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Mild and Effective Removal of Dithioketal Protecting Groups by Triarylamine Cation Radicals as Homogeneous Electron Transfer Agents[1)]

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1,3-Dithianes **2** can effectively be converted in to the parent carbonyl compounds **7** by a very mild oxidative procedure using tri-*p*-tolylammoniumyl ($\mathbf{1a}^{+\cdot}$) or tris(4-bromophenyl)ammoniumyl ($\mathbf{1b}^{+\cdot}$) as homogeneous electron transfer agents. The yields are equally good for the cleavage by stoichiometric amounts of the triarylammoniumyl hexachloroantimonates as well as for the indirect electrochemical procedure using catalytic amounts of the triarylamine together with electrochemical generation and regeneration of the cation radicals. In the case of 1,3-dithiolanes **3** the application of stoichiometric amounts of tris(4-bromophenyl)ammoniumyl hexachloroantimonate is very effective while during the indirect electrochemical procedure the deposition of polymeric sulfur compounds onto the electrode surface has to be prevented by the use of a flow-through cell. In all cases the conditions for the cleavage are so mild that hydroxy functions and double bonds are tolerated without problems.

Milde und effektive Abspaltung von Dithioketal-Schutzgruppen durch Triarylamin-Radikalkationen als homogene Elektronenüberträger

1,3-Dithiane **2** können durch eine äußerst milde oxidative Methode unter Verwendung von Tri-*p*-tolylammoniumyl ($\mathbf{1a}^{+\cdot}$) oder Tris(4-bromphenyl)ammoniumyl ($\mathbf{1b}^{+\cdot}$) als homogene Elektronenüberträger in effektiver Weise in die zugrunde liegenden Carbonylverbindungen **7** umgewandelt werden. Die Spaltung durch stöchiometrische Mengen Triarylammoniumyl-hexachloroantimonate oder mit Hilfe der indirekten elektrochemischen Methode unter Verwendung katalytischer Mengen an Triarylamin in Verbindung mit der elektrochemischen Erzeugung und Regeneration der Radikalkationen führt zu gleich guten Ausbeuten. Im Falle der 1,3-Dithiolane ist die Anwendung stöchiometrischer Mengen von Tris(4-bromphenyl)ammoniumyl-hexachloroantimonat sehr effektiv, während im Verlauf der indirekten elektrochemischen Umsetzung die Ablagerung polymerer Schwefelverbindungen auf der Elektrodenoberfläche durch Verwendung einer Durchflußzelle verhindert werden muß. In allen Fällen sind die Spaltbedingungen so mild, daß Hydroxyfunktionen und Doppelbindungen ohne Probleme toleriert werden.

1. Introduction and Basic Considerations

Dithioketal protecting groups are well established in preparative organic chemistry. Carbanions from 1,3-dithianes are the well known acyl anion equivalents in the famous umpolung reaction of carbonyl compounds[2)]. The 1,3-dithiolane function is a useful protecting group for carbonyl functions during the course of multistep syntheses[3)]. Its utility is, however, sometimes limited due to scarcity of suitable, mild reagents for the cleavage to ketones. The deprotection of dithioketals

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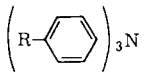
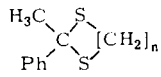
can either be performed by strong acidic, transition metal-induced[4], alkylative[5], and halogenative[6] hydrolysis. While the transition metal-induced deprotection is not advisable in the synthesis of pharmaceuticals because of remaining small transition metal residues[7], the alkylative and halogenative hydrolysis is not applicable in the case of nucleophilic substrates. Therefore a mild oxidative procedure could be a very attractive alternative in those cases.

Most of the known oxidative methods, however, are used in connection with quite strong oxidizing agents like hydrogen peroxide[8], nitrosonium and nitronium salts[9], benzeneselenic anhydride[10], thallium(III) and cerium(IV)[2] salts. Therefore the electrochemical deblocking would be of potential interest. However, the direct anodic removal of the 1,3-dithiane protecting group can be performed only in moderate yields (45 – 77%) at the relatively anodic potential of 1.6 V vs. NHE, if acetonitrile/water (9 : 1) is used as solvent and periodic pulsing to 0 V is applied to prevent electrode passivation[11]. 1,3-Dithiolanes are not cleaved efficiently because of severe electrode fouling[11]. Several mechanisms for this reaction have been proposed[12], which have to take into account that neither sulfoxides and sulfones nor sulfonium salts could be detected.



1a: R = CH_3
b: R = Br
c: R = CH_3CO



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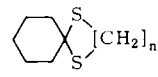
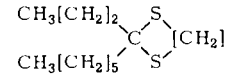
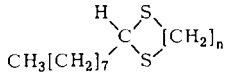
3a: n = 2



