Peculiar Aspects of the Anodic Oxidation of Vinylic Sulfides

GEORGES LE GUILLANTON [a] and JACQUES SIMONET [b]

[a] Laboratoire de Synthèse et Electrochimie organiques, Université Catholique de l'Ouest, B.P. 808, 49005 Angers Cedex, France and [b] Laboratoire d'Electrochimie organique, E.R.A. CNRS No. 896, Université de Rennes 1, Beaulieu, B.P. 25 A, 35042 Rennes Cedex, France

In the anodic oxidation of vinylic sulfides on platinum in acetonitrile, a non-classical sulfonium ion explains satisfactorily the transfer of the thioether group leading to an aldehyde in the presence of water, or its acetal in the presence of methanol. Some other reactions depend on the structure of the substrate, particularly the dimerization into anodically inactive forms likely to decompose during the work-up, to lead in some cases to masked ketenes having the structure of a *gem*-disulfide.

In aqueous solvents, the electrochemical oxidation of the sulfide group generally leads [1] to the sulfoxide and then to the sulfone. However, the use of non-nucleophilic solvents allows for reactions where the sole nucleophile reacting with cationic intermediates may be the sulfide group itself. Then coupling reactions [2] (to give dicationic disulfides) and electrophilic attack [3] (aromatic substitution) may occur and have demonstrated the ability to conduct electrolyses in non-aqueous systems. Recently, the anodic method was used in the deprotection of carbonyl groups (of ketones,[4] aldehydes [4] and sugars [5]) since the electrochemical oxidation of the bond is in some cases highly selective and leads under well-defined conditions to the corresponding carbonyl compounds $R^1R^2C=O$. Examples where anodic deprotection may be considered more efficient than classical chemical methods are available.[4,5] It is worth mentioning that the reaction can be also conducted by indirect means [6] with continuous electrochemical generation of an intermediate possessing adequate oxidizing properties in solution.
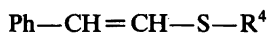
In such a field of investigation the anodic behaviour of vinylic sulfides *1*

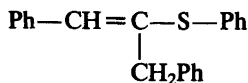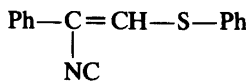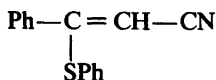$$R^1 \diagdown \atop R^2 \diagup C=C \diagup \atop \diagdown \substack{R^3 \\ S-R^4}$$

1
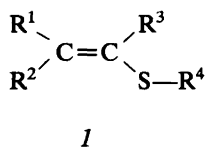
is of high interest and depends obviously on the nature of substituents R. At least four general reactions are expected, namely (i) anodic addition to the double bond, (ii) anodic cleavage of the C–S bond, (iii) classical addition to the sulfur atom and (iv) two-electron oxidation with deprotonation (when R^1 or R^3 are H) with formation of a cation, stabilized by the vicinity of the electron-rich sulfur atom. The aim of the present study is to discuss the different pathways and also to emphasize the possibility of new preparative aspects in the electrochemistry sulfur compounds.

RESULTS

Substrates possessing the general structure *1* have been prepared and oxidized according to the procedures described in the experimental section. The vinylic sulfides studied here are:

$$Ph-CH=CH-S-R^4$$

1a. $R^4=Ph$
1b. $R^4=n\text{-}C_3H_7$
1c. $R^4=n\text{-}C_4H_9$
1d. $R^4=i\text{-}C_4H_9$
1e. $R^4=sec\text{-}C_4H_9$

Ph—CH=C—S—Ph
$\quad\quad\quad$|
$\quad\quad\quad$CH$_2$Ph

1f

Ph—C=CH—S—Ph
$\quad$|
$\quad$NC

1g. Z isomer
1h. E isomer

Ph—C=CH—CN
$\quad$|
$\quad$SPh

1i

(a). *Cyclic voltammetry.* Compounds *1a–1i* exhibit an irreversible two-electron step at a platinum anode in superdry acetonitrile (in the presence of activated alumina). The electrolyte was Bu$_4$NBF$_4$. With compounds *1b, 1c, 1d* and *1e,* another poorly defined two-electron step was also observed at a rather positive potential. The data concerning the first step are reported in Table 1. It has to be emphasized that the peak currents are larger when R^3 is different from H (for example for *1f* and *1i*).

