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The Electrochemistry of Organic Sulfur Compounds Part VI.[1] The Anodic Dimerization of α-(1′, 2′-Dithiol-3′-ylidene)-acetophenones

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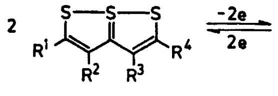
A series of aryl substituted α-(1′,2′-dithiol-3′-ylidene)acetophenones, *1*, has been examined by voltammetric and exhaustive electrochemical techniques. One electron oxidation of compounds *1* was accompanied by the formation of the corresponding dimeric dications, *2*, which were not capable of undergoing further electrochemical oxidation. Reaction of *2* with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) resulted in hydrogen abstraction and formation of a new dication, *4*, which upon electrochemical reduction gave the uncharged dimer of *1*, the bi[α-(1′,2′-dithiol-3′-ylidene)-phenacyl], *3*. The effect of the nature and degree of substitution on the reaction is discussed. By reaction with P_2S_5, the dimers, *3*, could be converted to the corresponding dimeric 1,6,6aλ^4-trithiapentalenes, *5*.

In part III of this series we reported the reversible electrochemical interconversion of several 1,2-dithiol-3-thiones.[2] Anodic oxidation resulted in formation of dimeric dications, linked through a disulfide bond, from which the starting materials could be regenerated by reduction. A similar reversible process was observed for a series of 1,6,6aλ^4-trithiapentalenes, *6*, during the oxidation of which *7* were formed.[3] We have now extended the study to include the structurally related α-(1′,2′-dithiol-3′-ylidene)-acetophenones, *1*, and this paper deals with the results obtained by anodic oxidation of compounds having an unsubstituted α-position. Compounds *1* can be prepared by oxidative desulfuration of *6*,[4] but further oxidation of the dithiolylidene ketones has not been observed. We now report the non-destructive anodic oxidation of a series of aryl substituted compounds *1*.



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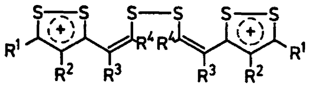

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RESULTS

For convenience of reference, the structures of the compounds studied are tabulated in Table 1.

Voltammetry of α-(1′,2′-dithiol-3′-ylidene)-acetophenones, 1. All of the compounds showed essentially the same voltammetric behavior in acetonitrile or the mixed solvent acetonitrile/dichloromethane (1/1) containing sodium perchlorate as supporting electrolyte (0.1 M). The voltammogram of *1f* in the mixed solvent is illustrated in Fig. 1. On the anodic sweep an irreversible oxidation peak, O_1, was observed

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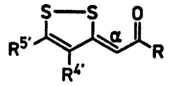
Table 1. Structures of α-(1′,2′-dithiol-3′-ylidene)acetophenones, *1.*



Structure[a]	$R^{5'}$	$R^{4'}$	R
1a	Phenyl	H	Phenyl
1b	*p*-*tert*-Butylphenyl	H	Phenyl
1c	*p*-Methoxyphenyl	H	Phenyl
1d	H	Phenyl	Phenyl
1e	H	*p*-Methylphenyl	Phenyl
1f	Phenyl	Phenyl	Phenyl
1g	Phenyl	Phenyl	*p*-Bromophenyl

[a] The same letters, *a*–*g*, are used for the corresponding substitution in compounds *2*–*5*.

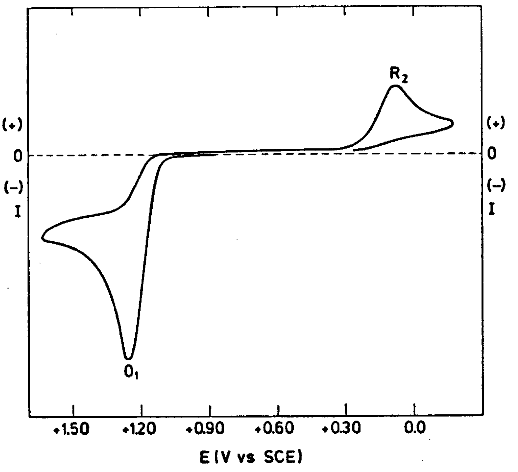


Fig. 1. Cyclic voltammetry of *1f* in acetonitrile/dichloromethane (1/1) containing sodium perchlorate (0.1 M). Sweep-rate = 86 mV/s.

at +1.26 V.* On the reverse sweep a reduction peak, R_2, appeared at +0.18 V. An increase of the sweep-rate from 86 mV/s to 20 V/s did not bring about any significant change in this picture. The voltammetric data for all the compounds are tabulated in Table 2.