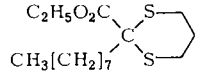
2b
3b



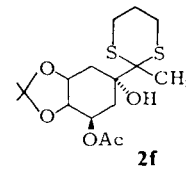
2c
3c



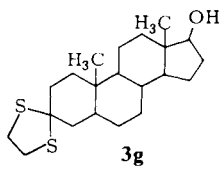
2d: n = 3
3d: n = 2



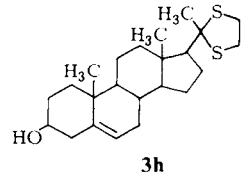
2e



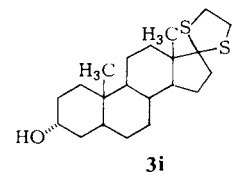
2f



3g



3h

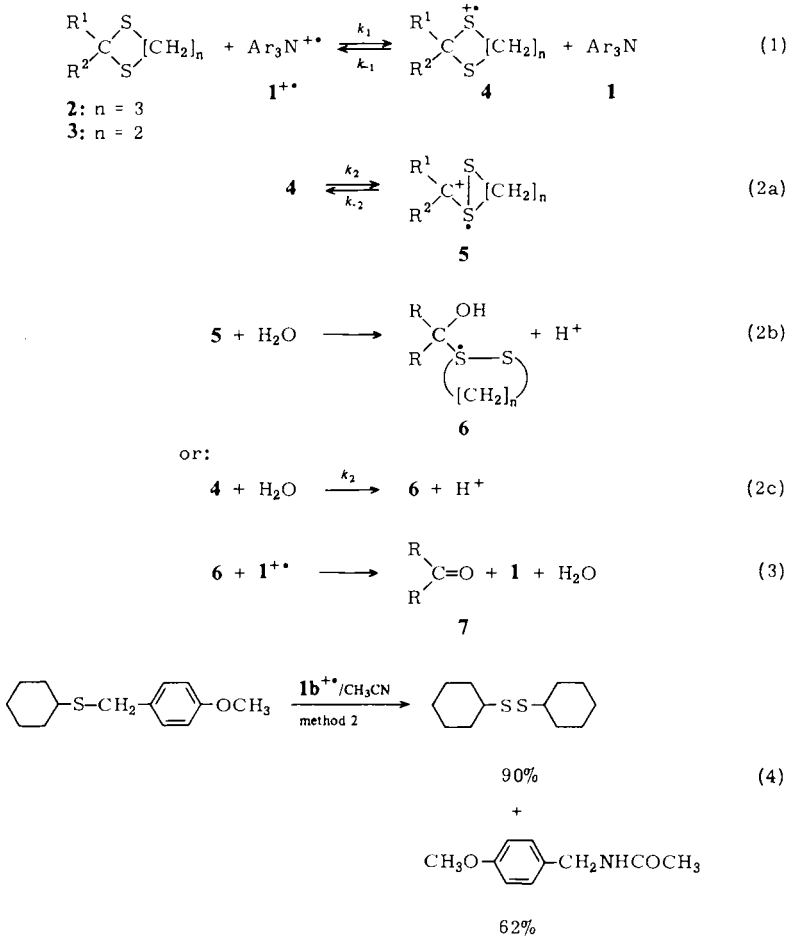


3i

Because of the problems in direct electrolysis, like moderate yields, relatively high potentials, and electrode fouling, we developed a mild and effective oxidative procedure for the cleavage of dithioketals **2** and **3**. This method is based on the homogeneous electron transfer between the protected carbonyl compound and a chemically stable organic electron transfer agent against the standard potential gradient in the presence of an inorganic base (Scheme 1). The driving force of this reaction is supposed to be the cleavage of the carbon sulfur bond in the substrate cation radical $\mathbf{2}^{+\cdot}$ and $\mathbf{3}^{+\cdot}$ with or without the asistence of the attacking nucleophile (eq. 2). This fast and irreversible follow-up reaction is shifting the thermodynamically unfavourable electron transfer equilibrium (eq. 1) to the product side. The possibility for this mild oxidative carbon sulfur bond cleavage was first observed by us using 4-methoxybenzyl or allyl thioether substrates which under the influence of triarylamine cation radicals are forming

disulfides and follow-up products of the 4-methoxybenzyl and allyl cations, respectively (eq. 4)[13]. This procedure has successfully been applied to the synthesis of cystine containing peptides[13].

Scheme 1. Proposed Mechanisms for the Oxidative Cleavage of Dithioketals by Triarylamine Cation Radicals, Eq. 1 – 3



As electron transfer agents cation radicals of the easy to prepare triphenylamines[14], tri-4-tolylamine (**1a**), tris(4-bromophenyl)amine (**1b**), and tris(4-acetylphenyl)amine (**1c**), have been applied to the deprotection of the carbonyl group from dithioketals. The cation radicals can be generated and regenerated by three different methods:

Method 1: The stable and crystalline triarylammoniumyl hexachloroantimonates[14], generated by reaction of the amine with $SbCl_5$, are applied in stoichiometric amounts in CH_3CN or CH_2Cl_2 containing $NaHCO_3$ as a base. After the reaction 70 – 90% of the amine can be recovered.

Method 2: The triarylamine cation radicals are electrochemically generated and regenerated "*in situ*" using a divided cell so that far less than stoichiometric amounts of **1** are necessary. The **1**:**2** ratio in most cases was 1:10, the **1**:**3** ratio 1:4.

Method 3: The triarylammoniumyl is generated in stoichiometric amounts by a pre-electrolysis of the amine in a divided cell and subsequently treated with the substrate within the electrochemical cell after total electrolysis had been achieved.

2. Analytical Studies

The chance for the success of the electron transfer against the standard potential gradient can be evaluated by the cyclic voltammetric method (CV) by which not only values of the redox potentials are measured (Table 1) but also the presence of a redox catalytic mechanism, as depicted in Scheme 1 with $\mathbf{1}^{+\cdot}$ being electrochemically generated, can be indicated by the so-called catalytic effect[15]. In the case of an oxidation with electrochemical regeneration of the homogeneous electron transfer agent (indirect electrolysis) the anodic peak current for the electron transfer agent (mediator) in the presence of the substrate, i_p, is increased as compared to the peak current of the mediator in the absence of the substrate, i_{pd}, by the amount of an catalytic current[16]. At the same time the cathodic peak current is lowered by the same amount. The size of the catalytic current is dependent on the potential scan rate, v, the ratio of the concentrations of the substrate and the mediator (sometimes called "excess factor"), γ, in some cases also on the absolute concentration of the mediator, and always on the overall reaction rate for the regeneration of the mediator in its reduced form. This reaction rate is not only dependent on the difference of the standard redox potentials of the mediator and the substrate, which determines the equilibrium constant for the homogeneous electron transfer step (eq. 1), but also by the rate of the follow-up chemical reaction, the cleavage of the carbon-sulfur bond (eq. 2). To examine the size of the catalytic effect cyclic voltammograms have to be recorded for different potential scan rates, concentrations of the substrates and mediators, and the amount of added nucleophiles.

Table 1. Redox Potentials of Compounds **1**, **2**, and **3** in Acetonitrile (0.3% H_2O)/0.2 M $LiClO_4$ *vs.* the Normal Hydrogen Electrode

Compound	E_{pa} [V][a]	Compound	E_{pa} [V][a]	Compound	E^0 [V][b]
2a	1.38	**3a**	1.63	**1a**	1.0
2b	1.43	**3b**	1.69	**1b**	1.3
2c	1.44	**3c**	1.68	**1c**	1.5
2d	1.47	**3d**	1.71		
2f	1.50	**3g**	1.65		
		3h	1.60		
		3i	1.70		

[a] Anodic peak potential. – [b] Standard potential.

Figure 1 shows cyclic voltammograms of tris(4-bromophenyl)amine (**1b**) in acetonitrile in the presence of different amounts of the 1,3-dithiolane **3g** and water. The

oxidation potential of **1b** is 350 mV lower as compared with **3g**. The catalytic effect for the 1,3-dithiane **2a** in the presence of **1a** as electron transfer agent is considerably smaller. In this case the potential difference between mediator and substrate is 380 mV.

