Rearrangement of *trans*-stilbene into diphenylacetaldehyde acetals induced by direct anodic oxidation

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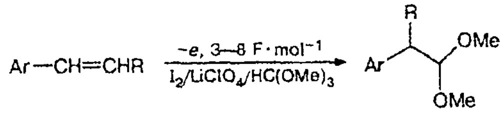
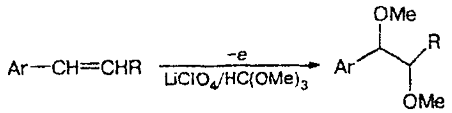
Direct anodic oxidation of *trans*-stilbene in lower alcohols and in some other solvents in the presence of KF or Bu_4NBF_4 is accompanied by its electrooxidatve rearrangement into diphenylacetaldehyde acetals; a competing reaction yields 1,2-dialkoxy-1,2-diphenylethanes.

Key words: *trans*-stilbene, electrooxidation, rearrangement.

Previously, the electrooxidative rearrangement of unsubstituted styrene and of β-methyl-, β-methoxymethyl-, 4-methyl-, 4-chloro-, and 4-methoxycarbonyl-substituted styrenes into arylacetaldehyde dimethyl acetals, induced by indirect electrooxidation of these substrates in trimethyl orthoformate in the presence of 0.25 or more equivalents of iodine, has been reported.[1]

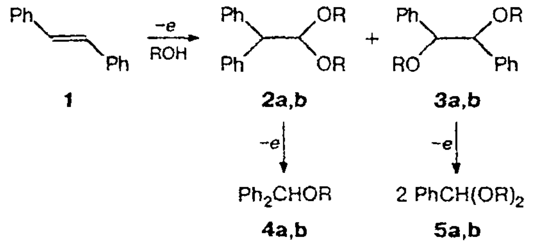


Under the same conditions but in the absence of iodine, the electrooxidative rearrangement of styrenes does not occur: in this case, they are converted into α,β-dimethoxyalkylarenes, which are typical products of direct electrooxidation of arylalkenes in methanol.[2—4]



We found that in the case of *trans*-stilbene (**1**), an electrooxidative rearrangement, similar to that observed for styrenes, can occur without iodine during anodic oxidation in lower alcohols, in their mixtures with acetonitrile, and in alkyl acetates containing the corresponding trialkyl orthoformate in the presence of potassium fluoride or tetrabutylammonium tetrafluoroborate as a supporting electrolyte. The process requires 2 F of electricity per mole of the substrate. As a result of this electrooxidative rearrangement and competing α,β-dialkoxylation,[5,6] compound **1** is converted into diphenylacetaldehyde acetals (**2a,b**) and 1,2-dialkoxy-1,2-diphenylethanes (**3a,b**). In addition, the process yields[7] minor amounts of alkyl diphenylmethyl ethers (**4a,b**) and benzaldehyde dialkyl acetals (**5a,b**) resulting from the electrochemical cleavage of the benzylic C—C bonds in compounds **2a,b** and **3a,b** (Scheme 1).

Scheme 1



R = Me (**a**), Et (**b**)

The ratio between acetal **2** and diether **3** formed in this reaction and the selectivity of transformation of **1** into these products depend mostly on the supporting electrolyte and the solvent; in addition they depend markedly on the temperature (Table 1). When the electrooxidation of **1** is carried out in the presence of KF or Bu_4NBF_4 in MeOH at 60 °C using a platinum or graphite anode, products **2a** and **3a** are formed in a nearly 1 : 1 ratio, and their overall yield is 81—91% for an 87—88% degree of conversion of **1** (entries *2* and *3*). When the electrolysis is conducted in a mixture of methyl acetate and trimethyl orthoformate (1 : 1) or in a mixture of acetonitrile and methanol (20 : 1), all other conditions being the same, the ratio of **2a** to **3a** increases to 3.5 : 1 or 10 : 1, respectively. This is accompanied by a sharp decrease in the selectivity of transformation of **1** into **2a** and **3a** (to 11—18%) and in a decrease in the degree of conversion of **1** (to 35—45%, entries *4* and *5*). When the temperature of the electrolysis of **1** in EtOH increases from 20 to 80 °C, the degree of conversion of **1** substantially increases (from 42 to

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Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 12, pp. 2202—2205, December, 1997.