When the electrolysis solution contains a noticeable concentration of nucleophile such as water or methanol, a second step is observed at a potential a little more anodic than the main one with compounds *1a–1f.* Its peak potential and its current are bound to the nucleophile concentration in the bulk (Fig. 1). An increase of the main

Table 1. Cyclic voltammetry of vinylic sulfides *1.* $C=3.10^{-3}$ M l^{-1}; 0.1 V s^{-1}; reference electrode: Ag/Ag$^+$ 0.01 M CH$_3$CN; Bu$_4$NBF$_4$ 0.1 M in acetonitrile in the presence of activated alumina–platinum disk.

Compounds	First peak E_{p_v}	$I_{p_{\mu A}}$
1b	0.87	8.5
1c	0.88	10.8
1d	0.88	11
1e	0.88	12
1a	0.97	14
1f	1.11	26
1g	1.31	10.8
1h	1.38	13
1i	1.60	15.3
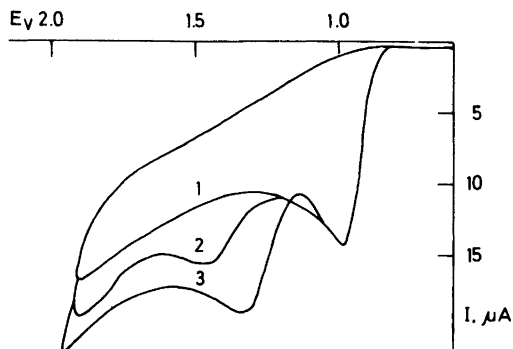
Fig. 1. Cyclic voltammetry of Ph–CH=CH–S–Ph; 3.10^{-3} M l^{-1} in CH$_3$CN–Bu$_4$NBF$_4$ 0.1 M l^{-1}; platinum disk –Ag/Ag+ 0.01 M–0.1 V s^{-1}.
1. In dry acetonitrile (activated alumina1).
2. In acetonitrile plus water (3.10^{-3} M l^{-1}).
3. In acetonitrile plus methanol (3.10^{-3} M l^{-1}).

wave is observed with *1g/h* and *1i* (Fig. 2). Whatever the electrolyte and the nature of the solvent may be, the presence of a base (lutidine in excess or Na$_2$CO$_3$) does not affect at all the current and the potential of the first and main peak.

(b). *Macroscale electrolyses.* Generally the results depend on the nature of the substituents on the ethylenic double bond, According to the nature of R^1, R^2. R^3 and R^4, the main results are listed below.

(1). *Migration of the sulfide group.* Compounds *1a–1e* lead to the aldehydes 5,

