCl_3$ or D_2O using tetramethylsilane (TMS) sodium 3-trimethylsilylpropanesulfonate or acetonitrile (δ 1.3 relative to TMS) as internal standards. IR spectra were obtained on a Nicolet 20-SXC FT-IR spectrometer. Mass spectra were recorded on an AEI MS-902 spectrometer at 70 eV (IP) and 200°C inlet temperature. Exact mass measurements were performed by peak matching using perfluorokerosene as the standard to provide the reference masses. GLC analyses were performed on a Varian 3700 gas chromatograph equipped with BP-1 and BP-5 capillary columns (25 m). HPLC analyses were done on a Perkin–Elmer LC-600 system using an LC-30 RI refraction index detector and an 25 cm APEX Prepsit ODS 8U column. Melting points are uncorrected.

Synthesis of 2-alkylthiirane, **3***: general procedure.* Thiourea (0.055 mol, 4.19 g) was dissolved in metanol (30 ml). To this solution was added 0.05 mol of the epoxide, **2**, over a period of 5 min. The reaction mixture was stirred at room temperature for 48 h. Water (30 ml) was then added, and the reaction mixture extracted with diethyl ether. The organic phases were dried over anhydrous magnesium sulfate, filtered and concentrated under reduced pressure, yielding the crude product, **3**.

2-Hexylthiirane, **3a**. The yield was 6.93 g (96%) of the crude product (99% by GLC). ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 0.89 (t, 3 H, J = 6.8 Hz), 1.30 (m, 6 H), 1.48 (m, 3 H), 1.80 (m, 1 H), 2.10 (dd, 1 H, J = 4.9 and J < 1 Hz), 2.44 (dd, 1 H, J = 6.4 and J < 1 Hz), 2.83 (m, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 14.1, 22.7, 25.7, 29.1, 29.4, 31.9, 35.8, 36.7. IR (NaCl, neat): 3063, 2987, 2956, 2927, 1466, 1459, 1439, 1378, 1065, 1038, 912, 724, 619 cm^{-1}. MS [m/z (% rel. int.)]: 144 (M^+, 10), 112 (29), 97 (11), 84 (25), 83 (34), 82 (10), 81 (11), 71 (16), 70 (59), 69 (43), 68 (16), 67 (10), 64 (11), 57 (24), 56 (72), 55 (81), 54 (13).

2-Decylthiirane, **3b**. The yield was 7.23 g (90%). The purity was better than 99% by GLC. ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 0.88 (t, 3 H, J = 6.8 Hz), 1.27 (m, 14 H), 1.48 (m, 3 H), 1.80 (m, 1 H), 2.12 (d, 1 H, J = 5.9 Hz), 2.47 (d, 1 H, J = 6.4 Hz); 2.85 (m, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 14.1, 22.8, 25.8, 29.4, 29.4, 29.6, 29.7, 32.0, 35.9, 36.7. IR (NaCl, neat): 3058, 2986, 2955, 2870, 1466, 1440, 1378, 1351, 1311, 1037, 912, 721, 670 cm^{-1}. MS [m/z (% rel. int.)]: 200 (M^+, 12), 168 (14), 126 (6), 112 (8), 111 (16), 98 (20), 97 (44), 96 (21), 87 (11), 85 (11), 84 (37), 83 (59), 82 (26), 81 (13), 74 (22), 71 (21), 70 (55), 69 (66), 68 (19), 67 (17), 57 (56), 56 (72), 55 (93), 54 (18).

2-(4-Ethyl-2-oxaoctyl)thiirane, **3c**. The yield was 98.6 g (97.4%) of 98% purity by GLC. ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 0.87 (t, 3 H, J = 7.6 Hz), 0.89 (t, 3 H, J = 7.3 Hz), 1.27 (m, 8 H), 1.50 (m, 1 H), 2.19 (t, 1 H, J = 4.9 Hz), 2.50 (t, 1 H, J = 5.1 Hz), 3.05 (m, 1 H), 3.31 (m, 2 H), 3.37 (m, 1 H), 3.62 (m, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 11.1, 11.1, 14.1, 14.2, 23.1, 23.8, 23.9, 29.1, 29.2, 30.5, 32.2, 39.7, 74.1, 75.6. IR (NaCl, neat): 2958, 2928, 2872, 2800, 1464, 1415, 1378, 1336, 1315, 1267, 1248, 1099, 1043, 910, 893, 770, 729, 708, 619 cm^{-1}. MS [m/z (% rel. int.)]: 202 (M^+), 144 (27), 115 (7), 113 (10), 112 (31), 103 (11), 102 (9), 84 (11), 83 (20), 74 (21), 73 (81), 71 (46), 70 (63), 69 (23), 58 (30), 57 (100), 56 (28), 55 (35).

