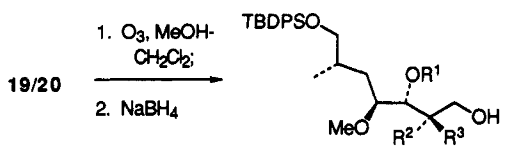
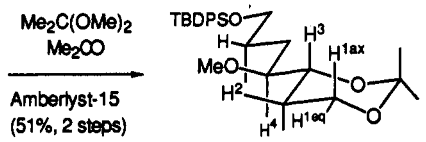


24 $R^1 = H, R^2 = Me, R^3 = H$
25 $R^1 = Me, R^2 = Me, R^3 = H$
26 $R^1 = Me, R^2 = H, R^3 = Me$

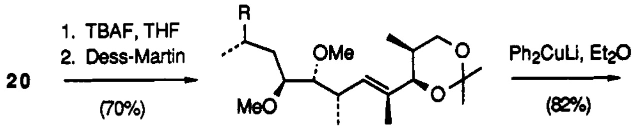


27

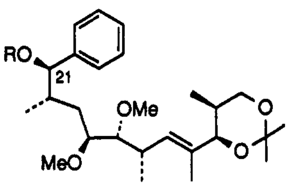
$J_{1ax,2} = 2.6$ Hz
$J_{1eq,2} = 1.5$ Hz
$J_{2,3} = 2.4$ Hz
$J_{3,4} = 8.6$ Hz

the OH-substituted vinyloxirane **15** proceeds with high anti selectivity, whereas addition to the methyl ether **16** is highly syn selective. Previous studies with TBS and MTM ether prototypes of **16** showed moderate to excellent preferences for anti addition.[4] It is not clear at this point if the methoxy substituent, the use of $BF_3{\cdot}OEt_2$, or some conformational factor is responsible for the ususual syn selectivity observed for **16**.

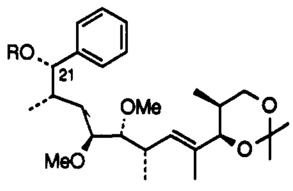
To explore the possibility of using acetonide **20** as a synthetic precursor of the macbecins, we prepared aldehyde **29** by silyl ether cleavage and Dess-Martin oxidation.[9] Addition of Ph_2CuLi to **29** yielded a separable 5.5:1 mixture of diastereomers favoring the Cram-Felkin-Ahn adduct **30**. The stereochemistry of this alcohol, ascertained by ^1H NMR analysis of the *O*-methyl mandelates,[16] is that required for elaboration to the macbecin family of natural products.[17] Therefore, by using an analogous cuprate derived from the aryl subunit described by Kallmerten[2b] in his recent synthesis, it should be possible to convert aldehyde **29** to macbecin I along the route previously employed by Baker, et al.[2a]



28 $R = CH_2OH$
29 $R = CHO$



30 R = H
31 R = (*S*)-PhCH(OMe)CO
32 R = (*R*)-PhCH(OMe)CO



33 R = H

Acknowledgment. This work was supported by a research grant (CHE-8912745) from the National Science Foundation.

---

(16) Trost, B. M.; Belletire, J. L.; Godleski, S.; McDougal, P. G.; Balkovec, J. M.; Baldwin, J. J.; Christy, M. E.; Ponticello, G. S.; Varga, S. L.; Springer, J. D. *J. Org. Chem.* **1986**, *51*, 2370.

(17) Satisfactory IR, ^1H NMR, and mass spectra/or combustion analyses have been obtained for all previously unknown synthetic intermediates.

Articles

Medium and Structure Effects on the Anodic Oxidation of Aryl Arylmethyl Sulfides

Enrico Baciocchi,[*,†] Cesare Rol,[‡] Emanuela Scamosci,[‡] and Giovanni V. Sebastiani[‡]

Dipartimento di Chimica, Università di Roma, Piazzale A. Moro, 00185 Roma, Italy, and Dipartimento di Chimica, Università di Perugia, Via Elce di Sotto, 06100 Perugia, Italy

Received August 21, 1990

The anodic oxidation of a number of $XC_6H_4CH_2SC_6H_4Y$ has been investigated under a variety of conditions ($AcOH/AcO^-$, $AcOH/NO_3^-$, $AcOH/ClO_4^-$, CH_3CN/ClO_4^-) and the relative weight of the various reaction paths available to the intermediate radical cation (C_α–H deprotonation, C–S bond cleavage, attack on sulfur) evaluated via product analysis. It has been observed that in $AcOH/AcO^-$ (presence of a strong base) the main reaction is C_α–H deprotonation, which is also favored when X is an electron-withdrawing substituent and depressed by electron-donating Y. The C–S bond cleavage reaction is particularly important in CH_3CN/ClO_4^-; its relative contribution is enhanced by an electron-donating X, which makes the benzyl carbocation more stable. The pathway leading to sulfoxides is favored in $AcOH/NO_3^-$ and, to a lesser extent, in $AcOH/ClO_4^-$. Formation of sulfoxide is also favored when Y is an electron-donating group.

