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ELECTROREDUCTIVE CLEAVAGE OF CARBON-SULPHUR BONDS IN DITHIOACETALS

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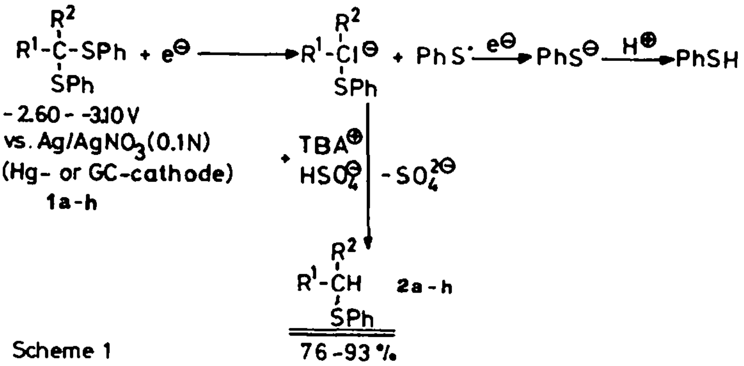
Abstract. The carbon-sulphur bond in aliphatic diphenyldithioacetals, α-carbonyldiphenyldithioacetals and α-carbonylketene dimethyldithioacetals can be cleaved cathodically on mercury (Hg) or glassy carbon (GC) electrodes. In the presence of tetrabutylammoniumhydrogensulphate ($TBAHSO_4$) as a proton donor one thiophenyl- respectively thiomethyl group is substituted by hydrogen to provide the corresponding phenylthioethers (phenylthiomethyl)ketones or methylthiovinylketones in very good yields. At a Hg cathode the electroreduction of α-carbonyldiphenyldithioacetals is self-catalyzed.

Polarity conversion (umpolung) of the reactivity of carbonyl compounds by transformation to sulphur containing derivatives, a very important principle in organic synthesis, is based on the effective stabilization of a carbanion in α-position.[1] Because of the same reason the reductive cleavage of one carbon-sulphur bond in dithioacetals or ketene dithioacetals is favoured. Reduction reagents like Ca/NH_3,[2] tributylstannyllithium [3] or lithium naphthalide [4] have been used for the cleavage and the resulting nucleophilic carbon can be trapped by electrophiles. A convenient alternative to the reduction with those chemical reagents, which are mostly quite difficult to handle, would be the electroreductive cleavage of carbon-sulphur bonds.[5,6] We are able to present a very simple and effective cathodic method for the cleavage of carbon-sulphur bonds in aliphatic diphenyldithioacetals, α-carbonyldiphenyldithioacetals and α-carbonylketene dimethyldithioacetals.

Aliphatic diphenyldithioacetals can be easily converted electroreductively into the corresponding phenyl thioethers in isolated yields of 76 to 93%, replacing one thiophenyl group by a proton using a mercury (Hg) or glassy carbon (GC) working electrode (Scheme 1).

The supporting electrolyte tetrabutylammoniumhydrogensulphate ($TBAHSO_4$) at the same time acts as a proton donor for the cathodically generated carbanion. Electroanalytical studies showed that only diphenyldithio- but not dialkyldithioacetals have a reduction potential which is accessible in the potential range of the used electrolyte $CH_3CN/TBAHSO_4$. In Table 1 the results of the preparative electroreductive substitution reaction of one thiophenyl group by a proton in different diphenyldithioacetals are presented.



Scheme 1

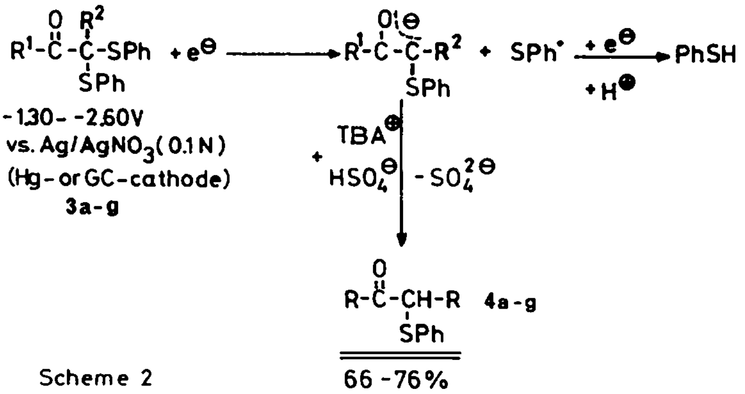
Table 1. Results of the preparative cathodic cleavage of diphenyldithioacetals in $CH_3CN/TBA^+HSO_4^-$

Substrate $R^1R^2C/SPh)_2$ R^1	R^2	Substrate Number	Turnover (%)	Charge Consumption (F/mol)	Working Potential (V *vs.* NHE)[d]	Product R^1R^2CHSPh (%)[a]	Product Number
$PhCH_2CH_2$	CH_3	1a	100	2.1	-2.43	76	2a
$-(CH_2)_5-$		1b	100	2.3	-2.43	82	2b
$-(CH_2)_5-$		1b	100	2.4	-2.43	73[b]	2b
$(CH_3)_3C$	CH_3	1c	100	2.3	-2.48	77	2c
$(CH_3)_2CH$	CH_3	1d	100	2.4	-2.43	78	2d
$CH_3CH_2CH_2$	H	1e	100	2.7	-2.48	79	2e
$EtO-CO-CH_2$	CH_3	1f	95	2.3	-2.03	85 (89)[c]	2f
3,3-bis(phenylthio)-5α-cholestane		1g	100	2.3	-2.48	86 (3β-SPh:3α=7:1)	2g
2,2-bis(phenylthio)-bicyclo[2.2.1]heptane		1h	75	2.5	-2.53	70 (93)[c] (endo:exo=5:3)	2h

[a] Material yield
[b] At a glassy carbon cathode; all other experiments at a Hg cathode
[c] Values in parentheses with respect to consumed substrate
[d] Calculated from values obtained with a Ag/AgNO$_3$ (0.1N) reference electrode (570 mV *vs.* NHE)

It is interesting to note that a carboxylic ester group in β-position to the sulphur substituents lowers the reduction potential of the substrate by about 500 mV, however, it remains unreduced in the reaction. The electroreduction of 3,3-bis-(phenylthio)-5α-cholestane and 2,2-bis(phenylthio)-bicyclo[2.2.1]heptane shows that steric effects have an influence on the stereoselectivity of the method with regard to the conversion of chiral dithioacetals. Thus, 3,3-bis(phenylthio)-5α-cholestane is predominantly reduced to the thermodynamically more stable 3β-thiophenylcholestane while 2,2-bis(phenylthio)-bicyclo[2.2.1]heptane is preferentially reduced to the kinetically more favourable *endo*-product. The latter result can be explained by the faster attack of the proton onto the carbanion from the less hindered *exo*-side. Other electrophiles than protons like triethylorthoformiate turned out to be too unreactive to provide the desired substituted thioethers or they themselves were reduced at the working potential like CO_2 or butanal.