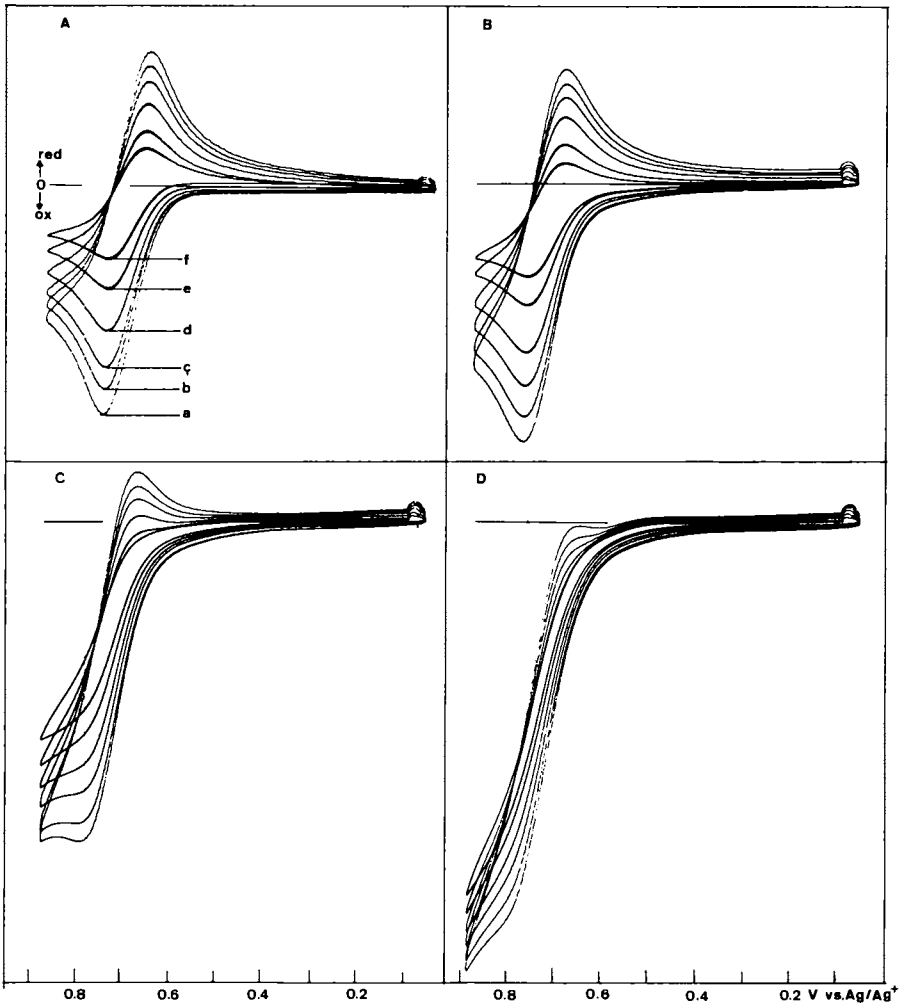


Figure 1. Cyclic Voltammograms of **1b** in the Absence and Presence of **3g** in CH_3CN (0.1 M $LiClO_4$, 0.3% H_2O)

a: 320 mV/s; b: 256 mV/s; c: 192 mV/s; d: 128 mV/s; e: 64 mV/s; f: 32 mV/s.
A: 1 mmol/l **1b**; B: 1 mmol/l **1b**; 1 mmol/l **3g**; C: 1 mmol/l **1b**, 5 mmol/l **3g**; D: 1 mmol/l **1b**, 5 mmol/l **3g**, 3% H_2O

From our experience with the cleavage of benzyl ethers[17] and esters[18] we can conclude that the catalytic effect is strong enough so that the preparative scale deprotection of 1,3-dithianes **2** by $\mathbf{1a}^{+\cdot}$ and of 1,3-dithiolanes **3** by $\mathbf{1b}^{+\cdot}$ should be possible

by all three methods. Because of the smaller catalytic effect in the presence of $\mathbf{1a}^{+\cdot}$ the 1,3-dithianes should react slower as compared with the system **1b/3**. To increase the speed of the deprotection of **2** the use of **1b** as mediator would be advisable.

It is, however, not only possible to deduce information on the potential success of a preparative experiment from CV data but also to get information about the mechanism. The dependence on the concentration of the value $i_p/i_{pd} \cdot \gamma$, which is the peak current ratio normalized for the excess factor, allows to determine, whether the homogeneous electron transfer step (eq. 1) is rate determining or the chemical follow-up reaction (eq. 2) with eq. (1) as a fast equilibrium. In the first case $i_p/i_{pd} \cdot \gamma$ for constant γ values is dependent on the mediator concentration while in the second case it is constant[16,19]. In the case of the system **1b/3g** in acetonitrile (0.3% H_2O) we therefore treated the CV data in the described manner (Table 2).

Table 2. Cyclic Voltammetric Data for the Redox-Catalytic Oxidation of **3g** by Electrogenerated $\mathbf{1b}^{+\cdot}$

v [a)] [V/s]	$c^0_{1b} \times 10^3$ [M b)]	γ c)	$i_p/\gamma \cdot i_{pd}$	log $(k \cdot k_1/k_{-1})$ d)	log k_1 e)
0.346	0.25	4	0.343	−1.09	3.30
0.346	0.5	4	0.348	−1.12	3.04
0.346	1.0	4	0.315	−1.22	2.53
0.277	0.25	4	0.369	−1.10	3.32
0.277	0.5	4	0.383	−1.05	3.05
0.277	1.0	4	0.325	−1.26	2.53
0.208	0.25	4	0.378	−1.19	3.23
0.208	0.5	4	0.347	−1.34	2.82
0.208	1.0	4	0.357	−1.24	2.54
0.138	0.25	4	0.420	−1.31	3.16
0.138	0.5	4	0.500	−1.04	3.10
0.138	1.0	4	0.378	−1.38	2.42
0.069	0.25	4	0.482	−1.03	3.03
0.069	0.5	4	0.506	−1.33	2.81
0.069	1.0	4	0.428	−1.50	2.32

a) Potential scan rate. – b) Initial concentration of mediator. – c) Excess factor. – d) Assuming kinetic control by (2) with (1) as fast equilibrium. – e) Assuming kinetic control by forward electron transfer.

It can be seen that the value of $i_p/i_{pd} \cdot \gamma$ is largely independent of the concentration of the redox catalyst. The kinetic term log $k_2 \cdot k_1/k_{-1}$ which can be obtained using working curves supplied by *Savéant* et al.[16] for kinetic control by eq. (2) with (1) as a pre-equilibrium is not drifting while changing concentrations and sweep rates. The value k_1, however, obtained from working curves for kinetic control by the forward electron transfer step in eq. (1), is drifting considerably. Therefore it must be concluded that under these conditions at least in the case of **3g** the chemical follow-up reaction is controlling the kinetics. This conclusion is different from the results which are obtained for the indirect electrochemical cleavage of 1,3-dithianes[12a,c]. The increase of the water content by a factor of 10, from 0.3 to 3%, only results in an increase of $k_2 \cdot k_1/k_{-1}$ by a

factor of about two to three indicating that the reaction order with respect to water is smaller than one. Therefore the direct assistance of the nucleophile to the carbon-sulfur bond cleavage as formulated in eq. (2c) is excluded. It could, however, be explained assuming a fast equilibrium of eq. (2a) with quasi-stationary concentration of **5**. As the uncatalyzed voltammograms of compounds **3** are severely influenced by adsorption of the substrate it is impossible to make a reliable analysis of the peak potentials as a function of the scan rate to obtain an independent relation between the standard potential of the substrate and the rate constant k_2[20]. Therefore we were unable to separate the value for $k_2 \cdot k_1/k_{-1}$ into the single rate constants according to *Savéant* et al.[19a]. We only can say that $k_2 \cdot k_1/k_{-1}$ equals 6×10^{-2} with k_2 being much smaller than 10^6 (condition for kinetic control by eq. (2) is $k_2 \ll k_{-1} \cdot [\mathbf{1b}]$ and assuming $k_{-1} = 5 \times 10^9\ s^{-1}\ M^{-1}$). To explain the very low yields for the direct anodic cleavage of 1,3-dithiolanes of about 5% it has been argued[21] that this is due to the intermediate formation of a highly strained system favouring side reactions. This is neither in agreement with our analytical data nor with our preparative results for the electron transfer-induced cleavage giving high yields of the carbonyl compounds. The low yields in direct electrolysis more likely are due to the instability of the 1,2-dithiethane which is polymerizing and thereby blocking the working electrode.