In the last few years there has been increasing concern with the role of electron-transfer (ET) processes in organic reactions.[1] Radical ions have been suggested as critical intermediates in a great variety of processes, and moreover,

---

[†] Università di Roma.
[‡] Università di Perugia.

(1) Eberson, L. *Electron Transfer Reaction in Organic Chemistry*; Springer-Verlag: Berlin, 1987.

0022-3263/91/1956-5498$02.50/0 © 1991 American Chemical Society

Table I. Product Yields[a] in Some Anodic Oxidations[b] of Aryl Arylmethyl Sulfides in Different Solvent/Supporting Electrolyte Systems

		products,[a] %										
						ArCH$_2$X, X =						
ArCH$_2$SAr′	solvent/ electrolyte	ArCH$_2$SOAr′	ArCH(OAc)-SAr′	ArCH-(OAc)$_2$	ArCHO	OAc	Cl	NHOAc	OH	ONO$_2$	OCH$_2$Ar
1	AcOH/AcONa	5	19	9							
2			7[c]	13							
3		5	44								
4		28				3					
5		13	31	10							
1	AcOH/LiNO$_3$	32			3						
2		12			11	6			5	21	
3		35	16		6						
5		23	25		3						
1	AcOH/LiClO$_4$	30				6	4				
2						29					
3		26				5	8				
4		33				3					
5		25		3		12					
1	CH$_3$CN/LiClO$_4$	11					5	26			
2							3	16	18		9
3		41					10				
4		10					7	20			
5		12					5	27			

[a] Percent determined by NMR analysis with respect to the starting material. The error is ±2. [b] Controlled potential (at 1.1–1.4 V vs. SCE), 1 F mol^{-1}. [c] Recovered as benzaldehyde (see Experimental Section).

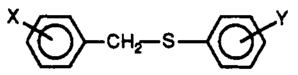
new concepts of organic reactivity have recently been developed where these species are models of the transition state of polar reactions.[2]

In this context a deeper knowledge of the general properties of radical ions and especially of their reactivity is certainly needed. Among other things, this information can have a diagnostic role with respect to the intervention of these intermediates in a given organic reaction.

As a further development of our recent study of the properties of benzyl phenyl ether radical cations,[3a] we have considered it worthwhile to undertake a corresponding investigation concerning the reactivity of benzyl phenyl sulfide radical cations. These species are of great interest since as many as four reaction paths are available to them. These are as follows: (a) C_α–H deprotonation to give a benzyl radical; (b) nucleophilic attack at sulfur to form a sulfur centered radical; (c) C–S bond cleavage to produce an arylmethyl cation and an arylthiyl radical; (d) nucleophilic attack at the aromatic ring. Moreover, the importance of sulfur-centered radicals and radical ions in biology is well-recognized.[3b]

Several examples concerning paths a–c have already been reported;[4–6] however, as far as we know, no systematic study concerning the role played by the medium and the substrate structure in the competition between the various reaction pathways has been carried out. In particular, little or no information is available on the effects of electron-donating and electron-withdrawing ring substituents as well as on those of the reaction medium.

To address these problems we have investigated the anodic oxidation of the benzyl phenyl sulfides 1–5 under



1: X = H, Y = H
2: X = 4–OCH$_3$, Y = H
3: X = 4–NO$_2$, Y = H
4: X = H, Y = 4–OCH$_3$
5: X = H, Y = 3–Cl

a variety of reaction conditions (AcOH/AcO$^-$, AcOH/NO$_3^-$, AcOH/ClO$_4^-$, CH$_3$CN/ClO$_4^-$). Anodic oxidations of aromatic sulfides, when carried out at the appropriate oxidation potential, are most probably ECEC processes,[4a] involving one-electron removal from the substrate with formation of a radical cation. This intermediate can undergo (Scheme I; Nu$^-$ is whatever nucleophile present in the medium) the reactions mentioned above, forming species that, after further oxidation and (or) reaction with a nucleophile, give side-chain-substituted products (path a), sulfoxides (path b), benzylic derivatives (path c), and ring-substituted compounds (path d). Thus, the relative contributions of the four reaction channels a–d available to the radical cation can directly be determined by the relative amounts of the products formed in the reaction.