Ph—CH—CHO
$\quad\quad$|
$\quad\quad$S
$\quad\quad$|
$\quad\quad$R^4

5
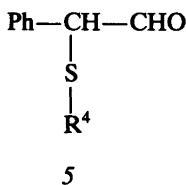
with a yield of the order of 50 %. Most of those aldehydes are not very stable and this fact may partly explain why the selectivity of the reaction is moderate. Such a formation of aldehydes of this series from *1* had been previously reported.[7] An interpretation is given here. Thus, a condition to observe such a reaction is that R^1 is a hydrogen. The other substituents and a basic medium may favor an ECE process (the chemical step here is the fast deprotonation of the radical cation) and allow the formation of a short-life intermediate having the structure of a vinylic cation probably stabilized by the vicinity of the
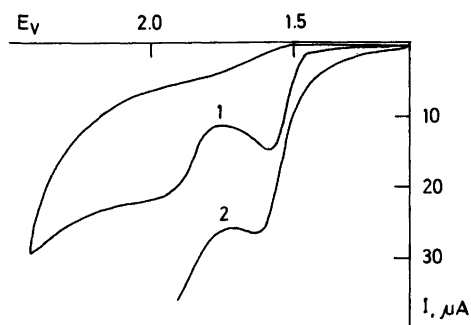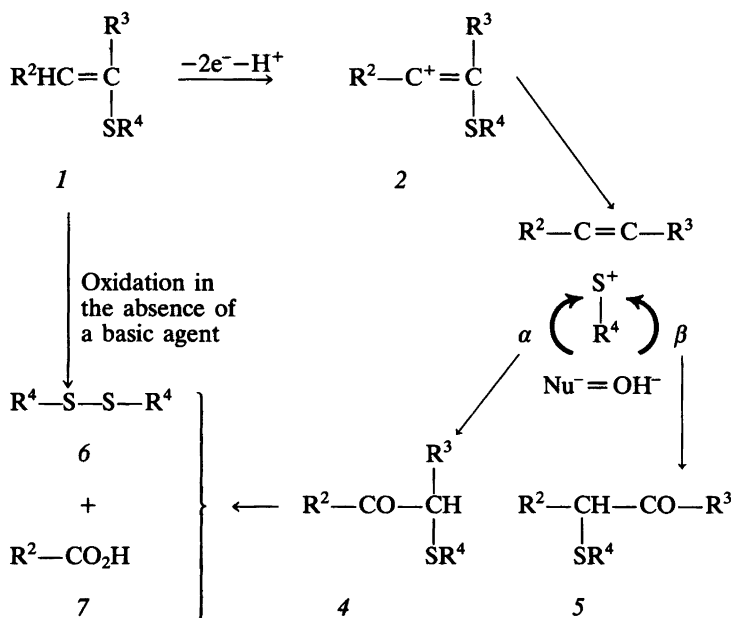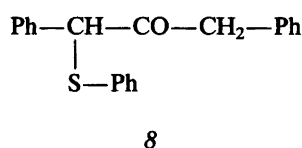
Fig. 2. Cyclic voltammetry of NC–CH=C(Ph)–S–Ph; 3.10^{-3} M l^{-1} in CH_3CN–Bu_4NBF_4 0.1 M l^{-1}; platinum disk –Ag/Ag+ 0.01 M–0.1 V s^{-1}.
1. In dry acetonitrile (activated alumina).
2. In acetonitrile plus methanol (6.10^{-3} M l^{-1}).

sulfur atom. Then a non-classical sulfonium ion [3,8] 3 may be suggested, reacting with nucleophiles according to two chemical routes a and β. (Scheme 1).

Where $R^2=C_6H_5$, benzoic acid 7 was isolated (yield between 10 and 30 %) and this involves an easy oxidation of the keto sulfide 4 at the fixed potential necessary to perform the anodic oxidation of 1. Similar fragmentation is probably

feasible from 5 but we failed in isolating and identifying most of the other oxidation products having obviously rather low molecular weights. However, organic disulfides R^4–S–S–R^4 6 were characterized. They may be obtained either from a final anodic fragmentation of 4 and 5 or from the cleavage of the radical cation of 1 when its deprotonation rate is not large enough. Actually, it was possible to demonstrate that the formation of the disulfide 6 could be *nearly* quantitative in the total absence of a basic agent (such as Na_2CO_3) in the electrolysis solution. As 4 and 5 are obviously candidates for further oxidation (leading to cleavage reactions) their yield appears to be strongly dependent on the water concentration; the higher the stability of the intermediate 3 in the bulk, the lower the occurrence of the fragmentation reactions.

In the same way the ketone 8 is also obtained from the vinylic sulfide 1f

$$Ph—CH—CO—CH_2—Ph$$
$$\quad\;\; |$$
$$\quad\;\; S—Ph$$

$$8$$

Scheme 1.

$$R^2-\underset{\underset{SR^4}{|}}{\underset{|}{CH}}-\underset{\underset{OCH_3}{|}}{CH}-OCH_3 \qquad \underset{\overleftrightarrow{}}{\overset{-CH_3OH}{\overset{(acid)}{}}} \qquad R^2-\underset{\underset{SR^4}{|}}{C}=CH-OCH_3$$