When the voltammetry of the compounds *1a*–*1c* was carried out in dichloromethane containing Bu_4NBF_4 (0.25 M) as supporting electrolyte, slightly different behavior was observed. This is illustrated by the voltammogram of *1a* in Fig. 2. The reduction peak R_2 was barely visible (not shown in Fig. 2) and instead a redox couple, R_3–O_3, appeared at +0.72 V (R_3) and +0.96 V (O_3).

Exhaustive electrolysis of 2 mM solutions (50 ml) of *1d*–*1g* in the acetonitrile/dichloro-

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* All peak potentials refer to the aqueous saturated calomel electrode (SCE).

Table 2. Voltammetric data for α-(1′,2′-dithiol-3′-ylidene)acetophenones, *1*, bi[α-hydro-α-(1′,2′-dithiol-3′-ylio)phenacyl]s, *2*, and bi[α-(1′,2′-dithiol-3′-ylidene)phenacyl]s, *3*.

Structure	$E_{O_1}{}^a$	Structure	$E_{R_2}{}^a$	Structure	$E_{O_3}{}^b$	$E_{R_3}{}^b$
1a	+1.24	*2a*	−0.14	*3a*	+0.96	+0.72
1b	+1.22	*2b*	−0.19	*3b*	+0.97	+0.61
1c	+1.20	*2c*	−0.30	*3c*	+0.90	+0.63
1d	+1.24	*2d*	+0.31	*3d*	+0.88	+0.60
1e	+1.25	*2e*	+0.27	*3e*	+0.87	+0.52
1f	+1.26	*2f*	+0.18	*3f*	+0.89	+0.45
1g	+1.27	*2g*	+0.15	*3g*	+0.94	+0.49

[a,b] Peak potentials in V *vs.* SCE measured at a platinum button electrode at the sweep-rate 86 mV/sec. [a] Solvent = acetonitrile/dichloromethane (1/1) containing sodium perchlorate (0.1 M). [b] Solvent = dichloromethane containing Bu_4NBF_4 (0.25 M). Substrate conc. = 1.0×10^{-3} M.

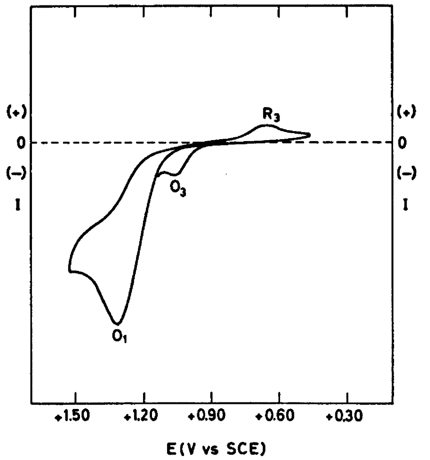


Fig. 2. Cyclic voltammetry of *1a* in dichloromethane containing Bu_4NBF_4 (0.25 M). Sweeprate = 86 mV/s.

methane solvent mixture, using constant current coulometric techniques,[5] demonstrated that one F/mol was transferred resulting in species which reduce at R_2. When $R^{4'} = H$ (*1a – 1c*) coulometric *n*-values ranging from 1.0 to 1.8 were found. Voltammetry of the resulting solutions showed the presence of a mixture of the compounds responsible for R_2 and R_3. *1d – 1g* could be regenerated by coulometric reduction (~1 F/mol) in nearly quantitative yields as judged from the corresponding peak currents. However, when $R^{4'} = H$ the products connected with O_2 were present as well.