Results

Anodic oxidations were carried out, under nitrogen, at controlled potential (1.1–1.4 V vs SCE)[7] in an undivided cell, and the reaction was always stopped after the passage of 1 F mol^{-1}. Current yields were between 85–100%, assuming that all products are formed by an overall two-electron transfer.

Generally, the reaction mixture, after usual workup, was chromatographed and the various products were characterized by spectroscopic methods (^{1}H NMR, GCMS, and MS) and/or by comparison with authentic specimens and literature data. Yields were determined by ^{1}H NMR

---

(2) Kochi, J. K. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1227. Pross, A. *Adv. Phys. Org. Chem.* **1985**, *21*, 99. Pross, A.; Shaik, S. *Acc. Chem. Res.* **1983**, *16*, 363.

(3) (a) Baciocchi, E.; Piermattei, A.; Rol, C.; Ruzziconi, R.; Sebastiani, G. V. *Tetrahedron* **1989**, *45*, 22. (b) *Sulfur Centered Reactive Intermediates in Chemistry and Biology*; Chatgilialogu, C.; Asmus, K. D., Eds.; Nato Asi Series; Plenum Press: New York, 1990.

(4) (a) Torii, S. *Electroorganic Syntheses. Part 1: Oxidations*; VCH: Weinheim, 1985. (b) Uneyama, K.; Torii, S. *Tetrahedron Lett.* **1971**, 329. (c) Aldmal, K.; Hammerich, O. *Sulfur Lett.* **1984**, *2*, 1. (d) Nokami, J.; Hatate, M.; Wakabayashi, S.; Okawara, R. *Tetrahedron Lett.* **1980**, *21*, 2557. (e) Watanabe, Y.; Oae, S.; Iyanagi, T. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 188. (f) Fuchigami, T.; Nakagawa, Y.; Nonaka, T. *Tetrahedron Lett.* **1986**, *33*, 3869. (g) Cottrell, P. T.; Mann, C. K. *J. Electrochem. Soc.* **1969**, *116*, 1499.

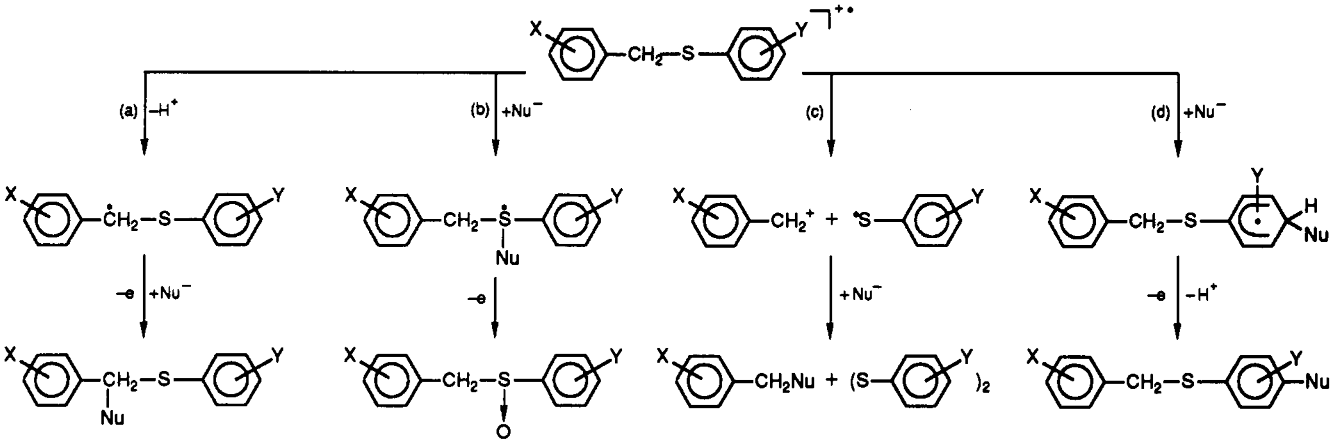
(5) Path d is extremely rare. One example of such a path is the formation of diphenyl[4-(phenylthio)phenyl]sulfonium ion in the anodic oxidation of diphenyl sulfide.[6] In this case, the substrate itself is the nucleophile that performs ring attack at the radical cation.