Synthesis of 1,2-dithiols, **4***: general procedure.* A solution containing 4.44 g, 0.06 mol of sodium hydrosulfide monohydrate in 100 ml of ethanol was cooled in an ice-bath and then saturated with hydrogen sulfide. Then 5.83 g, 0.04 mol of the 2-alkylthiirane in 25 ml of ethanol was added dropwise over 10 min. The reaction was continued for another 3 h, during which time a slow stream of hydrogen sulfide was passed through the solution. Water (100 ml) was then added and the reaction mixture acidified with ca. 1 M sulfuric acid. The reaction mixture was then neutralized with a solution of sodium bicarbonate and then extracted with diethyl ether. The organic layer was dried over anhydrous magnesium sulfate and the solvent evaporated off under reduced pressure, leaving behind the crude product.

Octane-1,2-dithiol, **4a**. The yield was 7.15 g (100%), which was 97% pure by GLC. The crude product was distilled under reduced pressure to give 4.61 g (65%) of the pure product (better than 99% pure by GLC). B.p. 49°C at 0.1 mmHg. ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 0.89 (t, 3 H, J = 6.8 Hz), 1.29 (m, 6 H), 1.35 (m, 1 H), 1.49 (m, 2 H), 1.64 (t, 1 H, J = 8.5 Hz), 1.70 (d, 1 H, J = 6.8 Hz), 1.77 (m, 1 H), 2.74 (m, 2 H), 2.89 (m, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 14.1, 22.6, 27.1, 28.9, 31.7, 33.9, 36.7, 3.8. IR (NaCl, neat): 2956, 2927, 1870, 2855, 2556, 1466, 1460, 1458, 1440, 1422, 1378, 1296, 1282, 1252, 1218, 1267, 1250, 723 cm^{-1}. MS [m/z (% rel. int.)]: 178 (M^+, 32), 144 (13), 131 (29), 112 (14),

97 (18), 87 (14), 84 (9), 83 (16), 81 (11), 74 (21), 70 (45), 69 (46), 68 (10), 67 (12), 60 (17), 59 (7), 58 (10), 57 (10), 56 (43), 55 (100), 54 (10).

Dodecane-1,2-dithiol, **4b**. The crude yield was 14.0 g, 99.5% of 60% purity by GLC. After distillation at 0.5 mmHg, the pure product was obtained (better than 99% by GLC) (9.42 g, 67%). B.p. 139–141°C at 0.5 mmHg. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 0.88 (t, 3 H, J = 6.8 Hz), 1.27 (m, 14 H), 1.35 (m, 1 H), 1.48 (m, 2 H), 1.64 (dt, 1 H, J < 1 Hz, J = 8.5 Hz), 1.70 (dd, 1 H, J < 1 Hz, J = 6.8 Hz), 1.76 (m, 1 H), 2.73 (m, 2 H), 2.87 (m, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 14.1, 22.7, 27.1, 29.3, 29.3, 29.5, 29.6, 31.9, 33.9, 36.6, 43.8. IR (NaCl, neat): 2955, 2924, 2853, 2665, 2640, 2558, 1466, 1421, 1377, 1353, 1343, 1300, 1287, 1272, 1251, 1228, 1188, 1168, 1122, 1076, 1045, 980, 890, 721 cm^{-1}. MS [m/z (% rel. int.)]: 234 (M^+, 26), 187 (48), 168 (13), 111 (16), 101 (11), 98 (18), 97 (52), 96 (18), 87 (17), 85 (14), 84 (37), 83 (71), 82 (24), 81 (13), 74 (21), 71 (25), 70 (56), 69 (84), 68 (17), 67 (21), 60 (18), 57 (60), 56 (63), 55 (100), 54 (17), 53 (10).