Preparative anodic oxidation of α-(1′,2′-dithiol-3′-ylidene)acetophenones. Constant current oxidation of *1* on a millimolar scale in acetonitrile/dichloromethane (1/1) containing sodium perchlorate as supporting electrolyte (0.1 M) gave products dependent on the substitution in the 4′-position of the starting material as expected from the voltammetric experiments. For *1a – 1c* mixtures of the corresponding *2* and *3* were obtained, the product ratio varying with both the nature of $R^{5'}$ and the solvent composition. When $R^{4'}$ = aryl quantitative formation of *2* as the perchlorate salt was observed.

Attempts to deprotonate *2d – 2g* in order to obtain *3d – 3g* were unsuccessful, as were attempts to electrochemically oxidize *2d – 2g* to *4d – 4g*. However, the latter oxidation was found to take place when 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) was added to the voltammetric solutions and *4* were obtained in good yields. Compounds *3* could now be prepared by electrochemical reduction with consumption of one F/mol (corresponding to starting material). By following this procedure, increased yields of *3a – 3c* were also obtained. Isolated yields of the dimers are given in Table 3 as well as melting points and visible spectral data.

The dimers, *3*, are coupled through the α-positions. This was shown by an experiment with the C_6D_5 analogue of *1d*, *1d*(d_{10}). The ^1H NMR spectrum of this compound consisted of only two peaks, H(5′), δ 7.78 and H(α), δ 7.30. Preparative oxidation according to the procedure described above resulted in the isolation of a product, the ^1H NMR spectrum of which showed only the presence of a single peak at δ 7.87 consistent with the structure *3d*(d_{10}).

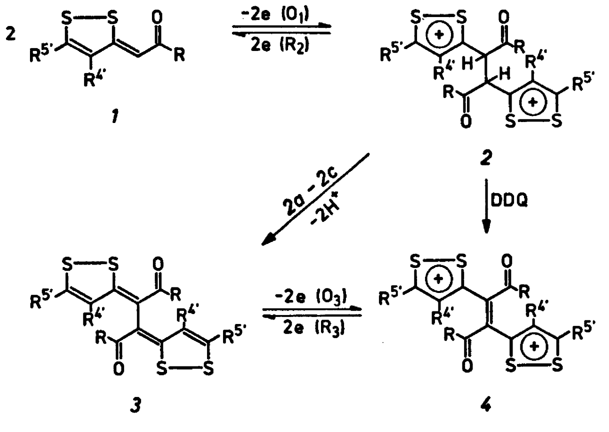


Table 3. Isolated yields, melting points and visible spectral data for bi-[α-(1′,2′-dithiol-3′-ylidene)phenacyl]s,*3*.

Structure	Yield[a]/%	M.p./°C	λ_{max}/nm[b]	ε[b]
3a	39	266–267	473	31 900
3b	37	205–206	472	34 000
3c	28	248–249	472	36 000
3d	68	299–300	467	26 100
3e	49	283–284	473	29 000
3f	54	282–283	475	27 100
3g	49	303–304	483	32 000

[a] After purification by chromatography (see experimental section). [b] In dichloromethane.

Voltammetry of bi[*α-(1′,2′-dithiol-3′-ylidene)-phenacyl*]*s*. The voltammetric measurements on all of the dimers, *3*, gave very similar results, and will only be described for one model compound, *3f*. The cyclic voltammogram in dichloromethane containing Bu_4NBF_4 (0.25 M) as supporting electrolyte is shown in Fig.3. During the anodic scan a single irreversible peak, O_3, was observed at +0.89 V. A cathodic counterpart, R_3, at +0.45 V appeared when the direction of the scan was changed. Voltammetric data for all the dimers are listed in Table 2. Constant current coulometry demonstrated that two electrons per molecule were transferred.

The resulting solution showed no signs of instability even after standing for several hours. Reduction back to starting material required two F/mol, and comparison of the height of peak O_3 before and after the experiment showed that *3f* was regenerated in 97 % yield. It was not possible to detect the presence of any intermediate cation radicals during this procedure.