(6) Uneyama, K.; Torii, S. *J. Org. Chem.* **1972**, *37*, 367.

(7) The anodic peak potentials (E_p) of sulfides are in the range 1.4–1.7 V (vs SCE).[8]

(8) Baciocchi, E.; Intini, D.; Rol, C.; Piermattei, A.; Ruzziconi, R. *Gazz. Chim. Ital.* **1989**, *119*, 649.

Scheme I



analysis of the crude reaction product in the presence of an internal standard (1,4-dimethoxybenzene or 4-nitrotoluene). The mass balance was, in each case, 90% or more. Details are in the Experimental Section, and the results are reported in Table I.

Acetic Acid/Sodium Acetate. Anodic oxidation in this solvent–electrolyte system led to the formation of substituted α-acetoxybenzyl phenyl sulfides, aryl aldehyde acylals, sulfoxides, and diaryl disulfides. The latter compounds were always found in amounts corresponding to those of the C–S bond cleavage products. In one case (reaction of 4), a small amount of benzylic acetate was detected.

The formation of α-acetoxy-substituted compounds can be reasonably ascribed to the deprotonation of the radical cation, (path a of Scheme I), which should be a quite easy process, in view of the extremely strong acidity of these species (pK_a ca. −3).[9,10]

Aryl aldehydes acylals most probably derive by partial oxidation of the first formed α-acetoxybenzyl sulfides. Acetolysis of the latter compounds can be excluded since it has been checked that α-acetoxy derivatives are stable in the reaction medium. Thus, the yields of aryl aldehyde acylals have been added to those of α-acetoxybenzyl sulfides to evaluate the relative weight of the deprotonation process.

The presence of sulfoxides is certainly indicative of attack at the sulfur atom of the radical cation, presumably by AcO$^-$,[11] as well as the formation of benzyl acetate indicates the operation of the C–S bond cleavage pathway (paths b and c in Scheme I, respectively). Path c in Scheme I is indicated as unimolecular, but some nucleophilic assistance is certainly possible.

Acetic Acid/Lithium Nitrate. With compounds 1–3 and 5, the formation of sulfoxides is accompanied by that of α-acetoxybenzyl sulfides and/or aryl aldehydes derived therefrom (presumably aryl aldehydes acylals cannot survive under these reaction conditions). However, aryl aldehydes might also derive from α-nitroxybenzyl sulfides formed by path a in Scheme I (Nu$^-$ = NO$_3^-$). In both cases the formation of these compounds can certainly be ascribed to the operation of the deprotonation channel.

With 2, substantial amounts of benzyl derivatives are obtained by path c in Scheme I, together with an equivalent amount of diphenyl disulfide. Probably, 4-methoxybenzyl alcohol derives from solvolysis of the corresponding benzyl nitrate during the workup procedure. Control experiments showed that 4-methoxybenzaldehyde is not formed by partial oxidation of 4-methoxybenzyl alcohol.

It can be suggested that, in this reaction medium, sulfoxides are mainly formed by the reaction of the intermediate radical cation with NO$_3^-$, in line with previous observations.[8,12]

Finally, with 4 fast formation of sulfoxides in the reaction medium, before the electrolysis, was observed. Therefore, no anodic oxidation of this compound was carried out in AcOH/NO$_3^-$.

Acetic Acid/Lithium Perchlorate and Acetonitrile/Lithium Perchlorate. In both these reaction media the main products are sulfoxides and benzylic derivatives. Formation of benzyl acetates and benzyl acetamides in AcOH and CH$_3$CN, respectively, is certainly due to the operation of path c of Scheme I. However, a quite surprising observation is the presence of substantial amounts of benzyl chlorides in the reaction product, especially in CH$_3$CN/LiClO$_4$. In view of the sometimes observed capacity of ClO$_4^-$ to quench carbocations,[13] we tentatively suggest that LiClO$_4$ may play a role in the formation of sulfoxides by reacting with the intermediate radical cation and thereby forming chloride ions, presumably in a number of steps, which are responsible for the formation of benzyl chlorides. On the other hand, it can be excluded that sulfoxides are formed by reaction of the radical cation with the small amount of water present in the medium, since the yield of these compounds remained unchanged even when CH$_3$CN was rigorously dry (0.005% of water). Finally, the possibility that sulfoxides are formed via chemical oxidation by HClO$_4$ produced by the electrochemically generated protons[4g] is also unlikely since the same product composition was observed in the pres-