3. Preparative Results

3.1. Removal of the 1,3-Dithiane Protecting Group

The results of the cleavage of 1,3-dithianes by $\mathbf{1a}^{+\cdot}$ or $\mathbf{1b}^{+\cdot}$ using method 2 are reported in Table 3.

Table 3. Results of 1,3-Dithiane Cleavage by Electrogenerated $\mathbf{1a}^{+\cdot}$ or $\mathbf{1b}^{+\cdot}$ (Method 2)

1,3-Dithiane	Mediator	Carbonyl Compound **7**, Yield (%)
2a	**1a**	95[a]
2b	**1a**	95[a]
2c	**1a**	85[a]
2d	**1a**	97[b]
2e	**1a**	70[c]
2f	**1b**	90[d]

[a] Determined by GLC. – [d] Determined by isolation as *O*-methyloxime. – [c] Determined by distillative isolation. – [d] Determined by LC isolation.

Acetonitrile containing small amounts of water (0.3 – 3%) has been used as solvent. $NaHCO_3$ is necessary to maintain neutral conditions in the anolyte. The electrochemical regeneration is easy to perform and does not present any problems. If equipment for the electrochemical generation of the mediator cation radicals from catalytic amounts of the triarylamines is not at hand, it is equally possible to use stoichiometric amounts of the hexachloroantimonate salts (method 1). This is demonstrated by the deprotection of **2c** by the hexachloroantimonates of $\mathbf{1a}^{+\cdot}$ and $\mathbf{1b}^{+\cdot}$ yielding 4-decanone (**7c**) in 92 and 82%, resp., isolated yield. Method 2 is especially useful as only small

amounts of the mediator are necessary and separation of the products is facilitated. Passivation of the electrodes has never been observed. Therefore, periodic pulsing of the anode potential is unnecessary in contrast to the direct anodic oxidation[11]. In the case of compounds **2e** and **f** reaction with $\mathbf{1a}^{+\cdot}$ is rather slow. Therefore, $\mathbf{1b}^{+\cdot}$ with its higher oxidation potential is recommended. Deprotection of **2f** was realized without problems. If the acetonide function is replaced by a double bond, the reaction with electrochemically generated stoichiometric amounts of $\mathbf{1a}^{+\cdot}$ or $\mathbf{1b}^{+\cdot}$ (method 3), however, leads to many unidentified products. The reason for this behaviour is not understood, as in other cases even allylic alcohol functions are stable to $\mathbf{1a}^{+\cdot}$ and $\mathbf{1b}^{+\cdot}$ under the reaction conditions[22].

3.2. Removal of the 1,3-Dithiolane Protecting Group

As 1,3-dithiolanes exhibit an oxidation potential which with a value of ca. +1.7 V (*vs.* NHE) is about 250 mV more positive than the one of the 1,3-dithianes (see section 2) only $\mathbf{1b}^{+\cdot}$ and $\mathbf{1c}^{+\cdot}$ are effective for the deprotection. While the direct anodic oxidation of 1,3-dithiolanes even at very positive potentials does not lead to appreciable amounts of the carbonyl compounds mainly due to very severe blocking of the electrode[11], the indirect electrolysis using electrogenerated triarylamine cation radicals is effective at considerably lower potentials. However, in contrast to the very clean indirect electrochemical cleavage of 1,3-dithianes the tendency of the formed polymeric sulfur compound $(-S-[CH_2]_2-S-)_n$ to deposit onto the electrode surface can not totally be suppressed. To prevent this it is advisable to continously add the dithiolane during the indirect electrolysis in such a way that the blue colour of unreacted oxidant is partially maintained during the whole reaction. This target together with faster turnover of the substrate can be achieved by using a divided parallel plate cell with circulating electrolytes. No problems are, however, encountered by using method 1. Within 0.5–1 hours the reaction of the substrate with the cation radical salt is complete. The triarylamine can be recovered in 70–90% yield depending on the reaction scale and can externally be regenerated to the cation radical by $SbCl_5$. The results are reported in Table 4.

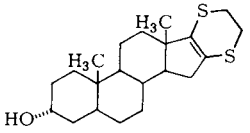
Table 4. Results of 1,3-Dithiolane Cleavage by $\mathbf{1b}^{+\cdot}$

1,3-Dithiolane	Carbonyl Compound **7**, Yield (%) Method 1	Method 2	Method 3
3a	91[a]	84[c]	
3b	81[b]	74[b]	
3c	83[a]	75[a]	
3d	74[a]	83[b]	
3g	83[d]	77[d]	91[d]
3h			74[d]
3h			100[d,e]

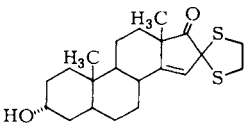
[a] Determined by GLC. – [b] Determined by Isolation as *O*-methyloxime. – [c] Determined by bulb-to-bulb distillation. – [d] Determined by LC isolation. – [e] Using $\mathbf{1c}^{+\cdot}$ instead of $\mathbf{1b}^{+\cdot}$.

In the case of the steroids **3g** and **h** we were able to demonstrate that unprotected hydroxy functions and double bonds are stable under the reaction conditions. This is equally true under the even milder conditions for the deprotection of 1,3-dithianes. Reaction of $\mathbf{1b}^{+\cdot}$ with the steroid **3i** did not yield the unprotected ketone presumably because of sterical hinderance by the C-18 methyl group to the attack of the nucleophile at C-17.

Instead, compounds **8** and **9** are formed in 55 and 32%, resp., yield (eq 5). In this case water is attacking the sulfur atom to form the dihydro-1,4-dithiine **8** *via* the intermediate sulfoxide as reported for the oxidation of 1,3-dithiolanes by *m*-chloroperbenzoic acid (MCPBA)[23]. Product **9** can be rationalized by follow-up oxidation and rearrangement of **8**.



8 (55%)



9 (32%)

(5)

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Experimental Part

IR spectra: Perkin-Elmer 177 and Pye Unicam SP 1100. – Mass spectra: Varian MAT 111 and A. E. I. MS-30 and MS-50. – ^{1}H-NMR spectra: Jeol PMX-60; Varian EM-360; Bruker WH-90; Bruker WM-400 (δ values, TMS internal standard). – ^{13}C NMR spectra: Bruker WP-60; Bruker WH-90; Bruker WM-400 (δ values, TMS internal standard). – GC/MS combination: Gaschromatograph Varian 1440 in combination with mass spectrometer Varian MAT 111. – Melting points (uncorrected): Kofler micro heating table (Reichert). – Microanalyses: CH analyzer, Perkin-Elmer model 240.