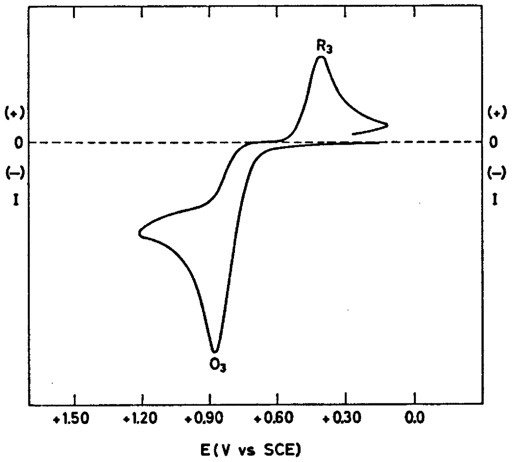
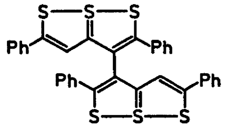


Fig. 3. Cyclic voltammetry of *3f* in dichloromethane containing Bu_4NBF_4 (0.25 M). Sweep-rate = 86 mV/s.

The identity of the products from coulometric oxidation was supported by oxidation of *3e* by $SbCl_5$. The resulting compound showed satisfactory analysis for a dication salt, *4e*, $Sb_2Cl_{12}^{2-}$, and the voltammetric behavior was indistinguishable from that of the solution from coulometric oxidation.

Reaction of bi[*α-(1′,2′-dithiol-3′-ylidene)-phenacyl*]*s with P_2S_5*. The compounds *1* can be transformed into 1,6,6aλ^4-trithiapentalenes, *6*, upon reaction with phosphorus pentasulfide.[4,6] The reaction of *3a* with P_2S_5 resulted in formation of the corresponding dimeric trithiapentalene, *5a*. Such compounds have hitherto been unknown. The structure of *5a* was supported by mass spectrometry and visible spectroscopy.



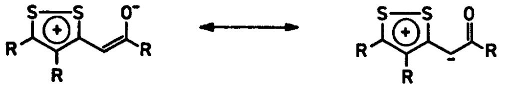
5a

DISCUSSION

Scheme 2 explains the experimental results.

The voltammetric and coulometric oxidation of *1* is consistent with a one-electron charge transfer to form the cation radicals $1^{+\cdot}$, which dimerize to the dications *2*. Under conditions where *2* are not consumed in further reactions, reduction regenerates *1*. This type of voltammetric behavior has earlier been reported for other reactions including the anodic oxidation of 1,2-dithiole-3-thiones[2] and 1,6,6aλ^4-trithiapentalenes[3] and the cathodic reduction of 1,2-dithiolylium ions.[1,7]

The peak potentials of *1* vary surprisingly little with the degree of substitution and the nature of the substituents (Table 2). Substitution of phenyl by the electron donating *p*-methoxyphenyl at C(5′) facilitates oxidation by 40 mV (*1a* and *1c*) and introduction of an extra phenyl group at C(4′) results only in a 20 mV increase of the peak potential (*1a* and *1f*). For comparison the corresponding changes observed for the trithiapentalene series were 140 mV and 290 mV, respectively.[3] Since the molecular geometry of *1* is very similar to that of *6*, the reason for the observed differences has to be sought in the electronic structure of the two types of molecules. The presence of one oxygen and two sulfur atoms in *1* instead of three sulfur atoms as in *6* makes the distribution of charge more uneven. Dipole moments[8] and ESCA spectra[9] suggest a strong contribution of mesoionic forms like *8a*, and from studies of the carbonyl vibration in ^{18}O enriched compounds it was found that the contribution of ketonic forms in some cases is as low as 27 %.[10] It is also believed that the observed oxidation potentials reflect this dipolar structure, the nearly constant values being associated with the high electron density in the oxygen containing part of the molecule (*8a*–*8b*). Substitution in the dithiole ring does not affect the polarity of the molecule significantly as measured from dipole moments.[8,11]