9   10
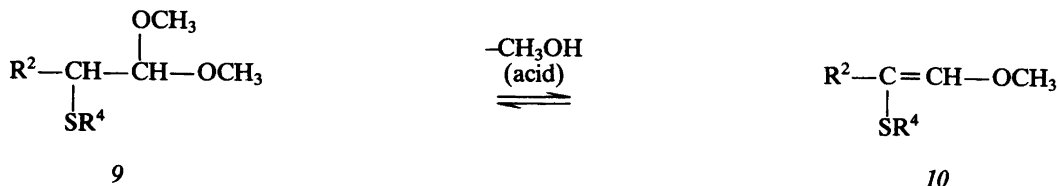
Scheme 2.

(2). Oxidation in the presence of methanol. With sulfides of the type *1a–1e*, the oxidation in the absence of water (when the electrolyses are performed in a glove box) in dry methanol–acetonitrile mixture (30–70 % v/v) leads to the acetal *9* of the aldehyde *5* previously isolated in the course of electrolyses conducted in the presence of moisture. The acetal *9* may be transformed reversibly into the enol ether *10* obviously formed during the attack of the intermediate *3* by the nucleophile MeO⁻. A similar reaction occurs in the presence of butanol.

The yields of *9* are higher than those observed for *5* (this experimental evidence could be due to the protection of the aldehyde) and may reach 70 %. However, small amounts (up to 10 %) of benzoic acid ($R^2=C_6H_5$) are also obtained. Nevertheless, it is worth mentioning that with *1f* under such experimental conditions, the rearranged ketone *8* is the main compound (yield: 25 %) even in the presence of methanol.
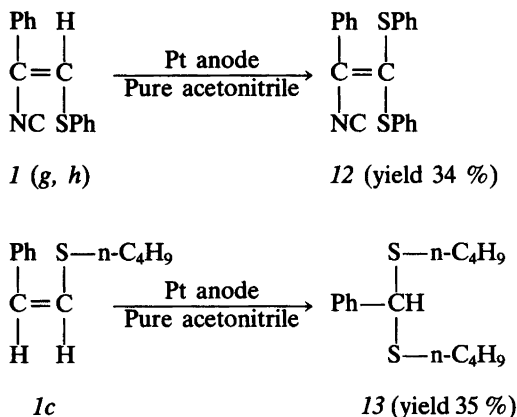
(3). Anodic addition to the ethylenic double bond. When the ethylenic double bond is strongly activated by an electron-withdrawing group such as the cyano substituent, the results of the anodic oxidation are dramatically changed. Then, in the presence of methanol, for example with *1g*, a vicinal dimethoxy thioether possessing the structure *11* appears to be the main electrolysis product

$$Ph-\underset{\underset{CN}{|}}{\overset{\overset{OCH_3}{|}}{C}}-\underset{\underset{S\,Ph}{|}}{\overset{\overset{OCH_3}{|}}{CH}}$$

11
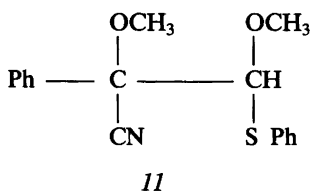
and is isolated with a yield of 43 %. The absence of a potential leaving proton in the β position of the thioether group and the withdrawing effect of the cyano group are responsible for the strong

electrophilic character of the radical cation generated by a first electron transfer; these evidences consequently suggest an ECE process where the chemical reaction is a nucleophilic attack.

(4). Other reactions. The formation of electrophilic groups or atoms in the molecules already possessing the thioether substituent may lead to other kinds of reactions. Thus, after the work-up, some products of the anodic oxidation of the series *1* have the structure of *gem*-disulfides; Scheme 3.

$$\underset{\underset{NC}{|}}{\overset{\overset{Ph}{|}}{C}}=\underset{\underset{SPh}{|}}{\overset{\overset{H}{|}}{C}} \quad \xrightarrow[\text{Pure acetonitrile}]{\text{Pt anode}} \quad \underset{\underset{NC}{|}}{\overset{\overset{Ph}{|}}{C}}=\underset{\underset{SPh}{|}}{\overset{\overset{SPh}{|}}{C}}$$