6-Ethyl-4-oxa-decane-1,2-dithiol, **4c**. The yield of the crude product was 26.4 g (112%), containing ca. 90% dithiol (GC). After distillation the yield was 8.77 g (37%) of the pure product (99% by GLC). B.p. 122°C at 0.1 mmHg. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 0.87 (*t*, 3 H, J = 7.6 Hz), 0.89 (t, 3 H, J = 7.1 Hz), 1.28 (m, 8 H), 1.48 (m, 1 H), 1.59 (t, 1 H, J = 8.5 Hz), 1.87 (d, 1 H, J = 8.8 Hz), 2.83 (ddd, 2 H, J < 1 Hz, J = 6.1 Hz, J = 8.5 Hz), 3.05 (m, 1 H), 3.32 (m, 2 H), 3.46 (m, 1 H), 3.60 (m, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 11.1, 11.1, 14.1, 23.1, 23.9, 29.1, 30.0, 30.5, 39.6, 42.2, 73.3, 73.7. IR (NaCl, neat): 295, 2928, 2872, 2859, 2790, 2718, 2558, 1479, 1462, 1422, 1379, 1362, 1311, 1279, 1269, 1248, 1216, 1113, 1100, 1049, 1012, 987, 785, 771, 727, 668 cm^{-1}. MS [m/z (% rel. int.)]: 236 (M^+, 1), 202 (6), 113 (21), 112 (9), 106 (41), 98 83 (11), 73 (26), 71 (64), 70 (17), 69 (11), 57 (100), 56 (18), 55 (20), 47 (10), 45 (13). Observed M^+: 236.1265. Calcd. for $C_{11}H_{24}OS_2$: 236.1269.

Synthesis of 4-alkyl-1,3-dithiolane-2-thione, **7***: general procedure.* To a stirred solution containing 150 mmol, 8.4 g, of potassium hydroxide in 36 ml of methanol were added 180 mmol, 13.7 g of carbon disulfide. 60 mmol of the epoxide, **2** were then added dropwise. The reaction was exothermic. The reaction mixture was stirred at room temperature for 4 days. The precipitate formed was isolated by filtration, washed with water and dried under reduced pressure at room temperature. Alternatively the reaction mixture was extracted with diethyl ether and the product isolated upon evaporation of the solvent under reduced pressure.

4-Decyl-1,3-dithiolane-2-thione, **7b**. The yield was 14.9 g (90%). M.p. 31–32°C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 0.89 (t, 3 H, J = 6.8 Hz), 1.27 (m, 14 H), 1.43 (m, 2 H), 1.94 (m, 2 H), 3.72 (dd, 1 H, J = 7.8 Hz, J = 11.7 Hz), 3.97 (dd, 1 H, J = 5.4 Hz, J = 11.7 Hz), 4.40 (m, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 14.1, 22.7, 28.3, 29.2, 29.3, 29.4, 29.5, 29.5, 31.9, 33.5, 48.2, 61.0, 228.0. IR (NaCl, neat): 3479, 3180, 2924, 2852, 2729, 2682, 1711, 1652, 1464, 1440, 1377, 1357, 1290, 1266, 1220, 1193, 1148, 1104, 1067, 1010, 920, 871, 812, 775, 721, 679 cm^{-1}. MS [m/z (% rel. int.)]: 276 (M^+, 100), 261 (2), 244 (7), 243 (40), 166 (10), 163 (9), 149 (33), 135 (13), 111 (17), 101 (16), 97 (43), 96 (27), 95 (16), 87 (31), 84 (14), 83 (56), 82 (30), 81 (27), 76 (27), 74 (31), 73 (12), 71 (14), 70 (24), 69 (72), 68 (25), 67 (35), 60 (24), 59 (21), 57 (36), 56 (30), 55 (99), 54 (20), 53 (10). Observed for M^+: 276.1043. Calcd. for $C_{13}H_{24}S_3$: 276.1040.