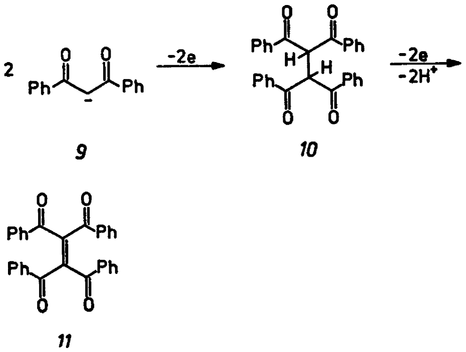


8a *8b*

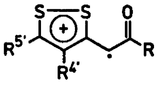
Considering now the reduction potentials of *2* the figures in Table 2 indicate that ions *2a*–*2c* are more difficultly reduced than ions carrying an aryl group at C(4′), *2d*–*2g*. The peak potentials found for *2a*–*2c* (approximately −0.20 V) are close to those observed (approximately −0.30 V) for the analogous 3,5-diaryl-1,2-dithiolylium salts.[1] Molecular models of *2* show that the presence of large substituents in the 4′-position causes considerable steric interactions, which could be released by reduction to *1*. Thus, the anodic shift in peak potentials observed for *2d*–*2g* can be rationalized from the effect of steric acceleration of the bond cleavage resulting in a kinetic shift of the reduction potential.

The reactivity of *2* is likewise significantly dependent on the nature of $R^{4'}$. Where $R^{4'}$ = aryl, dications, stable on the time scale of coulometry, were formed which only very slowly reverted to starting materials in an unknown redox process. When $R^{4'}$ = H, *2* deprotonated to *3* in a solvent dependent chemical step. The lack of reactivity of *2* substituted at C(4′) can be explained on steric grounds. The preferred conformation of *3* seems to be one in which the two planar halves of the molecule are twisted around the C(α)–C(α) bond. This is supported by the observation that $\lambda_{\max}$ of *3* (Table 3) are only approximately 17 nm higher than $\lambda_{\max}$ for *1*,[12] indicating little or no increase in conjugation. However, substitution at C(4′) effectively prevents a transition state involving planarity of the α-(1′,2′-dithiol-3′-ylidene)acetophenone ring system resulting in increased stability of *2*. The formation of *3* directly from *2* was only sufficiently rapid in dichloromethane to be observed by voltammetry. In the mixed solvent and in acetonitrile the only observable peak after changing the direction of the sweep was R_2. It is believed that the lower reactivity of *2* in the polar solvents reflects the better solvation of positive ions in these systems. In non-polar dichloromethane the uncharged *3* are favored.

The possibility of transforming the products from preparative electrolysis to dimeric 1,6,6aλ^4-trithiapentalenes, *5*, is only consistent with coupling between carbon atoms, and the actual position was shown by anodic oxidation of $1d(d_{10})$, the product of which, $3d(d_{10})$, was demonstrated to be a C(α)–C(α) dimer by ^{1}H NMR spectroscopy. Coupling through this position parallels the observation by VandenBorn and Evans,[13] who recently reported the formation of C(α)–C(α) dimers, *10*–*11*, from exhaustive oxidation of the enolate of dibenzoylmethane, *9*, which is analogous to the resonance structure *8b* for *1*.



The coupling took place *via* the free radical corresponding to *9*, and similarly a resonance structure like *12* for $1^{+\cdot}$ plays an important role in determining the nature of the resulting products.



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EXPERIMENTAL

General procedures, purification of solvents and supporting electrolytes and apparatus for voltammetry and coulometry have been decribed earlier.[5,14]

^{1}H NMR spectra were recorded on a Varian model A 60 spectrometer, mass spectra on a MS 902 spectrometer and visible spectra on a Bechman Acta III spectrometer.