Acetonitrile (Merck, for synthesis) was dried over P_2O_5 and K_2CO_3 and further purified by distillation; Acetonitrile (Merck, p. A.) was used as obtained. Dichloromethane was purified by distillation. $LiClO_4$ (Fluka) was used as obtained. $(n\text{-Bu})_4N^+ClO_4^-$ (TBAP) was prepared by treating a saturated aqueous solution of $(n\text{-Bu})_4HSO_4^-$ (Fluka) with a saturated aqueous solution of $NaClO_4$ or $HClO_4$ and subsequently extracting the mixture with dichloromethane. After evaporation of the solvent the salt was recrystallized from acetone/water.

1. General Procedures

TLC Analyses: TLC aluminium sheets, silica gel 60 F_{254} (Merck); mobile phase 1: dichloromethane/petrol ether (40–60°C)/ethyl acetate (8:3:2, v/v/v); mobile phase 2: petrol ether (40–60°C)/diethyl ether (9:1, v/v); mobile phase 3: dichloromethane/methanol/triethylamine (4:2:1, v/v/v).

Preparative LC Separations: Glass column, ∅ 30 mm, 0.35 m, silica gel 63/100 mesh (Merck) in combination with fraction collector LKB ultrorac, model 7000. Mobile phase 1.

Preparative HPLC Separations: Steel column, ∅ 16 mm, 0.5 m, LiChrosorb Si 60 (Merck) in combination with microprocessor controlled Gilson model 301 high pressure pump, Gilson model 260 double beam UV monitor and two-channel Linseis LS 4 X/t-recorder. Mobile phase 1.

Cyclic voltammetry: A Wenking potentiostat PCA 72 L (Bank) was used as current source in combination with a triggerable Wavetek 133 LF function generator, a Hewlett-Packard 7045 A X/Y-recorder, a Metrohm EA 875-20 electrolysis cell equipped with a glassy carbon (Metrohm) anode with 3 mm ∅, platinum sheet cathode (0.5 × 0.4 cm), and a reference electrode which was in contact with the electrolyte *via* a salt bridge. Either a $Ag/AgNO_3$ (0.1 M CH_3CN) reference electrode in combination with the electrolyte CH_3CN (0.1 M $LiClO_4$) or a $Ag/Ag_3I_4^-$ $(n\text{-}Bu)_4N^+$ reference electrode[24] in combination with the electrolyte CH_2Cl_2 (0.1 M TBAP) were applied. The cyclic voltammetric data are reported in Table 2.

Preparative Electrolyses: Wenking potentiostat LB 75 L or ST 72 (Bank) were used as current sources in combination with a digital coulometer based on voltage-to-frequency conversion and the following cells:

Two-compartment Beaker-type Glass Cell (Cell 1): A two-compartment beaker-type glass cell with cooling mantle was equipped with a 12-cm^2 platinum sheet anode, a $Ag/AgNO_3$ (0.1 M in acetonitrile) reference electrode, and a magnetic stirrer. The cathode compartment was formed by a glass cylinder closed by a G-4 glass frit and was equipped with a 5-cm^2 platinum sheet cathode.

Divided Flow-through Cell (Cell 2): The divided flow-through parallel plate cell with circulating electrolytes was formed by two Teflon halves, separated by a Nafion (Du Pont) cation exchange membrane and pressed together by a steel frame *via* thumb screws. The anode was formed by a 5 × 10 cm^2 platinum sheet or carbon felt of the same size. The cathode consisted of a platinum sheet of the same geometry. The reference electrode ($Ag/AgNO_3$) was in contact with the electrolyte *via* a Luggin capillary. The electrolytes were circulated by two Eheim pumps. The two circles of the flow-through system were completed by heat exchangers and buffer volume vessels.

General Procedure for the Oxidative Cleavage of 1,3-Dithianes **2** *and 1,3-Dithiolanes* **3** *(Method 1):* Between 0.4 and 2 mmol of **2** or **3** are dissolved in 10–40 ml of CH_3CN (0.3% H_2O)/CH_2Cl_2 (5:1) or CH_2Cl_2 (0.2% H_2O). For compounds **3g** and **i** CH_3CN (0.3% H_2O) was used as solvent. After addition of 0.5 g to 1.0 g of $NaHCO_3$ $\mathbf{1a}^{+\cdot}$ $SbCl_6^-$ (in the case of **2c**) or $\mathbf{1b}^{+\cdot}$ $SbCl_6^-$ is added in a molar ratio of 2.4:1 with respect to the substrate. Total decolouration of the mixture is indicating the end of the reaction (0.5–1 h). For work-up the solution is mixed with 40–100 ml of water, saturated with NaCl, three times extracted with 50 ml of ether, and the organic phase dried over $MgSO_4$. Product yields are determined from the organic phase by GLC, by bulb-to-bulb distillation, by transformation into the *O*-methyloxime followed by GLC analysis, or by LC (compounds **3g, i**). After distillation of the product crude triarylamine remains as solid. Recrystallization from chloroform/ethanol yields the amine in 70–90%.

General Procedure for the Oxidative Cleavage of 1,3-Dithianes **2** *by Indirect Electrolysis (Method 2):* 2.5 mmol of **2** and 143 mg (0.50 mmol) of **1a** or 240 mg of **1b** (compound **2f**) dissolved in 100 ml of CH_3CN (0.3% H_2O; 0.2 M $LiClO_4$) containing 1.0 g (12 mmol) of $NaHCO_3$ are electrolyzed in cell 1 at 20°C and a controlled potential of 0.5 V *vs.* $Ag/AgNO_3$ reference electrode (compound **1a**) or 0.8 V (compound **1b**). For work-up the acetonitrile solution is poured into 300 ml of water and three times extracted with ether. The organic phase is dried over $MgSO_4$. Product yields are determined by GLC, by bulb-to-bulb distillation, or by LC.

General Procedure for the Oxidative Cleavage of 1,3-Dithiolanes **3** *by Indirected Electrolysis (Method 2):* 1.2 g (2.5 mmol) of **1b** are dissolved in 200 ml of CH_3CN (0.3% H_2O)/CH_2Cl_2 (4:1; 0.2 M $LiClO_4$) as anolyte. 2.0 g (24 mmol) of solid $NaHCO_3$ is added. The catholyte consists of 200 ml of CH_3CN (0.2 M $LiClO_4$) and 10 ml of CH_3OH. Electrolysis takes place in cell 2 at a controlled potential of 0.8 V ($Ag/AgNO_3$). After consumption of 100 As and appearance of the blue colour of the cation radical 10 mmol of **3** dissolved in 30 ml of CH_3CN are slowly added

during the continuation of the electrolysis. The speed of the addition is controlled in such a way that the blue colour of the oxidant is maintained. After consumption of about 3500 As (0.035 F) total turnover is achieved. For work-up the anolyte is narrowed to 50 ml, mixed with 100 ml of water, saturated with NaCl, and extracted with ether or CH_2Cl_2. The organic phase is dried over $MgSO_4$. Product yields are determined from the organic phase by GLC, by transformation to the *O*-methyloxime followed by distillation, by bulb-to-bulb distillation, or by LC. After distillation of the product crude **1b** remains as a solid and can be recrystallized from chloroform/ethanol yielding the amine in 80%.