α-Carbonyldiphenyldithioacetals, easily prepared from esters and bis(phenylthio)-methyllithium, can be reduced at Hg or GC at a much less negative potential because the α-standing carbonyl group leads to an additional stabilization of the formed anion. In the presence of $TBAHSO_4$ the reduction of those substrates provides (phenylthiomethyl)ketones, which are valuable building blocks in organic synthesis and regioselective enol equivalents, in yields of 66 to 76% (Scheme 2).



Scheme 2

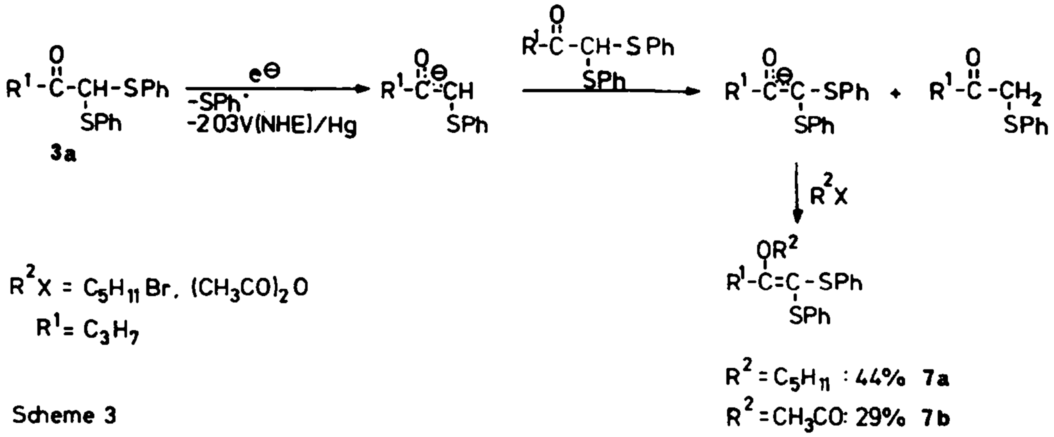
A survey of the structural variety of α-carbonyl-diphenyldithioacetals for this conversion is presented in Table 2. The reduction potentials are dependent on the substituents R. Double bonds with the exception of those being conjugated with the α-carbonyl group and carbonyl groups are not reduced under these conditions.

Table 2. Results of the preparative cathodic cleavage of α-carbonyldiphenyldithioacetals in $CH_3CN/TBA^{\oplus}HSO_4^{\ominus}$

Substrate R^1-CO-$CR^2(SPh)_2$ R^1	R^2	Substrate Number	Turnover (%)	Charge Consumption (F/mol)	Working Potential (V vs. NHE)[d]	Product R^1-CO-CHR^2-SPh (%)[a]	Product Number
$CH_3CH_2CH_2$	H	3a	100	2.2	-2.03	72	4a
$PhCH_2$	H	3b	100	2.0	-1.73	70	4b
1-cyclohexenylmethyl	H	3c	100	2.0	-1.43	72	4c
cyclohexyl	H	3d	100	2.3	-2.03	73	4d
cyclohexyl	H	3d	100	2.0	-1.73	74[b]	4d
Ph	H	3e	100	2.0	-0.73	69	4e
Ph	H	3e	91	2.25	-1.63	53[b,c]	4e
CH_3-C(OEt)$_2$	H	3f	100	2.7	-1.73	72	4f
CH_3-C(OEt)$_2$	H	3f	100	2.2	-1.63	76[b]	4f
CH_3	CH_3-CO	3g	100	2.2	-0.73	66	4g

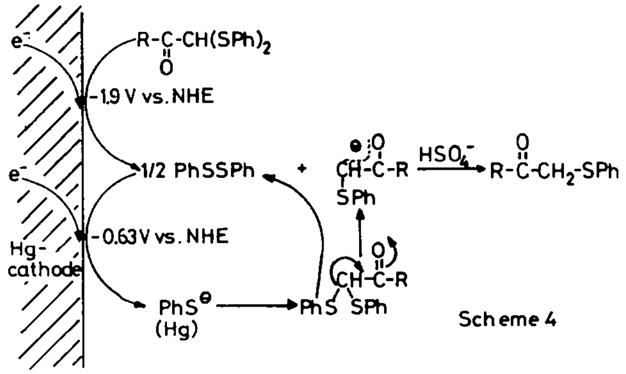
[a] Material yield
[b] At a glassy carbon cathode; all other experiments at a Hg cathode
[c] Accompanied by 20% acetophenone
[d] Calculated from values obtained with a $Ag/AgNO_3$ (0.1N) reference electrode (570 mV vs. NHE)

The use of pentylbromide or acetic anhydride as electrophiles to trap the generated carbanion leads to O-alkylated, respectively O-acylated substrates together with (phenylthiomethyl)ketones. This course of the reaction may be interpreted by the higher acidity of the α-protons in the α-carbonyldiphenyldithioacetal substrates compared with the (phenylthiomethyl)ketone (Scheme 3).



Scheme 3

At a Hg cathode the electroreduction of α-carbonyldiphenyldithioacetals in the presence of $TBAHSO_4$ is self-catalyzed. During electrolysis at constant current the potential increases to more positive values reaching a limiting value of -0.63 V *vs.* NHE which is the reduction potential of the diphenyldisulfide. The mechanistic explanation is given in Scheme 4.



Scheme 4

Hence the addition of 10 mol% diphenyldisulfide to the reaction mixture allows the electroreductive conversion of the α-carbonyldiphenyldithioacetals to the corresponding (phenylthiomethyl)ketones at a constant potential of -0.63 V *vs.* NHE.