---

(9) The pK_a of a radical cation can be estimated on the basis of thermochemical calculations: Nicholas, A. M. de P.; Arnold, D. R. *Can. J. Chem.* 1982, *60*, 2165. In our case, however, the problem is complicated by the lack of reliable values for the standard oxidation potentials ($E°$) and the C–H bond dissociation energies of the neutral substrate. Anyway, we have estimated a pK_a value of ca. −3 for $1^{•+}$ by using the E_p value determined in MeCN for benzyl phenyl sulfide[8] as $E°$ and by taking the C–H bond dissociation energy as 77 kcal mol^{-1} (8 kcal mol^{-1} less than for toluene). Presumably, the real value should be more negative since the $E°$ value is probably higher than E_p.

(10) The α-acetoxy-substituted compound might also be formed by a Pummerer rearrangement of an α-acetoxysulfonium ion (path b, Nu$^-$ = OAc$^-$); however, this possibility is unlikely since our conditions are much milder than those of the Pummerer rearrangement (at room temperature the equilibrium $R_2S^+–OAc + AcO^- \rightleftharpoons R_2SO + Ac_2O$ should be shifted completely to the right).

(11) Hammerich, O.; Parker, V. D. *Acta Chem. Scand.* 1983, *37*, 303.

(12) Shine, H. J. In *The Chemistry of Sulfonium Group*; Stirling, C. J. M., Ed.; John Wiley & Sons: Chichester, 1981; Part 2, p 566.

(13) Capozzi, G.; Modena, G.; Pasquato, L. In *The Chemistry of Sulphenic Acids and Their Derivatives*; Patai, S., Ed.; Wiley: New York, 1990; Chapter 10, p 431.

Table II. Yields (%) of Products Deriving from Sulfur Attack and C_α–H and C–S Bond Cleavage of Aryl Arylmethyl Sulfides Subjected to Anodic Oxidation in Different Solvent/Supporting Electrolyte Systems

$ArCH_2SAr'$	solvent/ electrolyte	sulfur attack	C–H bond cleavage	C–S bond cleavage
1	AcOH/AcONa	5	28	
2			20	
3		5	44	
4		28		3
5		13	41	
1	$AcOH/LiNO_3$	32	3	
2		12	11	32
3		35	22	
5		23	28	
1	$AcOH/LiClO_4$	30		10
2				29
3		26		13
4		33		3
5		25	3	12
1	$CH_3CN/LiClO_4$	11		31
2				55
3		41		10
4		10		27
5		12		32

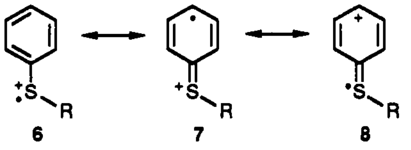
ence of a base ($CaCO_3$) or a proton trap like 1,2-epoxybutane.

Whereas, of course, the above suggestions have to be considered tentative, there is little doubt that formation of benzyl chlorides is due to the C–S bond cleavage pathway of the intermediate radical cation. Moreover, the presence of 4-methoxybenzyl alcohol and bis(4-methoxybenzyl) ether, observed in the product of anodic oxidation of **2**, can also be ascribed to further reactions of 4-methoxybenzyl chloride during the workup procedure.

Discussion

In Table II are reported the relative contributions of the various reaction pathways (Scheme I) for the compounds and the reaction media studied, evaluated according to the foregoing considerations. However, before discussing the data of Table II it is appropriate to briefly comment on the structure of the radical cations involved in these reactions.

Since the ionization potential of thioanisole[14] is much lower than that of toluene[15] it is most reasonable to assume that in the radical cations of the compounds investigated ($\mathbf{2}^{\bullet+}$ can however be an exception, vide infra) the electron is removed from the sulfur-bearing ring, the SOMO orbital resulting from mixing of the sulfur p-type lone pair orbital, n_s, and the symmetric π molecular orbital of the aromatic ring, $e_{1g}(S)$.[16] The radical cations can be therefore described by the resonance structures **6**-**8**.



6 **7** **8**

The contribution of the structures **7** and **8** depends on the conformation of the radical cation. When R = CH_2Ar, PES experiments[17] suggest that the most stable conformer of the radical cation is that with the Ar–SR bond perpendicular to the aromatic system with most of the charge, therefore, localized on the sulfur atom.