General Procedure for the Oxidative Cleavage of 1,3-Dithiolanes **3** *(Method 3):* 1.0 mmol of **1b** dissolved in 80 ml of CH_3CN (0.3% H_2O; 0.2 M $LiClO_4$) or 3 mmol of **1c** dissolved in 40 ml of CH_2Cl_2 and 60 ml of CH_3CN (0.3% H_2O; 0.2 M $LiClO_4$) are electrolyzed in cell 1 after addition of 1 g of silica gel, 60 – 100 mesh, at a controlled potential of 0.86 V ($Ag/AgNO_3$) (**1b**) or 1.05 V ($Ag/AgNO_3$) (**1c**) until total turnover of the amine to the cation radical was achieved indicated by a large decrease of the current density. The charge consumption ranged from 480 As (**1b**) to 900 As (**1c**). After addition of 2 g of solid $NaHCO_3$ 1 mmol of **3g** or **h** were added and the mixture stirred for 2 h. Work-up was performed as described before. Separation took place by LC. In this way between 83 and 86%, resp., of the mediators **1b** and **1c** could be recovered.

2. Preparation of the Substrates

Preparation of the Triarylamines and their Cation Radical Hexachloroantimonates: **1a**[25], **1a**$^{+\cdot}$ $SbCl_6^-$ [26], **1b**[27], **1b**$^{+\cdot}$ $SbCl_6^-$ [14,28], and **1c**[27] were prepared according to the literature. The preparation of **1a** could be improved by lithiating **1b** with *n*-BuLi in ether followed by alkylation with CH_3I yielding **1a** in 90%[29]. Spectral data and physical constants were identical with the literature values.

Preparation of the 1,3-Dithianes **2**: Compounds **2a, b, c,** and **d** were prepared according to a published method[4]. **2e** was synthesized by acylation of **2d** with $ClCO_2Et$ analogous to a literature procedure[4]. **2f** was obtained as a gift[30].

2-Methyl-2-phenyl-1,3-dithiane (**2a**): Yield 87%; m. p. 36 – 37 °C (Lit.[31] 35 °C). – ^1H NMR (CCl_4): in agreement with the literature[32]. – IR (KBr): 3084, 3063, 2863, 1491, 1450, 1428, 911, 863, 761, 704 cm^{-1}. – MS (70 eV): *m/e* = 210 (46%), 195 (6), 177 (10), 148 (12),135 (100).

$C_{11}H_{14}S_2$ (210.4) Calcd. C 62.81 H 6.71 Found C 62.84 H 6.69

1,5-Dithiaspiro[5.5]undecane (**2b**): Yield 85%; m. p. 42 – 43 °C (Lit.[33] 40.5 – 41 °C). – IR (KBr): 2937, 2860, 903 cm^{-1}. – ^1H NMR (CCl_4): δ = 1.20 – 2.18 (12H, m, CH_2), 2.71 – 2.83 (4H, m, SCH_2). – MS (70 eV): *m/e* = 188 (83%), 155 (20), 145 (53), 114 (79), 81 (100), 71 (19), 67 (9) 58 (7), 41 (17).

$C_9H_{16}S_2$ (188.4) Calcd. C 57.39 H 8.56 Found C 57.57 H 8.46

2-Hexyl-2-propyl-1,3-dithiane (**2c**): Yield 82%; b. p. 90 – 98 °C/0.015 Torr (bulb-to-bulb distillation). – IR (film): 2962, 2942, 2880, 2865, 916 cm^{-1}. – ^1H NMR (CCl_4): δ = 0.84 – 1.02 (6H, t, CH_3), 1.20 – 1.65 (10H, m, CH_2), 1.71 – 2.06 (6H, m, S – C – CH_2), 2.70 – 2.81 (4H, m, SCH_2). – MS (70 eV): *m/e* = 246 (22%), 203 (51), 189 (10), 171 (42), 161 (100), 102 (88), 74 (84), 69 (63), 55 (60).

$C_{13}H_{26}S_2$ (246.5) Calcd. C 63.35 H 10.63 Found C 63.40 H 10.45

2-Octyl-1,3-dithiane (**2d**): Yield 90%; b. p. 80 – 90 °C/0.02 Torr (bulb-to-bulb distillation) (Lit.[34] 112 °C/0.5 Torr). – IR (film): 2935, 2861, 905 cm^{-1}. – ^1H NMR (CCl_4): δ = 0.71 – 1.04 (3H, t, CH_3), 1.1 – 2.2 (16H, broad m, CH_2), 2.7 – 2.9 (4H, m, SCH_2), 3.83 – 4.04 (1H, t, 2-H).

– MS (70 eV): *m/e* = 232 (21%), 185 (1), 157 (18), 119 (100), 101 (7), 87 (11), 75 (12), 55 (15), 41 (22).

$C_{12}H_{24}S_2$ (232.45) Calcd. C 62.01 H 10.41 Found C 62.22 H 10.23

Ethyl 2-Octyl-1,3-dithiane-2-carboxylate (**2e**): Yield 47%; b. p.110 – 120 °C/0.02 Torr (bulb-to-bulb distillation). – IR (film): 2961, 2935, 2865, 1755, 912 cm^{-1}. – ^{1}H-NMR ($CDCl_3$): δ = 0.67 – 1.02 (6H, 2t, CH_3), 1.07 – 1.90 (16H, broad m, CH_2), 2.81 – 3.05 (4H, m, SCH_2), 4.01 – 4.40 (2H, q, OCH_2). – MS (70 eV): *m/e* = 304 (3%), 231 (100), 205 (2), 191 (8), 163 (4), 133 (4), 119 (6), 107 (13), 87 (8), 73 (10), 55 (17).

$C_{15}H_{28}O_2S_2$ (high resolution MS) Calcd. 304.1530624 Found 304.1529970

Preparation of the 1,3-Dithiolanes **3**: Compounds **3a, b, c**, and **d** were prepared according to the literature[35] and isolated by bulb-to-bulb distillation. The steroid derivatives **3g, h**, and **i** were synthesized *via* two literature procedures using either catalysis by *p*-TosOH in HOAc (method 1)[36] or BF_3 in CH_3OH (method 2)[37]. The products were isolated by recrystallization (**3g, h**, method 2), or by HPLC (**3h, i**, method 1).

2-Methyl-2-phenyl-1,3-dithiolane (**3a**): Yield 89%; n_D^{20} = 1.6187 (Lit.[38] n_D^{25} = 1.6162). – IR (film): 3080, 3062, 2961, 2855, 758, 698 cm^{-1}. – ^{1}H NMR ($CDCl_3$): δ = 2.16 (3H, s, CH_3), 3.24 – 3.55 (4H, s, CH_2), 7.08 – 7.32 (3H, m, C_6H_5), 7.62 – 7.74 (2H, m, C_6H_5). – MS (70 eV): *m/e* = 196 (54%), 181 (100), 167 (67), 136 (21), 121 (40), 105 (26), 103 (23), 94 (8), 91 (6), 77 (36), 59 (4), 51 (6).