Table 3. Results of the preparative cathodic cleavage of α-carbonyldiphenyldithioacetals in $CH_3CN/TBAHSO_4$ in the presence of 10 mol% diphenyldisulfide as a catalyst

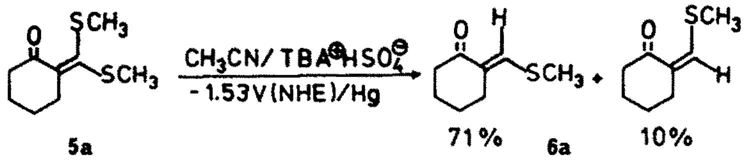
Substrate Number	Turnover (%)	Charge Consumption (F/mol Substrate)	Working Potential (V *vs.* NHE)	Product Number	(%)[a]
3a	82	2.0	-0.78	4a	69(84)[b]
3d	100	2.0	-0.68	4d	87

[a] Material yield

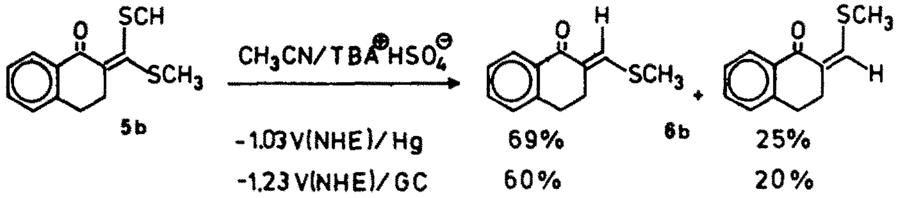
[b] Value in parentheses with respect to consumed substrate

In the presence of other electrophiles like methyl iodide catalysis by diphenyldisulfide is not observed because the generated thiophenolate ion is trapped by the electrophile.

The cathodic reduction of the α-carbonylketene dimethyldithioacetals 5a and 5b under the same conditions as described above leads to the corresponding (methylthiovinyl)ketones in yields of 80 to 94%. The thermodynamically favoured E-isomer is formed predominantly [7] (equation 1 and 2).

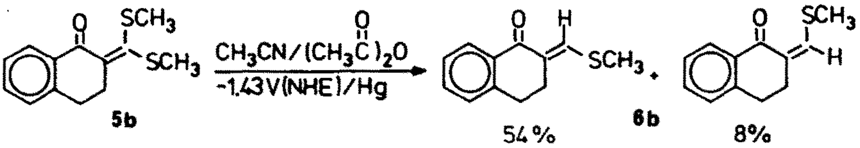


(1)

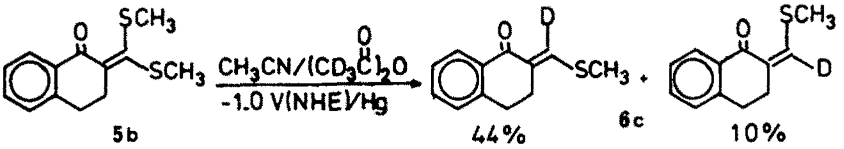


(2)

Acetic anhydride does not act as an acetylating agent but rather as a protonating agent at a Hg cathode. This was proved by using hexadeutero acetic anhydride (equation 3 and 4).



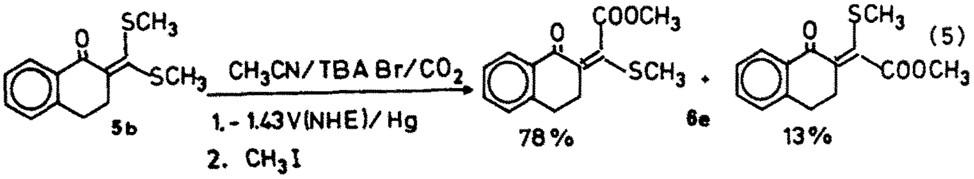
(3)



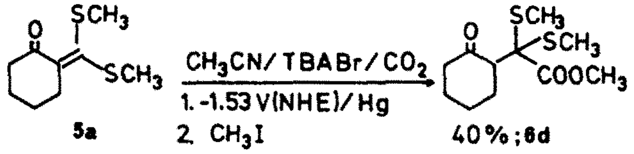
(4)

The difference in the E-/Z-isomer ratio using either TBAHSO$_4$ or acetic anhydride as a protonating agent may be due to a modified reaction mechanism. By using acetic anhydride the generated carbanion may undergo O-acylation first, followed by an intra- or intermolecular protonation at the carbon next to the remaining thiomethyl group.

The electroreduction of 2-bis(methylthio)methylene-1-tetralone (5b) in the presence of CO$_2$ provides the corresponding carboxylate ion which is trapped as methylester after the addition of methyl iodide. The use of CO$_2$ as an electrophile in this case was already demonstrated by H.Matschiner et al. [5,8]. In contrast to the reported results the reduction of 2-bis(methylthio)methylenecyclohexanone (5a) under our conditions in the presence of CO$_2$ leads to the addition product (6d) (equation 5 and 6).



(5)



(6)

EXPERIMENTAL

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, NMR spectra were measured with Varian EM-360, EM-390 and Bruker WH-90 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 with a data system. Liquid chromatography was performed on silica gel 63/100 mesh (Merck) on glass columns: 4 cm (diam.), 45 cm.
All solvents were purified by distillation, acetonitrile was dried over P_4O_{10} and K_2CO_3, and THF was dried over LAH.

Aliphatic diphenyldithioacetals (**1**).- Compounds **1a** - **1b** were prepared according to a literature procedure[9] from the corresponding ketones and thiophenol using $AlCl_3$ as a catalyst.

2,2-Bis(phenylthio)-4-phenyl-butane (**1a**).- Bright yellow oil (68%). (Found: C, 75.35; H, 6.43. $C_{22}H_{22}S_2$ requires C, 75.38; H,6.33); ν(film) 3080, 3045 (ar C-H), 2980, 2940 (C-H), 755, 700 (ar C-H) cm^{-1}; δ_H (90 MHz) 7.55-7.73 (m, 4H, ar H), 6.98-7.42 (m, 11H ar H), 2.75-3.02 (m, 2H, PhCH_2), 1.89-2.09 (m, 2H, Ph$CH_2C\underline{H}_2$), 1.44 (s, 3H, CH_3) ppm; δ_C (90 MHz) 141.64; 136.92; 131.96; 129.12; 128.63; 128.40 (ar C), 63.64 (-C-); 43.28 (Ph$\underline{C}H_2$), 31.36 (CH_2), 28.39 (CH_3) ppm; *m*/*z*= 241 (42%), 131 (90), 110 (26), 91 (100), 77 (10), 65 (20), 51 (9).