It should also be mentioned the tendency of organic sulfide radical cations to interact with the neutral sulfide to form complexes with a σ-σ three-electron bond. However, even though the equilibrium is shifted toward the complex, chemical reactions are given by the uncomplexed radical cation.[18]

Medium Effect. Data of Table II show that the deprotonation reaction is important in $AcOH/AcO^-$ and, to a lesser extent, in $AcOH/NO_3^-$. Clearly, the presence of a base is needed for the occurrence of this reaction and the ability of NO_3^- in this respect is remarkable and to some extent unexpected.

Attack at sulfur and (or) C_α–S bond breaking, paths b and c, respectively, are the predominant processes in $AcOH/ClO_4^-$ and CH_3CN/ClO_4^-. However, the former is more important in $AcOH/ClO_4^-$, the second in CH_3CN/ClO_4^- with radical cations of **1**, **4**, and **5**. No significant effect is noted with $\mathbf{3}^{\bullet+}$; with $\mathbf{2}^{\bullet+}$ only fragmentation is observed in both media.

Structure Effects. Our results indicate that the presence of a methoxy group in the benzylic ring significantly increases the contribution of the C–S bond cleavage channel. This is accordingly the only process observed for **2** in $AcOH/ClO_4^-$ and CH_3CN/ClO_4^- and the main process in $AcOH/NO_3^-$. Only in $AcOH/AcO^-$ is no C–S bond rupture observed, but exclusive deprotonation.

Preliminary PES experiments[17] suggest that in $\mathbf{2}^{\bullet+}$ most of the positive charge resides in the benzylic ring. Thus, for this radical cation, deprotonation and C–S bond cleavage are expected to be the major pathways under all experimental conditions. Of course, deprotonation predominates in $AcOH/AcO^-$ (effect of the strong base), whereas C–S bond cleavage is the major or the exclusive process under the other conditions.

With the 4-methoxy group in the sulfur bearing ring, the deprotonation path becomes almost negligible *under all the reaction conditions* (even in $AcOH/AcO^-$). Probably, in $\mathbf{4}^{\bullet+}$ the contribution of the π system to the π-n_s SOMO is higher than in the other substrates, due to the presence of the methoxy group. Positive charge density at sulfur should decrease with consequent decrease of the C_α–H bond acidity. Sulfoxide formation is the main reaction for the radical cation $\mathbf{4}^{\bullet+}$ in $AcOH/AcO^-$ and $AcOH/ClO_4^-$, whereas C–S bond cleavage is the preferred pathway in CH_3CN/ClO_4^-.

In $AcOH/AcO^-$ and $AcOH/NO_3^-$, the presence of an electron-withdrawing (EW) group, such as NO_2, in the benzylic ring favors the deprotonation reaction, which, accordingly, is more important with $\mathbf{3}^{\bullet+}$ than with $\mathbf{1}^{\bullet+}$, especially when the base is NO_3^-. This finding may be attributed to an acidifying effect of the 4-NO_2 group on the benzylic protons.

For $\mathbf{3}^{\bullet+}$ in CH_3CN/ClO_4^-, formation of sulfoxide prevails over C–S bond cleavage, whereas the reverse occurs with the other radical cations. This might be due to the fact that the 4-nitrobenzyl carbocation should be a very poor leaving group. Surprisingly, however, this explanation does not apply to $AcOH/ClO_4^-$ where the relative contribution of pathways b and c is nearly the same for $\mathbf{1}^{\bullet+}$, $\mathbf{3}^{\bullet+}$, and $\mathbf{5}^{\bullet+}$. On the other hand, the nature of the cleavage process (unimolecular or bimolecular) might be somewhat different in the two reaction media so as to lead to a different response to structural changes.

Interestingly, in $AcOH/NO_3^-$, when an EW group (3-Cl) is in the sulfur-bearing ring, deprotonation of the radical

---

[14] Reichenbach, G.; Santini, S.; Aloisi, G. G. *J. Chem. Soc., Faraday Trans. 1*, **1977**, 95.

[15] Fukuzumi, S.; Kochi, J. K. *J. Am. Chem. Soc.* **1981**, *103*, 7240.

[16] Glass, R. S.; Broeker, J. L.; Yatcko, M. E. *Tetrahedron* **1989**, *45*, 1263.