1 (g, h)   *12* (yield 34 %)

$$\underset{\underset{H}{|}}{\overset{\overset{Ph}{|}}{C}}=\underset{\underset{H}{|}}{\overset{\overset{S-n\text{-}C_4H_9}{|}}{C}} \quad \xrightarrow[\text{Pure acetonitrile}]{\text{Pt anode}} \quad Ph-\underset{\underset{S-n\text{-}C_4H_9}{|}}{\overset{\overset{S-n\text{-}C_4H_9}{|}}{CH}}$$

1c   *13* (yield 35 %)

Scheme 3.

Compound *12* is particularly interesting as it corresponds to the masked structure of a ketene. In the absence of nucleophile and of any possibility of fast deprotonation, oxidized forms of *1g* and *1h* may lead to dimers possessing a structure of disulfonium $-S^+-S^+-$ which can react with nucleophiles mainly during the work-up. Such dimeric structures are known and their formation has been demonstrated for both monosulfides [2] and cyclic macrodisulfides.[9] Thus, the *gem*-disulfide *12* could result from the reaction of such a dimer according to the following process:

$$Ph—C=CH—S^+—Ph$$
$$\underset{CN}{|}$$

2 (*1g* or *1h*) $\xrightarrow[\text{dimerisation}]{-2e^-}$ $$Ph—C=CH—S^+—Ph$$ $\xrightarrow{-H^+}$
$$\underset{CN}{|}$$

$$Ph—C=C—S—Ph$$
$$\underset{CN}{|} \quad \diagdown$$
$$S^+—Ph$$ $\xrightarrow{Nu^-}$ $\left\{ \begin{array}{c} \\ \\ \end{array} \right.$ $$Ph—C=C$$
$$Ph—C=CH \diagup$$
$$\underset{CN}{|}$$

$$\begin{array}{c} SPh \\ | \\ Ph—C=C \\ | \quad | \\ CN \ SPh \\ \textit{12} \end{array}$$
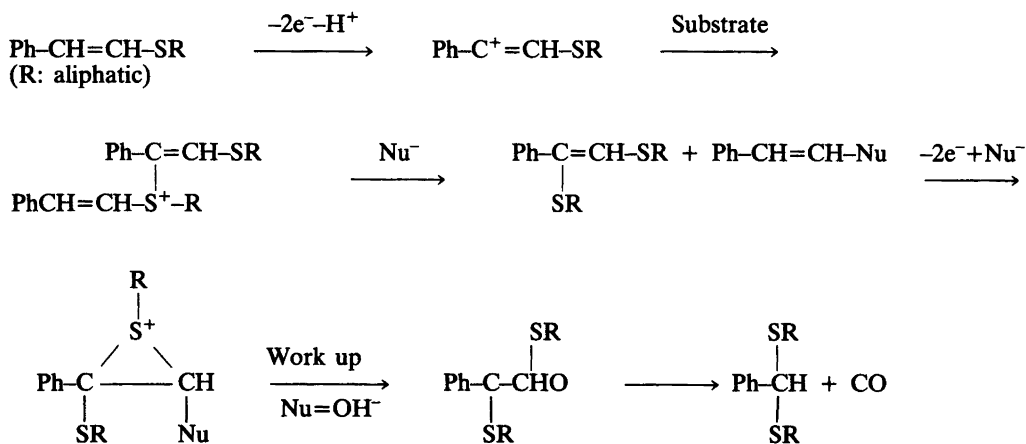
+