1,1-Bis(phenylthio)-cyclohexane (**1b**)[9], 2,2-Bis(phenylthio)-3,3-dimethyl-butane (**1c**)[10] and 1,1-Bis(phenylthio)-butane (**1e**)[11].- Physical and spectroscopic data compared well with those reported.

2,2-Bis(phenylthio)-3-methyl-butane (**1d**).- Colourless oil (45%). (Found: C, 70.81; H, 6.99. $C_{17}H_{20}S_2$ requires C, 70.78; H, 6.99); ν(film) 3098, 3000 (ar C-H), 3000, 2960, 2900 (C-H), 795, 745-760 (br.), 710, 700 (ar C-H) cm^{-1}; δ_H (60 MHz) 7.13-7.73 (m, 10H, ar H), 2.0 (m, 1H, CH), 1.26 (s, 3H, CH_3), 1.2 (d, 6H, $C\underline{H}_3$-CH) ppm; *m*/*z*= 288 (M^+, 0.1%), 259 (1.1), 179 (100), 135 (27), 110 (82), 109 (25), 69 (81), 41 (65).

3,3-Bis(phenylthio)-ethylbutyrate (**1f**).- Colourless oil (31%). (Found: C, 65.08; H, 6.07. $C_{18}H_{20}O_2S_2$ requires C, 65.03; H, 6.06); ν(film) 3080, 3000 (ar C-H), 3000, 2960, 2920 (C-H), 1720-1750 (br.) (C=O), 1190, 1155 (C-O), 785, 750, 735, 690 (ar C-H) cm^{-1}; δ_H (90 MHz) 7.57-7.83 (m, 4H, ar H), 7.27-7.57 (m, 6H, ar H), 4.18 (q, 2H, CH_2O), 2.75 (s, 2H, CH_2), 1.65 (s, 3H, CH_3), 1.28 (t, 3H, CH_2-$C\underline{H}_3$) ppm; *m*/*z*= 287 (0.1%), 259 (0.8), 223 (100), 177 (78), 149 (95), 134 (32), 110 (76), 109 (49), 77 (21).

3,3-Bis(phenylthio)-5α-cholestane (**1g**).- Colourless needles (76%). M.p. 89-90°C. (Found: C, 79.61; H, 9.62. $C_{39}H_{56}S_2$ requires C, 79.53; H, 9.58); δ_H (90 MHz) 7.49-7.89 (m, 4H, ar H), 7.22-7.49 (m, 6H, ar H), 0.44-1.96 (m, 29H) ppm; *m*/*z*= 479 (42%), 478 (100), 371 (5), 369 (12), 162 (70), 123 (11), 110 (41), 109 (10), 81 (32).

2,2-Bis(phenylthio)-bicyclo[2.2.1]heptane (**1h**).- Colourless needles (67%). M.p. 49°C. (Found: C, 72.84; H, 6.50. $C_{19}H_{20}S_2$ requires C, 73.03; H, 6.45); δ_H (90 MHz) 7.44-7.7 (m, 4H, ar H), 7.2-7.4 (m, 6H, ar H), 2.0-2.5 (m, 5H, $C\underline{H}_2$, C$\underline{H}$), 1.2-1.7 (m, 5H, $C\underline{H}_2$, C$\underline{H}$) ppm; *m*/*z*= 312 (M^+, 0.03%), 203 (100), 174 (42), 123 (51), 110 (38), 109 (23), 93 (72), 77 (27), 67 (21), 65 (23).

α-Carbonyldiphenyldithioacetals (**3**).- Compounds **3a** - **3g** were prepared from the corresponding carboxylic esters and bis(phenylthio)methyllithium: To a solution of 10 mmol bis(phenylthio)methane[7] in 25 ml abs. tetrahydrofurane (THF), stirred under argon at 0°C, 11 mmol of n-butyllithium (n-buLi) in n-hexane was added slowly. This mixture was cooled down after 10 minutes stirring to -78°C and 10 mmol of the ester was added dropwise. The dark yellow reaction mixture changed to bright yellow while warming up to r.t. The stirring was continued for four hours, the reaction mixture then poured into four times its' volume of water and the product extracted with three 100 ml portions of ether. After drying the combined ether phases over $MgSO_4$ the solvent and the unreacted ester were removed by distillation under vacuum and the crude product was purified by column chromatography on silica gel (eluate: petroleum ether/ether 10:1).

1,1-Bis(phenylthio)-2-pentanone (**3a**).- Colourless needles (42%). M.p. 52°C. (Found: C, 67.56; H, 6.04. $C_{17}H_{18}OS_2$ requires C, 67.51; H, 6.00). ν(KBr) 3140, 3040, 3000 (ar C-H), 3000, 2940 (C-H), 1740 (C=O), 770, 720, 670 (ar C-H) cm^{-1}; δ_H (90 MHz) 7.23-7.5 (m, 10H, ar H), 4.83 (s, 1H, -CH), 2.6 (t, 2H, CH_2-CO), 1.57 (dq, 2H,CH_3-$C\underline{H}_2$), 0.73 (t, 3H, $C\underline{H}_3$) ppm; *m*/*z*= 302 (M^+, 3.5%), 231 (100), 153 (10), 123 (35), 121 (28), 109 (18), 77 (15), 45 (19), 43 (18).

1,1-Bis(phenylthio)-3-phenyl-2-propanone (**3b**).- Colourless needles (38%). M.p.40°C. (Found: C, 72.10; H, 5.13. $C_{21}H_{18}OS_2$ requires C, 71.97; H, 5.18); ν(KBr) 3080, 3060 (ar C-H), 2980, 2950, 2880 (C-H), 1730 (C=O), 750, 705, 695 (ar C-H) cm^{-1}; δ_H (60 MHz) 7.0-7.4 (m, 15H, ar H), 4.87 (s, 1H, CH), 3.83 (s, 2H, CH_2) ppm; *m*/*z*=

350 (M^+, 4%), 231 (100), 153 (8), 131 (30), 121 (32), 110 (20), 109 (20), 91 (56), 77 (12).