$C_{10}H_{12}S_2$ (196.3) Calcd. C 61.18 H 6.04 Found C 61.29 H 6.18

1,4-Dithiaspiro[4.5]decane (**3b**): Yield 85%; n_D^{20} = 1.5668 (Lit.[38] n_D^{25} = 1.5650); b. p. 140 – 143 °C/12 Torr (Lit.[33] 148 – 148.5 °C/17 Torr). – IR (film): 2946, 2928, 2850 cm^{-1}. – ^{1}H NMR ($CDCl_3$): δ = 1.30 – 1.79 (6H, broad m, CH_2), 1.94 – 3.02 (4H, t, S – C – CH_2), 4.26 (4H, s, SCH_2). – MS (70 eV): *m/e* = 174 (53%), 146 (49), 131 (100), 118 (13), 114 (17), 81 (65), 71 (28).

$C_8H_{14}S_2$ (174.3) Calcd. C 55.12 H 8.09 Found C 55.07 H 7.99

2-Hexyl-2-propyl-1,3-dithiolane (**3c**): Yield 90%; n_D^{20} = 1.5093. – IR (film): 2943, 2975, 2870 cm^{-1}. – ^{1}H NMR ($CDCl_3$): δ = 0.89 – 1.02 (6H, t, CH_3), 1.22 – 1.64 (10H, broad m, CH_2), 1.93 – 2.00 (4H, m, S – C – CH_2), 3.28 (4H, s, SCH_2). – MS (70 eV): *m/e* = 232 (9%), 189 (60), 171 (3), 147 (100), 105 (10), 87 (10), 61 (12).

$C_{12}H_{24}S_2$ (232.5) Calcd. C 62.01 H 10.41 Found C 61.95 H 10.62

2-Octyl-1,3-dithiolane (**3d**): Yield 93%; b. p. 101 – 105 °C/2 Torr, n_D^{20} = 1.5103. – IR (film): 2941, 2971, 2861 cm^{-1}. – ^{1}H NMR ($CDCl_3$): δ = 0.80 – 0.93 (3H, t, CH_3), 1.20 – 1.63 (14H, broad m, CH_2), 1.83 – 1.96 (1H, t, 2-H), 3.22 (4H, s, CH_2S). – MS (70 eV): *m/e* = 218 (13%), 186 (1), 174 (5), 158 (15), 157 (6), 105 (100).

$C_{11}H_{22}S_2$ (218.4) Calcd. C 61.62 H 10.34 Found C 61.40 H 10.10

17β-Hydroxy-5α-androstan-3-one 1,2-Ethanediyl Dithioacetal (**3g**): Yield (method 2) 93%; m. p. 193 – 195 °C (CH_3OH/H_2O = 3:1). – IR (KBr): 3600 – 3300, 2940, 2920, 2975 cm^{-1}. – ^{13}C NMR ($CDCl_3$): δ = 11.13, 11.94 (C-18, -19), 20.59 (C-11), 23.37 (C-15), 28.19 (C-6), 30.49 (C-16), 31.36 (C-7), 35.51 (C-8), 36.71 (C-10, -12), 37.38 (C-1), 38.36, 38.91 (SCH_2CH_2S), 38.74 (C-2), 43.02 (C-13), 45.15 (C-4), 46.51 (C-5), 51.51 (C-14), 54.15 (C-9), 69.01 (C-3), 81.92 (C-17) (assignment by comparison with data for 17β-hydroxy-5α-androstan-3-one[39]). – MS (70 eV): *m/e* = 366 (100%), 338 (9), 305 (23), 273 (20), 255 (10), 235 (11), 83 (77).

$C_{21}H_{34}OS_2$ (366.6) Calcd. C 68.80 H 9.35 Found C 68.95 H 9.40

3β-Hydroxy-5-pregnen-20-one 1,2-Ethanediyl Dithioacetal (**3h**): Yield (method 1) 74% together with 23% of 3β-acetoxy-5-pregnen-20-one 1,2-ethanediyl dithioacetal; yield (method 2)

90%; m. p. 195–197°C (CH_3OH/H_2O = 10:1) (Lit.[40] 195–196°C). – IR and MS in agreement with literature data[41]. – ^{13}C NMR ($CDCl_3$): δ = 13.14 (C-18), 19.34 (C-19), 20.97 (C-11), 24.05 (C-15), 26.99 (C-16), 31.62 (C-8), 31.75 (C-2, -7), 35.54 (C-21), 36.51 (C-10), 37.25 (C-1), 37.38 (C-12), 39.84, 41.33 (SCH_2CH_2S), 42.30 (C-4), 44.02 (C-13), 49.94 (C-9), 56.68 (C-14), 60.72 (C-17), 71.37 (C-20), 71.76 (C-3), 121.57 (C-6), 140.83 (C-5) (assignment by comparison with data for 3β-hydroxy-5-pregnen-20-one)[42].

$C_{23}H_{36}OS_2$ (392.7) Calcd. C 70.43 H 9.24 Found C 70.15 H 9.42

3α-Hydroxyandrostan-17-one 1,2-Ethanediyl Dithioacetal (**3i**): Yield (method 1) 68% together with 16% 3α-acetoxyandrostan-17-one 1,2-ethanediyl dithioacetal; m. p. 176–177°C (CH_3OH/H_2O = 10:1). – IR (KBr): 3600–3300, 2945, 2915, 2860 cm^{-1}. – ^{13}C NMR ($CDCl_3$): δ = 11.23 (C-19), 17.39 (C-18), 20.42 (C-11), 23.82 (C-15), 28.45 (C-6), 29.00 (C-2), 31.72 (C-12), 32.17 (C-1, -7), 35.90 (C-10), 36.15 (C-4), 36.96 (C-8), 39.10 (C-5), 39.23, 39.55 (SCH_2CH_2S), 42.95 (C-16), 49.13 (C-13), 52.53 (C-14), 53.83 (C-9), 66.48 (C-3), 80.60 (C-17) (assignment by comparison with data for 3α-hydroxyandrostan-17-one[39]). – MS (70 eV): *m/e* = 366 (22%), 338 (45), 306 (3), 305 (5), 272 (7), 246 (32), 118 (100).

$C_{21}H_{34}OS_2$ (366.6) Calcd. C 68.80 H 9.35 Found C 68.56 H 9.40

3. Oxidative Cleavage of 1,3-Dithianes 2

Method 2: Compounds **2a–f** underwent oxidative cleavage to the carbonyl compounds **7** by method 2 according to the general procedure. Identification of the products took place by comparison of their physical and spectral data with those of authentical samples. All data are summerized in Table 5.

Table 5. Experimental Data for the Oxidative Cleavage of **2** by Method 2

Compound	Amount of **2** [mg (mmol)]	Amount of **1a** [mg (mmol)]	Yield of **7** [% (mg, mmol)]	Consumed Charge [As]
2a	525 (2.5)	143 (0.5)	95 (285, 2.38)[a]	538
2b	495 (2.5)	143 (0.5)	95 (233, 2.38)[a]	532
2c	615 (2.5)	143 (0.5)	85 (332, 2.13)[a]	527
2d	581 (2.5)	143 (0.5)	97[b]	542
2e	761 (2.5)	143 (0.5)	70 (375, 1.75)[c]	536
2f	478 (1.32)	240 (0.5)[d]	90 (324, 1.19)[e]	300

[a] GLC analysis. – [b] Isolated and identified by an authentical sample as *O*-methyloxime (423 mg, 2.43 mmol) by a literature procedure[43]. – [c] Isolated by distillation. – [d] **1b** was used as mediator. – [e] Isolated by GLC.