$$Ph—C=CH—Nu$$
$$\underset{CN}{|}$$
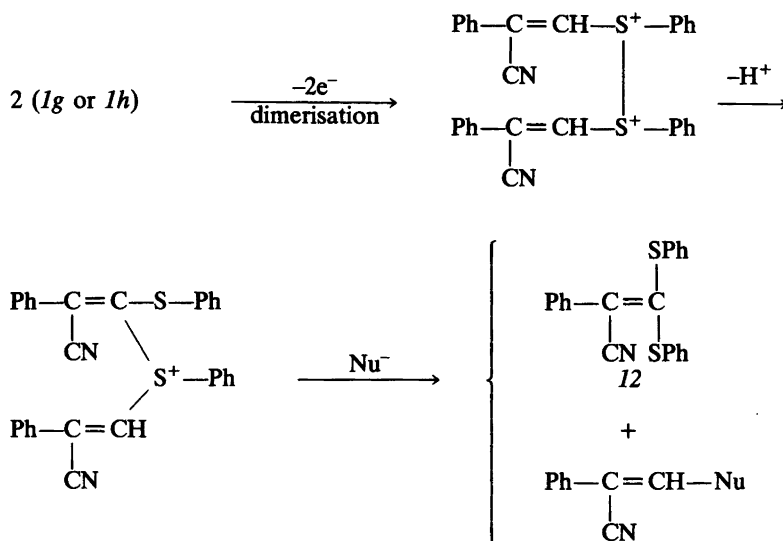
Scheme 4.

However, the formation of *13* observed only in pure acetonitrile which could also proceed through a sulfonium dimer is more problematic to explain. Nevertheless, an oxidation mechanism may be proposed taking into account the nucleophilic effect of the non-oxidized thiogroup (under such conditions, the formation of the sulfonium cation would not be intramolecular as mentioned previously for *1a*) and the occurrence of an easy decarbonylation [10] during the work-up.

CONCLUSION

The present work describes the different chemical pathways observed in the oxidation of vinylic sulfides. It is obvious that the reactions are dramatically controlled by both the structure of the substrate and the nature of the medium. Most of the possible anodic reactions observed in general for the different classes of thioethers are seen for only one series of unsaturated sulfides.

Under conditions where the deprotonation of

$$Ph–CH=CH–SR \xrightarrow{-2e^-–H^+} Ph–C^+=CH–SR \xrightarrow{Substrate}$$
(R: aliphatic)

$$Ph–C=CH–SR$$
$$\underset{PhCH=CH–S^+–R}{|} \xrightarrow{Nu^-} \quad Ph–C=CH–SR + Ph–CH=CH–Nu \xrightarrow{-2e^-+Nu^-}$$
$$\underset{SR}{|}$$

$$\begin{array}{c} R \\ | \\ S^+ \\ \diagup \diagdown \\ Ph–C————CH \\ | \qquad | \\ SR \quad\ Nu \end{array} \xrightarrow[\text{Nu=OH}^-]{\text{Work up}} \begin{array}{c} SR \\ | \\ Ph–C–CHO \\ | \\ SR \end{array} \xrightarrow{\qquad} \begin{array}{c} SR \\ | \\ Ph–CH + CO \\ | \\ SR \end{array}$$

13

Scheme 5.

Table 2. Main products from macroscale electrolyses.

Sub-strate	In presence of water						In presence of methanol					
	E(V)	Prod-uct	Yield %	IR ν_{CO}	NMR ppm	MS	E(V)	Prod-uct	Yield %	IR ν_{C-O-C}	NMR ppm	MS
1a	1.0	5	35	1715	4.75 (CH) / 9.5 (CHO)	228	1.0	9ᵃ	65	1070–1115	3.30 and 3.45 (OCH$_3$) / 4.35–4.7 (CH–CH)	274
1b	0.9	5	62	1700	9.1 (CHO)		0.9	9	70	1090–1120	3.25–3.45 (OCH$_3$) / 4.0–4.8 (CH–CH)	
1c	0.9	5 / 13	26 / 35	1705	9.1 (CHO)	268	0.9	9	60	1070–1115	3.25–3.45 (OCH$_3$) / 4.06–4.63 (CH–CH)	
1d	0.9	5	57	1710	9.1 (CHO) / 2.45 (CH)		0.9	9	65	1080–1115	3.34–3.45 (OCH$_3$) / 4.06–4.65 (CH–CH)	
1e	0.9	5	48	1715	9.4 (CHO)		0.9	9	45	1070–1120	3.24–3.48 (OCH$_3$) / 4.06–4.63 (CH–CH)	
1b	1.10	8	30	1710	3.3 (CH$_2$) / 4.68 (CH)		1.0	8	25	ν_{CO}=1710		
1g/1h	1.25	12	34	ν_{CN} 2210	only aromatic protons	345	1.25	11	43	1080–1110 / ν_{CN} 2250	3.32–3.55 (OCH$_3$) / 4.4 (CH)	318