1,1-Bis(phenylthio)-3-(cyclohexene-1-yl)-2-propanone (**3c**).- (The corresponding ester was prepared according to a literature procedure[12,13]). Colourless oil (28%). ν(film) 3100, 3030 (ar C-H), 2960, 2880, 2860 (C-H), 1750 (C=O), 750, 700 (ar C-H) cm^{-1}; δ_H (90 MHz) 6.7-7.13 (m, 10H, ar H), 5.3 (m, 1H, CH=C), 4.83 (s, 1H, CH), 3.1 (s, 2H, CH_2-CO), 1.3-2.1 (m, 8H, CH_2) ppm; m/z= 354 (M^+, 0.4%), 231 (100), 154 (18), 123 (40), 121 (48), 110 (47), 109 (68), 95 (49), 77 (48), 65 (40), 41 (38), 39 (44). (Found M^+, 354.1101. $C_{21}H_{22}OS_2$ requires M, 354.1112).

1,1-Bis(phenylthio)-2-cyclohexyl-2-ethanone (**3d**).- Colourless needles (41%). M.p. 112-113°C. (Found: C, 70.26; H, 6.57. $C_{20}H_{22}OS_2$ requires C, 70.14; H, 6.47). ν(KBr) 3100, 3080, 3040 (ar C-H), 2960, 2880 (C-H), 1715 (C=O), 900, 785, 762, 745, 695 (ar C-H) cm^{-1}; δ_H (60 MHz) 7.3-7.73 (m, 10H, ar H), 5.0 (s, 1H, CHS_2), 2.73 (m, br., 1H, CH), 1.1-2.0 (m, 10H, CH_2) ppm; m/z= 342 (M^+, 2%), 231 (100), 123 (21), 110 (20), 109 (18), 83 (28), 55 (21), 41 (18).

1,1-Bis(phenylthio)-acetophenone (**3e**).- Colourless needles (38%). M.p. 98°C. (Found: C, 71.58; H, 4.88. $C_{20}H_{16}OS_2$ requires C, 71.39; H, 4.79). ν(KBr) 3120, 3090, 3060 (ar C-H), 2970 (C-H), 1685 (C=O), 840, 810, 760, 750, 728, 700 (ar C-H) cm^{-1}; δ_H (60 MHz) 7.03-7.7 (m, 15H, ar H), 5.6 (s, 1H, CH) ppm; m/z= 336 (M^+, 3%), 231 (100), 121 (21), 110 (18), 109 (17), 105 (31), 77 (41).

1,1-Bis(phenylthio)-3,3-diethoxy-2-butanone (**3f**).- Colourless oil (51%). (Found: C, 63.85; H, 6.47. $C_{20}H_{24}O_3S_2$ requires C, 63.80; H, 6.42); ν(film) 3100, 3080, 3000 (ar C-H), 3000, 2945, 2905 (C-H), 1730 (C=O), 1210, 1180-1140 (br.), 1100, 1055, 1030 (C-O-C), 745, 690 (ar C-H) cm^{-1}; δ_H (60 MHz) 7.03-7.5 (m, 10H, ar H), 5.57 (s, 1H, CH), 3.07-3.4 (m, 4H, CH_2-O), 1.43 (s, 3H, CH_3-COO), 1.03 (t, 6H, CH_3-CH_2O) ppm; δ_C (90 MHz) 200.68 (C=O), 133.65 (ar C-S), 133.13; 129.02; 128.53 (ar C); 102.51 (CO_2), 59.62 (CS_2), 57.94 (CH_3), 22.50 (CH_3), 15.18 (CH_2) ppm; m/z= 231 (7%), 117 (100), 110 (41), 109 (48), 89 (76), 61 (100), 43 (97).

3,3-Bis(phenylthio)-2,4-pentanedione (**3g**).- This compound was prepared according to a literature procedure[14].

The dimethylketene dithioacetals **5a** and **5b** were prepared by literature procedures[15,16].

Equipment for preparative electrolyses.- Preparative electrolyses were performed using a stabilized current source, model NTN 1400M-350 (FUG, Rosenheim), modified as potentiostate together with a digital coulometer based on a voltage to frequency converter.

Electrochemical cell: Devided beaker type cell (150 ml), separated by a glass frit, with cooling mantle equipped with a Hg- (31.4 cm^2) or a GC (15 cm^2) working electrode, Pt- wire anode and Ag/$AgNO_3$ (0.1n) reference electrode. The temperature was 25°C. Argon atmosphere was maintained.

Electrolytes: 1) 0.1N solution of $TBAHSO_4$ in dry CH_3CN, 2) 0.1N solution of $TBAClO_4$ in dry CH_3CN, 3) 0.1N solution of $TBAHSO_4$ in dry CH_3CN/THF 1:1. All electrolytes were dried over molecular sieve before being used.

General procedure for direct electrolysis of aliphatic diphenyldithioacetals, α-carbonyldiphenyldithioacetals and ketendithioacetals in the presence of $TBAHSO_4$ as a proton donor.- 2 mmol of the substrate was dissolved in 45 ml electrolyte 1 (in the case of the conversion of 2,2-bis(phenylthio)-5α-cholestane (**1g**) electrolyte 3 was used). The electrolysis is terminated after the current has dropped to 10 mA or the charge consumption reaches 2.7 F/mol of the substrate. For work up the solvent was evaporated, the residue dissolved in 30 ml water and 30 ml ether, the organic phase separated and the water phase three times extracted with 30 ml ether. The combined ether phases were dried over $MgSO_4$ and the solvent was removed. The products were purified by column chromatography on silica gel and identified by spectroscopic methods.

1-Phenyl-3-phenylthio-butane (**2a**).- Eluent: cyclohexane/dichloromethane 10:1. Colourless oil. (Found: C, 79.13; H, 7.47. $C_{16}H_{18}S$ requires C, 79.29; H, 7.48); δ_H (90 MHz) 7.1-7.44 (m, 10H, ar H), 3.0-3.38 (m, 1H, CH), 2.78 (t, 2H, CH_2-Ph), 1.69-2.0 (m, 2H, CH_2-CH_2-Ph), 1.29 (d, 3H, CH_3); m/z= 242 (M^+, 35%), 132 (53), 117 (43), 110 (23), 109 (11), 92 (9), 91 (100), 65 (18).