Method 1: 98 mg (0.40 mmol) or 246 mg (1.0 mmol) of **2c** was treated with 520 mg (0.83 mmol) of $\mathbf{1a}^{+\cdot}$ $SbCl_6^-$ or 1.8 g (2.2 mmol) of $\mathbf{1b}^{+\cdot}$ $SbCl_6^-$ according to the general procedure. After work-up the yields of **7c** were determined by GLC to give 92% (57.4 mg, 0.37 mmol) in the case of $\mathbf{1a}^{+\cdot}$ and 82% (128 mg, 0.82 mmol) in the case of $\mathbf{1b}^{+\cdot}$.

4. Oxidative Cleavage of 1,3-Dithiolanes 3

Method 1: Compounds **3a–d**, **g**, and **i** underwent oxidative cleavage to the carbonyl compounds **7** by method 1 according to the general procedure. Identification of the products took place by comparison of their physical and spectral data with those of authentical samples. All data are summerized in Table 6.

Table 6. Experimental Data for the Oxidative Cleavage of **3** by Method 1

Compound	Amount of **3** [mg (mmol)]	Amount of $\mathbf{1b}^{+\cdot}$ $SbCl_6^-$ [mg, (mmol)]	Yield of **7** [% (mg, mmol)]
3a	245 (1.25)	2300 (2.82)	91 (120, 1.00)[a]
3b	218 (1.25)	2250 (2.76)	81 (128, 1.01)[b]
3c	291 (1.25)	2250 (2.76)	83 (162, 1.04)[a]
3d	273 (1.25)	2200 (2.69)	74 (158, 0.93)[a]
3g	449 (1.22)	2200 (2.69)	83 (295, 1.02)[c]
3i	402 (1.10)	1980 (2.43)	– [d]

[a] GLC analysis. – [b] Determined as *O*-methyloxime. – [c] Isolated by LC. – [d] No formation of **7c**, instead **8** (55%) and **9** (32%) were isolated by LC.

5',6'-Dihydro-3α-hydroxy-5α-androst-16-eno[16,17-b][1,4]dithiine (**8**): Yield 55%; m. p. 168 – 170°C (CH_3OH/H_2O = 4:1). – ^{13}C NMR ($CDCl_3$, 15.09 MHz): δ = 11.17 (C-19), 15.99 (C-18), 20.52 (C-11), 26.64 (SCH_2), 27.45 (C-7), 28.39 (C-6), 29.00 (C-2), 31.72 (C-15), 31.98 (C-1), 33.76 (C-8), 34.18 (SCH_2), 35.89 (C-4), 36.38 (C-10), 36.87 (C-12), 39.33 (C-5), 49.36 (C-13), 54.44 (C-14), 54.96 (C-9), 66.55 (C-3), 120.15 (C-16), 133.61 (C-17). – MS (70 eV): *m/e* = 364 (60%), 349 (100), 331 (7), 237 (8), 223 (3), 183 (6), 169 (4).

$C_{21}H_{32}OS_2$ (High resolution MS) Cacld. 364.18946 Found 364.1901

3α-Hydroxy-5α-androst-14-ene-16,17-dione 16-(1,2-ethanediyl dithioacetal) (**9**): Yield 32%; m. p. 259 – 262°C (CH_3OH/H_2O = 4:1). – IR (KBr): 3580, 3480, 2990, 2980, 2940, 2870, 1750, 1635, 1455, 1260, 1060, 1020, 880, 860, 785 cm^{-1}. – ^1H NMR ($CDCl_3$, 400 MHz): δ = 5.85 (1H, d, *J* = 2 Hz, 15-H), 4.03 – 4.08 (1H, m, 3-H), 3.59 – 3.69 and 3.38 – 3.50 (4H, m, SCH_2CH_2S), 2.18 – 2.25 (1H, m, 8-H), 1.85 – 1.93 (2H, m, CH_2-12), 1.20 – 1.25 (18H, several m), 0.85 (3H, s, CH_3-19). – ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 10.86 (C-19), 20.02 (C-11), 21.94 (C-18), 27.68 (C-7), 28.40 (C-6), 28.78 (C-2), 31.80 (C-1), 34.92 (C-12), 35.47 (C-8), 35.61 (C-4), 36.52 (C-10), 38.51 (C-5), 39.68 (SCH_2), 40.26 (SCH_2), 50.12 (C-13), 54.44 (C-9), 65.98 (C-3), 67.60 (C-16), 116.69 (C-15), 156.58 (C-14), 217.13 (C-17). – MS (70 eV): *m/e* = 378 (12%), 350 (23), 332 (1), 322 (65), 304 (5), 289 (10), 271 (11), 144 (100).

$C_{21}H_{30}O_2S_2$ (High resolution MS) Calcd. 378.1687 Found 378.1691

Method 2: Compounds **3a – d** and **g** underwent oxidative cleavage to the carbonyl compounds **7** by method 2 according to the general procedure. Identification of the products was achieved as described before (Table 7).

Table 7. Experimental Data for the Oxidative Cleavage of **3** by Method 2

Compound	Amount of **3** [g (mmol)]	Amount of **1b** [g (mmol)]	Yield of **7** [% g (mmol)]	Consumed Charge [As]
3a	1.96 (10.0)	1.21 (2.5)	84 (1.01, 8.4)[a]	3120
3b	2.00 (11.5)	1.39 (2.9)	74 (1.08, 8.5)[b]	3540
3c	2.26 (9.7)	1.20 (2.5)	75 (1.20, 7.3)[c]	3305
3d	2.16 (9.9)	1.20 (2.5)	83 (1.41, 8.22)[b]	3625
3g[d]	0.24 (0.65)	0.40 (0.8)	77 (0.15, 0.5)[b]	230

[a] Determined by bulb-to-bulb distillation. – [b] Determined by isolation as *O*-methyloxime. – [c] GLC analysis. – [d] Using cell 1.

Method 3: Compounds **3g** and **h** underwent oxidative cleavage to the carbonyl compounds **7** by method 3 according to the general procedure. Identification as described before (data in Table 8).

Table 8. Experimental Data for the Oxidative Cleavage of **3** by Method 3

Compound	Amount of **3** mg (mmol)	Amount of **1b** g (mmol)	Yield of **7** % (mg, mmol)	Charge Consumed As
3g	302 (0.82)	1.46 (3.03)	71 (170, 0.59)[a,b]	480
3h	396 (1.01)	1.45 (3.01)	74 (235, 0.74)[b]	500
3h	200 (0.51)	1.14 (3.06)[c]	100 (162, 0.51)[b]	900

[a] 91% with respect to consumption of **3g**; 0.18 mmol **3g** recovered. – [b] Isolated by LC. – [c] **1c** was used as mediator.

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