ᵃ In presence of butanol the acetal Ph–CH(S–Ph)–CH(O–n–C$_4$H$_9$)$_2$ is obtained (50 %).

the radical cation is fast, the occurrence of a non-classical sulfonioum ion may explain satisfactorily the moving of the thioether group. Such a concept was already given [8] in some nucleophilic displacement reactions concerning some classes of vinylic thioethers for which R^1 was the leaving group. The present results underline the potential of H^+ as a leaving group in anodic oxidations on organic sulfide substrates, and the similarity with SN reactions in organic chemistry where the existence of other types of leaving groups are necessary.

On the other hand, when deprotonation reactions are inhibited, anodic additions and cationic adducts formations may occur. Thus, the ability of the thioether group to behave as the main nucleophile allows probably the observation of new reactions. They are explained by the transient formation of unusual dimeric forms (anodically inactive) likely to decompose during the work-up into masked ketenes possessing the structure of *gem*-disulfides (obtained in a good yield if we consider that two molecules of substrate are necessary to build up one of protected ketene).

EXPERIMENTAL

^{1}H NMR spectra were recorded on a Perkin-Elmer-HITACHI R 24 A Spectrometer. IR spectra were taken with a PERKIN-ELMER 257 Spectrophotometer. Mass spectra were obtained on a MAT 311 VARIAN (Rennes). Elemental analysis were performed by Rhône-Poulenc and were in agreement with calculated values.

Substrates. Vinyl sulfides Ph–CH=CH–S–R (*1a–1e*) were prepared as follows: 5.10^{-2} M of appropriately dried sodium thiolate was dissolved in 30 ml of 1-methyl-2-pyrrolidone; then 5.10^{-2} M of β-bromostyrene was added and the mixture was heated for 2 h at 135 °C. The residue was diluted with 100 ml of ether and washed with water (3×100 ml). Yield=95 %. The substrates were sufficiently pure to be used for electrolysis. The separation of Z/E isomers was possible by chromatography on a silica gel column (Merck type 60) (elution with cyclohexane–ethyl acetate 98:2).

We used an already described procedure for the preparation of *1f*,[11] *1g*, *1h* and *1i*.[12]

Electrochemical experiments. Cyclic voltammetry experiments were performed with the use of a SOLEA-TACUSSEL potentiostat, equipped with a TP-PRT Plug-in and a SEFRAM TGM 100 XY recorder. Working electrode: Solea-Tacussel. Platinum disk electrode Pt 30, diameter of active platinum surface: 1 mm. Reference electrode: Ag/Ag^+ 0.01 M in CH_3CN.

Acetonitrile was purified as already described.[13] An H-cell was used for macroelectrolyses with a platinum anode (area: 16 cm^2), and a steel rod cathode. Substrate concentration: 0.1 M l^{-1}; supporting electrolyte: $LiClO_4$ or $NaClO$ 0.2 M l^{-1}.

After electrolysis the resulting solution was evaporated, diluted with 100 ml water and extracted with 100 ml ether. The organic layer was washed with 100 ml water three times and dried over anhydrous magnesium sulfate. After evaporation, the residue was chromatographed on a silica gel (Merck type 60) column. Results of electrolysis are collected in Table 2.

By-products, such as benzoic acid and diphenyldisulfide, were characterized from oxidation of β-thiophenylstyrene, *1a*, but the yields were lower in the presence of a basic agent (Na_2CO_3 or lutidine).

Experiments in methanol–acetonitrile mixture 4:6 were conducted in a glove box to avoid any trace of water.

The oxidation of phenyl-3-thiophenyl-3-propenonitrile *1i* is impossible owing to strong inhibition phenomena.

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