4-(4-Ethyl-2-oxaoctyl)-1,3-dithiolane-2-thione, **7c**. From the reaction of 2-ethylhexyl glycidyl ether (90 mmol, 16.8 g) was isolated 20.5 g (82%) of the desired product. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 0.88 (t, 3 H, J = 7.6 Hz), 0.88 (t, 3 H, J = 10 Hz), 1.27 (m, 6 H), 1.36 (m, 2 H), 1.50 (m, 1 H), 3.39 (m, 2 H), 3.62 (m, 1 H), 3.79 (dt, 1 H, J < 1 Hz, J = 9.3 Hz), 3.94 (ddd, 1 H, J = 2.6 Hz, J = 5.0 Hz, J = 11.8 Hz), 4.06 (ddd, 1 H, J = 1.8 Hz, J = 5.7 Hz, J = 12.0 Hz), 4.49 (m, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 11.1, 14.1, 23.0, 23.81, 29.0, 30.4, 39.5, 45.0, 58.6, 70.1, 74.2, 227.4. IR (NaCl, neat): 2957, 2927, 2871, 2858, 2795, 2733, 1461, 1424, 1378, 1365, 1267, 1189, 1108, 1079, 1036, 1006, 893, 863, 770, 729, 688, 671 cm^{-1}. MS [m/z (% rel. int.)]: 278 (M^+, 27), 245 (4), 169 (5), 150 (23), 136 (18), 135 (12), 113 (18), 76 (25), 74 (25), 73 (31), 71 (61), 70 (11), 69 (14), 57 (100), 56 (11), 55 (20). Observed M^+: 278.0829. Calculated for $C_{12}H_{22}OS_3$: 278.0833.

Oxidation of 1,2-dithiols, **4**, *to disodium 1,2-disulfonic acids,* **1**, *with sodium hypochlorite: general procedure.* To a solution containing 7 mmol of the dithiol, **4**, and 19.4 mmol, 2.06 g of sodium carbonate in 22 ml of water was added a 10% sodium hypochlorite solution (63 mmol, 47 ml). The reaction mixture was then heated to 75–80°C for 5 h. Another portion of 10% sodium hypochlorite solution (40 mmol, 30 ml) was then added and the reaction mixture was stirred overnight at room temperature. The mixture was neutralized with hydrochloric acid, concentrated under reduced pressure and then extracted with boiling methanol. The organic solution was concentrated under reduced pressure.

Disodium octane-1,2-disulfonate, **1a**. The crude yield was 2.28 g (100%). The product was recrystallized from methanol (70 ml) and the product dried under reduced pressure. The yield was 0.31 g (14%). M.p. > 250°C. ^{1}H NMR (400 MHz, D_2O): δ 0.95 (s, 3 H), 1.39 (m, 5 H), 1.63 (m, 3 H), 2.01 (m, 2 H), 2.38 (m, 1 H), 3.15 (dd, 1 H, J = 14 Hz, J = 10 Hz), 3.29 (m, 1 H), 3.44 (m, > 8 H), 3.53 (dd, 1 H, J = 14 Hz, J = 2 Hz), 4.12 (s, < 1 H), 8.53

(s). IR (KBr): 3454, 2958, 2931, 2857, 2815, 2778, 2711, 2683, 1895, 1655, 1612, 1365, 1355, 1207, 1052, 893, 816, 774, 765, 624 cm^{-1}.

Oxidation of 1,2-dithiols, **4**, *and 1,3-dithiolane-2-thiones,* **7**, *to disodium 1,2-disulfonic acids,* **1**, *with hydrogen peroxide: general procedure.* A well stirred solution containing 10 mmol of the 1,2-dithiol, **4**, or the 1,3-dithiolane-2-thione, **7**, in 15 ml of glacial acetic was heated at 60°C. Hydrogen peroxide (100 mmol, 9.72 g of a 35% solution) was then added dropwise, and the reaction stirred for another 16 h. The pH-value was at this stage between 0 and 1. The reaction mixture was concentrated under reduced pressure, with removal of the last traces of acetic acid as an azeotrope with water. The sulfonic acid was then neutralized with a solution of sodium bicarbonate, (to pH 3). The solvent was removed under reduced pressure and the product dried by azeotropic distillation with benzene. Finally the product was placed under oil pump vacuum to remove the last traces of solvents.