Phenylcyclohexylsulfide (**2b**).- Eluent: petroleum ether/ether 50:1. Colourless oil. (Found: C, 74.82; H, 8.58. $C_{12}H_{16}S$ requires C, 74.95; H, 8.39). δ_H (60 MHz) 7.0-7.53 (m, 5H, ar H), 2.9-3.23 (m, 1H, CH), 1.0-2.1 (m, 10H, CH_2) ppm; m/z= 192 (M^+, 22%), 110 (100), 84 (12), 83 (10), 55 (28).

2,2-Dimethyl-3-phenylthio-butane (**2c**).- Eluent: petroleum ether/ether 49:1. Colourless oil. (Found: C, 73.81; H, 9.12. $C_{12}H_{18}S$ requires C, 74.17; H, 9.34); δ_H (60

MHz) 7.1-7.63 (m, 5H, ar H), 3.1 (q, 1H, CH-SPh), 1.23 (d, 3H, CH_3-CH), 1.03 (s, 9H, CH_3) ppm; m/z= 194 (M^+, 41%), 137 (100), 110 (52), 85 (30), 84 (42), 69 (22), 57 (32), 43 (78), 41 (43).

2-Methyl-3-phenylthio-butane (2d) [17] and 1-phenylthiobutane (2e) [18].- Physical and spectroscopic data compared well with those reported.

3-Phenylthio-ethylbutyrate (2f).- Eluent: petroleum ether/ether 9:1. Colourless oil. ν(film) 3110, 3100, 3015 (ar C-H), 2990, 2960, 2940, 2900 (C-H), 1735-1755 (br., C=O ester), 860, 760, 710, 700 (ar C-H) cm^{-1}; δ_H (90 MHz) 7.1-7.53 (m, 5H, ar H), 4.07 (q, 2H, OCH_2), 3.53 (m, 1H, CH-S-Ph), 2.22-2.75 (m, 2H, CH_2-CO_2), 1.33 (d, 3H, CH_3-CH), 1.2 (t, 3H, CH_3-CH_2) ppm; m/z= 224 (M^+, 55%), 179 (7), 137 (43), 110 (100), 109 (41), 87 (19), 73 (18), 45 (18). (Found M^+, 224.0882. $C_{12}H_{16}O_2S$ requires M, 224.0871).

3-Phenylthio-5α-cholestane (2g).- For purification the crude product was dissolved in dichloromethane and the solution washed with 0.3N NaOH solution. After drying the organic layer over $MgSO_4$ and evaporation of the solvent a mixture of the 3β- and 3α-isomer (7:1) was isolated. After recrystallization (acetone) pure 3β-phenylthio-5α-cholestane was obtained (colourless needles). δ_H (90 MHz, mixture) 7.1-7.5 (m, 5H, ar H), 3.5-3.6 (m, 1/8 H, CH-S-Ph), 2.87-3.22 (m, 7/8 H, CH-S-Ph), 0.56-2.16 (m, 46H, CH_3, CH_2, CH) ppm; m/z= 480 (M^+, 100%), 371 (28), 217 (27), 203 (19), 163 (20), 110 (40), 109 (31), 95 (26), 81 (21), 55 (27), 43 (33), 41 (20); (Found: (3β-phenylthio-5α-cholestane): C, 82.50; H, 10.99. $C_{33}H_{52}S$ requires C, 82.43; H, 10.90).

2-Phenylthio-bicyclo[2.2.1]heptane (2h).- Eluent: petroleum ether/ether 50:1. Mixture of endo- and exo-isomer (5:3). Colourless needles. (Found: C, 76.55; H, 7.90. $C_{13}H_{16}S$ requires C, 76.42; H, 7.89). δ_H (90 MHz) 7.0-7.56 (m, 5H, ar H), 3.36-3.67 (m, 5/8 H, CH-S-Ph, endo-isomer), 3.07-3.27 (m, 3/8 H, CH-S-Ph, exo-isomer), 0.89-2.44 (m, 10H, CH_2, CH) ppm; m/z= 204 (M^+, 48%), 110 (33), 109 (17), 95 (100), 67 (29), 55 (14), 53 (10), 41 (29), 39 (22).

1-Phenylthio-2-pentanone (4a).- Eluent: petroleum ether/ether 4:1. Colourless needles. M.p. 25°C. (Found: C, 67.72; H, 7.26. $C_{11}H_{14}O_4S$ requires C, 68.00; H, 7.26); ν(KBr) 3110, 3090 (ar C-H), 2995, 2960, 2900 (C-H), 1720 (C=O), 750, 700 (ar C-H) cm^{-1}; δ_H (90 MHz) 7.16-7.38 (m, 5H, ar H), 3.64 (s, 2H, CH_2-S-Ph), 2.56 (t, 2H, CH_2-CO), 1.58 (m, 2H, CH_3-CH_2), 0.87 (t, 3H, CH_3) ppm; m/z= 194 (M^+, 30%), 124 (40), 123 (78), 110 (16), 109 (20), 77 (22), 71 (100), 65 (15), 51 (20), 45 (39), 43 (100).

1-Phenyl-3-phenylthio-2-propanone (4b).- Eluent: petroleum ether/ether 3:2. Colourless oil. ν(film) 3100, 3060, 3040 (ar C-H), 2980, 2960, 2880 (C-H), 1730 (C=O), 820, 750, 710 (ar C-H) cm^{-1}; δ_H (60 MHz) 6.87-7.47 (m, 10H, ar H), 3.7 (s, 2H, CH_2-CO), 3.6 (s, 2H, CH_2-S-Ph) ppm; m/z= 242 (M^+, 27%), 133 (32), 123 (51), 110 (12), 109 (10), 91 (100), 77 (9). (Found: M^+, 242.0777. $C_{15}H_{14}OS$ requires M, 242.0765).

3-(Cyclohexene-1-yl)-1-phenylthio-2-propanone (4c).- Eluent: petroleum ether/ether 9:1. Colourless oil. (Found: C, 73.11; H, 7.44. $C_{15}H_{18}OS$ requires C, 73.13; H, 7.36); ν(film) 3110, 3100, 3060, 3040 (ar C-H), 2960, 2890, 2870 (C-H), 1725 (C=O), 810, 750, 700 (ar C-H) cm^{-1}; δ_H (60 MHz) 6.97-7.5 (m, 5H, ar H), 5.27-5.57 (m, 1H, CH=C), 3.57 (s, 2H, CH_2-S-Ph), 3.07 (s, 2H, CH_2-CO), 1.17-2.1 (m, 8H, CH_2) ppm; m/z= 246 (M^+, 19%), 137 (31), 123 (100), 110 (22), 109 (21), 95 (68), 81 (15), 77 (30), 67 (32), 55 (48).