[17] Baciocchi, E.; Cauletti, C.; Rol, C.; Sebastiani, G. V.; Stranges, M. To be published.

[18] Asmus, K. D. *Acc. Chem. Res.* **1979**, *12*, 436.

cation is favored with respect to the case of the unsubstituted substrate.

No significant effect of the 3-Cl group is, however, noted in $AcOH/ClO_4^-$ and CH_3CN/ClO_4^- as the relative proportions of sulfoxide and C–S bond cleavage products are nearly the same for $1^{\cdot +}$ and $5^{\cdot +}$ in both reaction media.

Conclusions

Summing up, even though this study cannot provide us with unequivocal information on the effect of structural changes on each of the reaction channels available to the radical cation, some reasonable conclusion seems possible, which can also be useful when carrying out anodic oxidation for synthetic purposes.

First, it is sufficiently clear that C_α–H deprotonation of benzyl phenyl sulfides is strongly favored by the use of $AcOH/AcO^-$ as the reaction medium and by the presence of EW groups in the benzylic ring. The same reaction is depressed by the presence of ER substituents in the sulfur bearing ring.

Second, there is also evidence that CH_3CN/ClO_4^- is the most suitable medium when C–S bond cleavage is desired. The relative contribution of this process is enhanced by the presence of electron donating substituents in the benzylic ring, which can increase the stability of the benzyl carbocation fragment. Electron-withdrawing substituents appear to have the opposite effect.

Third, $AcOH/NO_3^-$ and, to a lesser extent, $AcOH/ClO_4^-$ favor the formation of sulfoxides. Formation of sulfoxides appears also favored by the presence of the 4-methoxy group in the sulfur-bearing ring.

Experimental Section

^1H NMR spectra were obtained from a Bruker WP 80 CW (at 80 MHZ) spectrometer, for solutions in $CDCl_3$. GCMS analyses were performed on a Hewlett-Packard gas chromatograph 5890A (SP85 capillary column, 30 m, at 45–300 °C) connected to a mass selective detector 5970 (at 70 eV). MS spectra were obtained on a Varian MAT 311A spectrometer. Elemental analyses were performed on a Carlo Erba Elemental Analyzer M1106. All melting points are uncorrected.

Starting Materials. Aryl arylmethyl sulfides were obtained from the reaction of the corresponding arylmethyl bromide or chloride with the phenyl-substituted thiol as previously described.[8,19] All compounds were solids, recrystallized to constant melting point (identical with literature data), and characterized by ^1H NMR and MS.

Anodic Oxidations. The electrochemical experiments were performed in a jacketed microcell with Pt as anode (4-cm² effective electrode area) and cathode. The magnetically stirred solutions were electrolyzed (1.1–1.4 V vs SCE, constant potential, and 5–20 mA/cm²), under nitrogen, by using an AMEL 552 potentiostat until 1 F mol^{-1} of charge was passed. To avoid drastic current decrease during electrolysis the principal circuit was opened periodically (ca. every 10 s). The sulfide (1.25 mmol) was dissolved in 30 mL of one of the following solutions: AcOH/AcONa (1 M), $AcOH/LiNO_3$ (0.1 M), $AcOH/LiClO_4$ (0.5 M), and $CH_3CN/LiClO_4$ (0.5 M). The reaction mixture was poured into cold saturated water and extracted with chloroform containing the internal standard (1,4-dimethoxybenzene or 4-nitrotoluene in the case of methoxy-substituted compounds). The combined organic extracts were washed with sodium bicarbonate and water, dried, and concentrated. The residue was analyzed by GCMS and ^1H NMR and chromatographed on silica gel eluting with light petroleum–diethyl ether (4:1), diethyl ether, and chloroform.