Disodium dodecane-1,2-disulfonate, **1b**. The yield from 2.35 g, 10.0 mmol of dodecane-1,2-dithiol, **4b**, was 4.27 g, 114% (hygroscopic), of a white solid material. The product decomposed at 220°C without melting. ^{1}H NMR (400 MHz, D_2O): δ 0.87 (t, 3 H, $J = 6.6$ Hz), 1.28 (m, 14 H), 1.55 (m, 2 H), 1.94 (m, 2 H), 3.06 (ddd, 1 H, $J = 14$ Hz, $J = 0$ Hz, $J = 1$–2 Hz), 3.19 (m, 1 H), 3.44 (dd, 1 H, $J = 14$ Hz, $J < 1$ Hz) ppm. ^{13}C NMR (100 MHz, D_2O): δ 14.3, 22.9, 27.0, 29.4, 29.6, 29.7, 30.4, 32.1, 52.1, 57.8 ppm. IR (KBr): 3437, 2956, 2924, 2874, 2853, 1724, 1625, 1468, 1418, 1380, 1249, 1233, 1179, 1151, 1113, 1073, 1068, 1046, 1040, 773, 734, 720, 638, 621 cm^{-1}.

As disulfonic acid. MS [*m*/*z* (% rel. int.)]: 330 (M^+, 0.2), 251 (4), 250 (9), 249 (7), 166 (9), 126 (9),, 124 (8), 111 (15), 110 (11), 109 (15), 98 (14), 97 (41), 96 (39), 95 (27), 85 (13), 84 (27), 83 (53), 82 (43), 81 (38), 80 (51), 71 (22), 70 (35), 69 (48), 68 (34), 67 (44), 64 (12), 57 (54), 56 (38), 55 (90), 54 (26).

Disodium dodecane-1,2-disulfonate, **1b**. The yield starting from 2.77 g, 10.0 mmol, of 4-decyl-1,3-dithiolane-2-thione, **7b**, was 4.53 g, 121% (hygroscopic), as a white solid material that decomposed at 220°C without melting. The product exhibited the same spectroscopic properties as the above product.

Disodium 6-ethyl-4-oxa-decane-1,2-disulfonate, **1c**. The yield from 2.36 g, 10.0 mmol of 6-ethyl-4-oxa-decane-1,2-dithiol, **4c**, was 3.75 g, 100% of a white hygroscopic crystalline material. The product decomposed at 220°C without melting. ^{1}H NMR (400 MHz, D_2O): δ 0.88 (t, 3 H, $J \approx 8$ Hz), 0.89 (t, 3 H, $J \approx 6$–8 Hz), 1.30 (m, 8 H), 1.59 (m, 1 H), 2.83 (s, > 1 H), 3.23 (ddd, 2 H, $J = 14$ Hz, $J = 10$ Hz, $J = 1$ Hz), 3.36–3.40 (m, 1 H), 3.40–3.52 (m, 2 H), 3.92–4.04 (m, 2 H) ppm. IR (KBr): 3439, 2960, 2931, 2874, 2861, 1727, 1633, 1465, 1416, 1379, 1231, 1206, 1187, 1125, 1108, 1066, 1042, 785, 745, 728, 689, 640, 615 cm^{-1}.

Disodium 6-ethyl-4-oxa-decane-1,2-disulfonate, **1c**. The yield starting from 2.79 g, 10.0 mmol, of 4-(4-ethyl-2-oxa-octyl)-1,3-dithiolane-2-thione, **7c**, was 4.98 g, 132% (hygroscopic). The product exhibited the same spectroscopic properties as the above product.