1-Cyclohexyl-2-phenylthio-1-ethanone (4d).- Eluent: petroleum ether/ether 9:1. Colourless needles. M.p. 34°C. (Found: C, 71.77; H, 7.82. $C_{14}H_{18}OS$ requires C, 71.75; H, 7.74); ν(KBr) 3120, 3100 (ar C-H), 2970, 2930, 2890 (C-H), 1712 (C=O), 745, 740, 710, 700 (ar C-H) cm^{-1}; δ_H (90 MHz) 7.0-7.3 (m, 5H ar H), 3.67 (s, 2H, CH_2-S-Ph), 2.33-2.83 (m, 1H, CH), 1.0-1.93 (m, 10H, CH_2) ppm; m/z= 234 (M^+, 15%), 111 (27), 110 (12), 109 (10), 83 (100), 55 (32).

1-Phenylthio-acetophenone (4e).- Eluent: petroleum ether/ether 7:1 and afterwards recrystallization from petroleum ether. Colourless needles. M.p. 53°C. (Found: C, 73.50; H, 5.26. $C_{14}H_{12}OS$ requires C, 73.65; H, 5.30); ν(KBr) 3150, 3120 (ar C-H), 2990, 2980, 2940, 2920 (C-H), 1685 (C=O), 815, 750, 730, 695, 660 (ar C-H) cm^{-1}; δ_H (60 MHz) 7.6-8.1 (m, 2H, ar H), 7.0-7.6 (m, 8H, ar H), 4.23 (s, 2H, CH_2) ppm; m/z= 228 (M^+, 23%), 123 (10), 110 (8), 109 (9), 105 (100), 77 (28).

3,3-Diethoxy-1-phenylthio-2-butanone (4f).- Eluent: petroleum ether/ether 4:1. Colourless oil. (Found: C, 62.70; H, 7.59. $C_{14}H_{20}O_3S$ requires C, 62.66; H, 7.51); ν(film) 3150, 3100, 3010 (ar C-H), 2970, 2930 (C-H), 1740 (C=O), 875, 750, 700 (ar C-H) cm^{-1}; δ_H (60 MHz) 6.93-7.4 (m, 5H, ar H), 3.73 (s, 2H, CH_2-S-Ph), 3.15 (q, 4H, CH_2-O), 1.33 (s, 3H, CH_3), 1.13 (t, 6H, CH_3-CH_2) ppm; δ_C (90 MHz) 203.55 (C=O), 135.51 (ar C-S), 129.80; 128.79; 126.50 (ar C), 102.32 (CO_2), 57.66 (CH_3), 40.77 (CH_2-S-Ph), 21.08 (CH_3), 15.15 (CH_2O) ppm; m/z= 223 (21%), 177 (0.8), 123 (9), 117 (100), 110 (10), 109 (9), 89 (39), 61 (86), 45 (14), 43 (58).

3-Phenylthio-2,4-pentandione (**4g**)[19].- Physical and spectroscopic data compared well with those reported.

2-(Methylthio-methylene)-cyclohexanone (**6a**).- Eluent: petroleum ether/ether 2:1. Isolated mixture of the *E*-[20] and *Z*-isomers (7:1). ν(film) 2960, 2890 (C-H), 1675 (C=O, br.), 1560 (C=C, br.) cm^{-1}; δ_H (90 MHz) 7.56 [t, 7/8 H, -CH=C, ^4J= 2 Hz (*E*-isomer)], 6.7 [t, 1/8 H, CH=C, ^4J= 1.3 Hz (*Z*-isomer)], 2.44 [s, 21/8 H, -SCH_3 (*E*-isomer)], 2.33 [s, 3/8 H, SCH_3 (*Z*-isomer)], 2.27-2.44 (m, 4H, CH_2), 1.7-2.0 (m, 4H, CH_2) ppm; δ_C (90 MHz) 196.31 (C=O), 143.78 (=C-S), 130.90 (C=C), 39.26; 27.71; 23.21; 22.92 (CH_2), 17.41 (CH_3) ppm (*E*-isomer); *m/z*= 156 (M^+, 41%), 141 (100), 109 (20), 81 (15), 79 (22), 61 (10). (Found: M^+, 156.0607. $C_8H_{12}OS$ requires M, 156.0609).

2-(Methylthio-methylene)-1-tetralone (**6b**).- The mixture of the *E*-[20] and *Z*-isomer can be separated by LC. Eluent: petroleum ether/ether 7:4. *E*-isomer: yellow needles. M.p. 60-62°C. (Found: C, 70.66; H, 6.05. $C_{12}H_{12}OS$ requires C, 70.55; H, 5.92). ν(KBr) 3100, 3060 (ar C-H), 2960, 2870 (C-H), 1665 (C=O), 1565 (C=C), 815, 790, 745, 710 (ar C-H) cm^{-1}; δ_H (90 MHz) 7.95-8.1 (m, 1H, ar H), 7.7 (t, 1H, -CH=C, ^4J= 1.2 Hz), 7.1-7.53 (m, 3H, ar H), 2.56-3.0 (m, 4H, CH_2), 2.44 (s, 3H, SCH_3) ppm; *m/z*= 204 (M^+, 33%), 189 (100), 157 (4), 128 (26), 115 (7), 90 (15), 77 (11), 45 (10).- *Z*-isomer: yellow oil. M.p. <20°C. ν(film) 3100, 3060 (ar C-H), 2960, 2930, 2870 (C-H), 1650 (C=O), 1545 (C=C), 850, 810, 790, 750, 725, 695 (ar C-H) cm^{-1}; δ_H (90 MHz) 8.0.8.16 (m, 1H, ar H), 7.13-7.53 (m, 3H, ar H), 6.93 (t, 1H, CH=C, ^4J= 0.9 Hz), 2.67-2.98 (m, 4H, CH_2), 2.36 (s, 3H, SCH_3) ppm. (Found: M^+, 204.0613. $C_{12}H_{12}OS$ requires M, 204.0608).