Reaction Products. All products formed in the anodic oxidation of compounds **1**–**5** are reported in Table I. These compounds have been isolated and their structures demonstrated on the basis of the spectral properties and/or by comparison with authentic specimens and literature data. The details are as follows: benzyl phenyl sulfoxide, benzyl acetate, benzaldehyde, benzyl chloride, *N*-benzyl acetamide, 4-methoxybenzaldehyde, 4-methoxybenzyl nitrate, 4-methoxybenzyl alcohol, 4-methoxybenzyl acetate, 4-methoxybenzyl chloride, *N*-(4-methoxybenzyl) acetamide, bis(4-methoxybenzyl) ether, 4-nitrobenzaldehyde, 4-nitrobenzyl acetate, and 4-nitrobenzyl chloride were commercial products or available from previous works;[20] α,α-diacetoxytoluene, mp 44–5 °C (lit.[21] mp 46 °C); α,α-diacetoxy-4-methoxytoluene, mp 62–3 °C (lit.[22] mp 64–5 °C); 4-nitrobenzyl phenyl sulfoxide, mp 164–5 °C (lit.[23] 163–4 °C); benzyl 4-methoxyphenyl sulfoxide [mp 128–9 °C; NMR δ 7.4–6.9 (m, 9 H, ArH), 4.3–3.9 (m, AB system, 2 H, CH_2), 3.87 (s, 3 H, OCH_3); MS *m/z* (rel intensity) 246 M^+, 198, 155, 91, 77, 65. Anal. Calcd for $C_{14}H_{14}O_2S$: C, 68.25; H, 5.74. Found: C, 68.36; H, 5.71]; benzyl 3-chlorophenyl sulfoxide [mp 106–7 °C; NMR δ 7.5–6.9 (m, 9 H, ArH), 4.2–3.9 (m, AB system, 2 H, CH_2); MS *m/z* (rel intensity) 252 $M^+ + 2$, 250 M^+, 236, 234, 159, 91 (100), 65. Anal. Calcd for $C_{13}H_{11}ClOS$: C, 62.26; H, 4.43. Found: C, 62.01; H, 4.40]; 4-methoxybenzyl phenyl sulfoxide [mp 129–130 °C; NMR δ 7.5–6.7 (m, 9 H, ArH), 4.2–3.8 (m, AB system, 2 H, CH_2), 3.79 (s, 3 H, OCH_3); MS (35 eV) *m/z* (rel intensity) 230 $M^+ - 16$, 121 (100), 109, 91, 78, 77, 65. Anal. Calcd for $C_{14}H_{14}O_2S$: C, 68.25; H, 5.74. Found: C, 68.40; H, 5.72]; α-acetoxybenzyl phenyl sulfide [NMR δ 7.7–7.2 (m, 10 H, ArH), 7.14 (s, 1 H, CH), 2.05 (s, 3 H, CH_3); MS *m/z* (rel intensity) 258 M^+, 149, 110, 107, 43 (100)], α-acetoxy-4-nitrobenzyl phenyl sulfide [NMR δ 8.05 (d, 2 H, ArH), 7.6–7.2 (m, 7 H, ArH), 7.14 (s, 1 H, CH), 2.14 (s, 3 H, CH_3); MS *m/z* (rel intensity) 303 M^+, 152, 110, 43 (100)], and α-acetoxybenzyl 3-chlorophenyl sulfide [NMR δ 7.7–7.2 (m, 9 H, ArH), 7.14 (s, 1 H, CH), 2.08 (s, 3 H, CH_3); MS *m/z* (rel intensity) 294 $M^+ + 2$, 292 M^+, 233, 149, 107, 43 (100)] were always recovered in a mixture with the corresponding benzaldehydes, formed by their partial decomposition during column chromatography; such a decomposition was complete in the case of α-acetoxy-4-methoxybenzyl phenyl sulfide, and evidence for the formation of this compound came from GCMS (*m/z* 229 $M^+ - 59$, 179, 137 (100), 135, 109, 77, 43) and NMR analysis (signal at δ 2.04) of the reaction mixture.

Acknowledgment. This work was supported by the Ministero della Universitá e della Ricerca Scientifica e Tecnologica (MURST) and by the Consiglio Nazionale delle Ricerche (Progetto Speciale su "Processi di Trasferimento Monoelettronico").

---

(19) Russel, G. A.; Pecoraro, J. M. *J. Am. Chem. Soc.* **1979**, *101*, 3331.

(20) Baciocchi, E.; Piermattei, A.; Ruzziconi, R. *Synth. Commun.* **1988**, *18*, 2167. Baciocchi, E.; Rol, C.; Sebastiani, G. V.; Serena, B. *Tetrahedron Lett.* **1984**, *25*, 1945. Baciocchi, E.; Bartoli, D.; Rol, C.; Ruzziconi, R.; Sebastiani, G. V. *J. Org. Chem.* **1986**, *51*, 3587.

(21) Fawcett, E. W.; Gibson, R. O. *J. Chem. Soc.* **1934**, 386.

(22) Gregory, M. J. *J. Chem. Soc. B* **1970**, 1201.

(23) Makosza, M.; Golinski, J.; Pankowski, J. *Synthesis* **1983**, 40.