Oxidation of dodecane-1,2-dithiol, **4b**, *with ozone.* A solution containing dodecane-1,2-dithiol (10.0 mmol, 2.34 g) in 50 ml of dichloromethane was cooled to −78°C. A stream of ozone was then passed through the solution until a blue color persisted. The reaction mixture was then allowed to reach room temperature and 10 ml of water were added. The more volatile organic solvent was removed under reduced pressure, and the aqueous solution was neutralized with sodium bicarbonate solution. The solution was concentrated under reduced pressure and dried *in vacuo* over P_2O_3. The yield was 3.57 g (103%, hygroscopic) of a product that was probably a peracid, as it gave a positive iodide–starch reaction. ^{1}H NMR (400 MHz, D_2O, TPS): δ 0.85 (t, 3 H, $J = 6.8$ Hz), 1.28 (m, 14 H), 1.53 (m, 2 H), 1.93 (m, 2 H), 3.05 (ddd, 1 H, $J = 14$ Hz, $J = 10$ Hz, $J < 0$ Hz), 3.20 (m, 1 H), 3.43 (ddd, 1 H, $J = 14$ Hz, $J = 1$ Hz, $J < 1$ Hz). IR (KBr): 3454, 2957, 2921, 2853, 1720, 1639, 1467, 1412, 1378, 1329, 1198, 1129, 1064, 1040, 789, 763, 721, 622, 591, 555 cm^{-1}.

As (per)disulfonic acid. MS [*m*/*z* (% rel.int.)]: 328 (0,6), 296 (4), 266 (4), 265 (4), 264 (27), 232 (4), 199 (17), 166 (15), 111 (13), 109 (10), 101 (14), 98 (11), 97 (36), 96 (24), 95 (24), 87 (30), 85 (12), 84 (20), 83 (50), 82 (36), 81 (44), 80 (10), 79 (13), 73 (13), 71 (19), 70 (30), 69 (68), 68 (52), 67 (48), 64 (34), 60 (14), 57 (51), 56 (37), 55 (94), 54 (49).

Disodium dodecane-1,2-disulfonate, **1b**, *from dodec-1-ene and disulfur dichloride.* To 15.62 g, 0.1 mol of dodec-1-ene under a nitrogen atmosphere was added 1.0 g of disulfur dichloride under reflux, and the mixture kept at that temperature for 30 min. The reaction mixture was then cooled in an ice–water bath and another 5.14 g of disulfur dichloride were added dropwise over a 120 min period. Altogether 6.14 g (0.045 mol) was added. The reaction was stirred overnight at room temperature and then refluxed for ca. 8 h until a negative iodine–starch reaction was obtained. The crude product was then dissolved in 50 ml of ethanol, cooled in an ice bath and treated with a solution containing 15.0 g, 0.2 mol, of sodium hydrosulfide in 200 ml of ethanol over a 15 min period. The resulting mixture was stirred for 5 h at room temperature, 200 ml of water were added and the mixture was extracted with diethyl ether (4 × 100 ml). The combined ether layers were dried over anhydrous magnesium sulfate and filtered and the solvent was evaporated off under reduced pressure, leaving behind the crude dithiol as a colorless liquid. This product was then dissolved in 100 ml of glacial acetic acid and heated to 60°C. Hydrogen peroxide, 84 g of a 35% aqueous solution

(0.86 mol), was then added dropwise to the well stirred solution. The reaction mixture was stirred for 13 h. The pH-value at this stage was between 0 and 1. The reaction mixture was concentrated under reduced pressure, with removal of the last traces of acetic acid as an azeotrope with water. The sulfonic acid was then neutralized with a solution of sodium bicarbonate, (to pH 3). The solvent was removed under reduced pressure and the product dried by azeotropic distillation with benzene. Finally the product was placed under light vacuum to remove the last traces of solvents. The crude yield was 19.5 g (0.052 mol, 52% overall) which may be recrystallized from methanol yielding disodium decane-1,2-disulfonate, **1b**, as a hygroscopic white crystalline product. The product decomposed at 250°C without melting. ^{1}H NMR (400 MHz, D_2O): δ 0.86 ppm (t, 3 H, J = 6.4 Hz), 1.28 (m, 14 H), 1.55 (m, 2 H), 1.94 (m, 2 H), 1.98 (s, < 1 H), 2.81 (s, < 1 H), 3.06 (ddd, 1 H, J = 14 Hz, J = 10 Hz, J < 1 Hz), 3.21 (m, 1 H), 3.35 (s, < 1 H), 3.44 (dd, 1 H, J = 14 Hz, J < 1 Hz), 3.76 (s, < 1 H). IR (KBr): 3445, 2955, 2925, 2854, 1716, 1618, 1470, 1417, 1380, 1179, 1131, 1108, 1066, 1038, 996, 760, 721, 639, 617, 552 cm^{-1}.

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