α-(1′,2′-Dithiol-3′-ylidene)acetophenones, 1, were prepared by conventional methods.[15–17]

Anodic oxidation of α-(1′2′-dithiol-3′-ylidene)-acetophenones, 1. The compound (1 mmol) to be oxidized was dissolved in acetonitrile/dichloromethane, 1/1, (60 ml), containing sodium perchlorate (0.1 M) as supporting electrolyte. This solution was subjected to constant current oxidation (50 mA) in a two-compartment cell kept at room temperature. The anode was a platinum gauze electrode and the cathode a platinum wire. When the calculated amount of current had been passed through the cell (32.2 min required for one F/mol at 50 mA) the electrolysis was stopped, and DDQ (0.6 mmol) was added together with sodium carbonate (250 mg). The solution was allowed to stand overnight after which it was dark red colored. Constant current reduction (50 mA) was now performed for another 32.2 min. The resulting solution was evaporated to near dryness in *vacuo* and then diluted with dichloromethane (200 ml) in which the supporting electrolyte is insoluble. This solution was washed several times with water, aqueous sodium carbonate and again water followed by drying over sodium sulfate. After evaporation of the solvent the residue was chromatographed on neutral alumina (100 g) (Woelm W 200, 10 % water). Elution was started with ligroin/dichloromethane (10/1) and continued with increasing amounts of dichloromethane in the mixture ending with a 1/1-mixture (total approximately 900 ml). Small amounts of purple and yellow biproducts were eluted with the less polar solvent mixtures and finally the bi[α-(1′,2′-dithiol-3′-ylidene)phenacyl]s, *3*. Some polymeric material and DDQH$_2$ were left on the column. Recrystallization was in general not necessary, but if very pure samples were wanted, *3* were recrystallized from 2-ethoxyethanol. Yields are given in Table 3. All compounds showed satisfactory elemental analysis. However, these data are not included because the monomers and the dimers have the same calculated analysis within the experimental error. Mass spectra showed in all cases the presence of M$^{+\cdot}$.

Anodic oxidation of α-(4′-pentadeuteriophenyl-1′,2′-dithiol-3′-ylidene)pentadeuterioacetophenone, 1d(d_{10}).[17] The procedure was essentially that described above. *1d*(d_{10}) (82 mg, 0.268 mmol) was dissolved in acetonitrile/dichloromethane (2/3) (25 ml) containing sodium perchlorate (0.1 M) as supporting electrolyte. The time of oxidation (50 mA) required for 0.268 mmol was 8.63 min, and the amount of DDQ was reduced to 0.3 mmol. After standing over night and cathodic reduction, work-up was as described above. Chromatography on alumina (25 g) gave 42 mg of *3d*(d_{10}), (52 %) * ^{1}H NMR (CDCl$_3$): δ 7.87 (s).

Oxidation of bi[α-(4′-(p-methylphenyl)-1′,2′-dithiol-3′-ylidene)phenacyl], 3e, by SbCl$_5$. Compound *3e* (13 mg) was dissolved in dichloromethane (1 ml). To this solution was added dropwise a solution of SbCl$_5$ in dichloromethane in excess. The resulting suspension was added to ether and filtered. The yellow precipitate was washed several times with ether and dried at +80 °C. (Found C 33.2; H 2.37; S. 9.95; Cl 31.9 Calc. for $C_{36}H_{28}O_2S_4Sb_2Cl_{12}$: C 33.5; H 2.03; S 9.89; Cl 33.4).

Reaction of bi[α-(5′-phenyl-1′,2′-dithiol-3′-ylidene)-phenacyl], 3a, with P$_2$S$_5$. Compound *3a* (50 mg) was refluxed for 2h with P$_2$S$_5$ (200 mg) in toluene (50 ml). The toluene solution was dried over sodium sulfate and evaporated *in vacuo*. The resulting dark residue was chromatographed on alumina (MERCK neutral, 4 % water) (cyclohexane). Recrystallization from cyclohexane gave 25 mg of *5a*. Yield 47 %, m.p. 214–216 °C, M$^{+\cdot}$ = 622 (52 %), λ_{max} (dichloromethane) = 480 nm, ε = 26 000.

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* The yield is lower than that obtained for *3d* (68 %). This is probably due to the smaller amount of material taken into work.

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