Direct electrolysis of 1,1-bis(phenylthio)-2-pentanone (**3a**), 2-bis(methylthio)-methylene-cyclohexanone (**5a**) and 2-bis(methylthio)methylene-1-tetralone (**5b**) in the presence of other electrophiles than protons.- 2 mmol of **3a**, **5a** or **5b** was dissolved in 45 ml electrolyte 2, a tenfold (in case of hexadeuterio acetic anhydride a 5fold) excess of the electrophile (pentyl bromide, acetic anhydride respectively hexadeuterio acetic anhydride) was added and the electrolyses were stopped after a charge consumption of 2.2 F/mol substrate. The work up was carried out as described in the general procedure and the products purified by column chromatography on silica gel.

1,1-Bis(phenylthio)-2-pentyloxy-1-pentene (**7a**).- Eluent: petroleum ether/dichloromethane 7:3. Colourless oil. ν(film) 3100 (ar C-H), 2990, 2960, 2900 (C-H), 1590 , 1570 (C=C), 790, 745, 700 (ar C-H); δ_H (90 MHz) 7.07 (s, 10H, ar H), 3.87 (t, 2H, CH_2O), 2.7 (t, 2H, CH_2-C=C), 0.6-1.83 (m, 14H, CH_2, CH_3) ppm; *m/z*= 372 (M^+, 52%), 302 (42), 301 (56), 263 (32), 123 (32), 110 (25), 109 (30), 71 (59), 43 (100). (Found: M^+, 372.1547. $C_{22}H_{28}OS_2$ requires M, 372.1582).

1,1-Bis(phenylthio)-2-acetoxy-1-pentene (**7b**).- Eluent: petroleum ether/dichloromethane 3:7. Colourless oil. ν(film) 3105, 3090 (ar C-H), 2980, 2960, 2900 (C-H), 1775 (C=O), 1590 (C=C), 790, 750, 700 (ar C-H) cm^{-1}; δ_H (60 MHz) 7.17 (s, 10H, ar H), 2.73 (t, 2H, CH_2-C=C), 2.17 (s, 3H, CH_3CO), 1.23-1.80 (m, 2H, $C\underline{H}_2$-CH_3), 0.77 (t, 3H, $CH_2C\underline{H}_3$); *m/z*= 344 (M^+, 15%), 302 (100), 193 (3), 121 (11), 43 (9). (Found: M^+, 344.0915. $C_{19}H_{20}O_2S_2$ requires M, 344.0905).

2-[(Methylthio)-deuteriomethylene]-1-tetralone (**6c**).- Eluent: petroleum ether/ether 7:4. Colourless needles. M.p. 66°C. Mixture of the *E*- and *Z*-isomer (5:1). (Found: C, 70.18; H, 5.54. $C_{12}H_{11}DOS$ requires C, 70.21; H, 5.40). ν(KBr) 3100 (ar C-H), 2960, 2940, 2870 (C-H), 1660 (C=O, br.), 1560 (C=C, br.), 810, 795, 775, 750, 710, 670 (ar C-H) cm^{-1}; δ_H (90 MHz) 8.0-8.22 (m, 1H, ar H), 7.16-7.62 (m, 3H, ar H), 2.67-3.09 (m, 4H, CH_2), 2.53 [s, 15/6 H, SCH_3 (*E*-isomer)], 2.42 [s, 3/6 H, SCH_3 (*Z*-isomer)]ppm; *m/z*= 205 (M^+, 41%), 190 (100), 158 (4), 129 (29), 90 (14), 89 (9), 77 (5), 46 (6), 45 (7).

Direct electrolyses of 2-[bis(methylthio)-methylene]-cyclohexanone (**5a**) and 2-[bis(methylthio)-methylene]-1-tetralone (**5b**) in the presence of CO_2.- 2 mmol of **5a** respectively **5b** was solved in 45 ml electrolyte 2. During the electrolysis a permanent flow of CO_2 was bubbled through the electrolyte which was cooled to 0°C[21]. After a charge consumption of 2.3 F/mol substrate, the electrolyses were stopped, a tenfold amount of methyl iodide was added, the reaction mixture stirred for three hours and worked up as described in the general procedure, the products being purified by column chromatography on silica gel (eluent: petroleum ether/ether 1:1).

2-[Bis(methylthio)-methyloxycarbonyl-methyl]-cyclohexanone (**6d**).- Yellow oil. ν(film) 2980, 2960, 2895 (ar C-H), 1720-1750 (C=O, br.) cm^{-1}; δ_H (90 MHz) 3.78 (s, 3H, OCH_3), 3.11-3.33 (m, 1H, CH), 2.27-2.44 (m, 4H, CH_2), 2.2 (s, 3H, SCH_3), 2.07 (s, 3H, SCH_3), 1.56-2.0 (m, 4H, CH_2) ppm; δ_C (90 MHz) 207.77 (C=O), 170.32 (CO_2), 62.02; 57.91 (CH, C), 52.70 (CH_3), 42.11; 29.49; 26.96; 25.21 (CH_2), 15.05; 13.34 (SCH_3) ppm; *m/z*= 262 (M^+, 11%), 215 (100), 199 (9), 183 (45), 155 (28), 127 (82), 79 (86), 47 (46).

2-(Methylthio-methyloxycarbonyl-methylene)-1-tetralone (**6e**).- Colourless needles. *E*- and *Z*-isomer (6:1). M.p. 82-84°C. (Found: C, 63.98; H, 5.43. $C_{14}H_{14}O_3S$ requires C, 64.10; H, 5.38); ν(KBr) 3090, 3020 (ar C-H), 2980, 2950, 2870 (C-H), 1737 (C=O, ester), 1656 (C=O, ketone), 1560 (C=C), 810, 790, 750, 735 (ar C-H) cm^{-1}; δ_H (90 MHz) 8.0-8.13 (m, 1H, ar H), 7.13-7.57 (m, 3H, ar H), 4.0; 3.9 (2s, 3H, CO_2-CH_3), 2.63-3.0 (m, 4H, CH_2), 2.33 [s, 3/7H, SCH_3 (*Z*-isomer)], 2.2 [s, 18/7H, SCH_3, (*E*-isomer)] ppm; *m*/*z*= 262 (M^+, 22%), 247 (100), 230 (28), 215 (12), 187 (34), 183 (37), 128 (28), 115 (38), 90 (28), 59 (12).

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