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Table 1. Direct anodic oxidation of *trans*-stilbene (**1**)[a]

Entry	Solvent	Electrolyte	T/°C	Anode	Degree of conversion (%)	Yield (%)				
						2	3	4	5	2/3
1[b]	MeOH	MeONa	60	Pt	98	0	64	—	—	0
2	MeOH	KF	60	C	87	46	45	<1	4	~1
3	MeOH	Bu_4NBF_4	60	C	88	41	40	<1	5	~1
4	$HC(OMe)_3$—AcOMe (1 : 1)	Bu_4NBF_4	60	C	35	14	4	—	—	3.5
5	MeCN—MeOH (20 : 1)	Bu_4NBF_4	60	C	45	10	1	—	—	10
6	EtOH	Bu_4NBF_4	20	C	42	31	24	24	19	1.3
7	EtOH	Bu_4NBF_4	80	C	92	52	21	20	4	2.5
8	$CO(OEt)_2$—EtOH (9 : 1)	Bu_4NBF_4	80	C	90	32	8	2	—	4.0

[a] 2 mmol of stilbene and 2 mmol of an electrolyte in 20 mL of a solvent were taken; 2 F mol^{-1} of electricity was passed; the current density was 100 mA cm^{-2}.

[b] See Ref. 5.

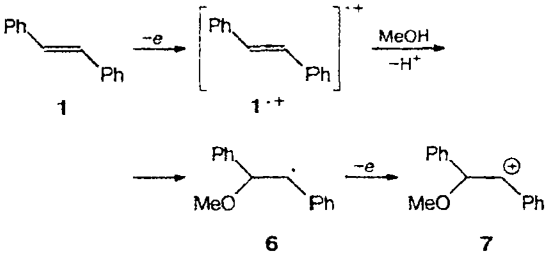
92%), and so does the ratio between the rearrangement and dialkoxylation products, *viz*., diphenylacetaldehyde diethylacetal (**2b**) and 1,2-diethoxy-1,2-diphenylethane (**3b**) (from 1.3 to 2.5). In these experiments, compounds **2b** and **3b** were obtained in an overall yield of 55—73% (entries *6* and *7*). In addition, appreciable amounts of products resulting from the electrochemical cleavage of the benzylic C—C bonds in compounds **2b** and **3b** are formed, namely, diphenylmethyl ethyl ether (**4b**) and benzaldehyde diethyl acetal (**5b**), mostly **4b** (at 80 °C). The (**2b** + **4b**) : (**3b** + **5b**) ratio increases to 2.8. A higher **2b** : **3b** ratio (4.0) was obtained when the electrolysis was carried out in a mixture of diethyl carbonate and EtOH (9 : 1); however, in this case the overall selectivity of conversion of **1** into **2b** and **3b** is moderate (entry *8*).

This effect of EtOH as the medium on the rearrangement proved to be the opposite to that expected from the chemical viewpoint: EtOH is a more active external nucleophile than MeOH; hence, it should oppose more effectively the rearrangement in a solution. Therefore, the observed effect is determined most probably by electrolytic processes, in particular, by the cathodic reduction of alcohols accompanied by electrogeneration of alkoxide anions. The latter are formed more readily from MeOH than from EtOH, because the reduction potential of MeOH is lower. Consequently, methanolic solutions contain larger quantities of alkoxide anions than ethanolic solutions; these anions are much stronger external nucleophiles and, therefore, they inhibit the rearrangement more efficiently.

The electrooxidative rearrangement of **1** into acetals **2**, like the related rearrangements of styrenes into arylacetaldehyde acetals[1] and of alkyl aryl ketones into methyl α-arylalkanoates,[8] is an electrochemical process based on the oxidative isomerization of the carbon skeleton of the initial substrate accompanied by the 1,2-migration of the aryl group. This is a particular example of the 1,2-shift of a substituent, which is a key step in many molecular rearrangements including those with a migration of aryl groups. The shift of an aromatic substituent in these rearrangements occurs *via* the intermediate formation of β-phenyl-substituted cationoid species and of arenonium ions and the fragmentation of the latter.[9]

Evidently, the electrooxidative rearrangement of stilbene **1** occurs by a similar mechanism. The corresponding cationoid intermediates are generated upon direct anodic oxidation of **1**; in the case of electrolysis in MeOH, this oxidation yields successively radical cation **1**$^{\cdot+}$, 1,2-diphenyl-2-methoxyethyl radical **6**, and then cation **7** (Scheme 2).

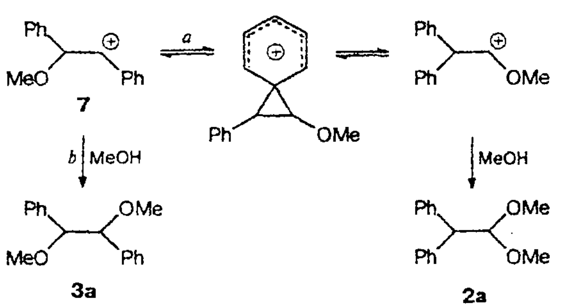
Scheme 2



The subsequent transformations of the electrically generated cation **7**, like those of its analogs obtained by traditional chemical methods (solvolysis, deamination, *etc*.), are determined by the competition between external (the solvent and counterions in the electrolytes) and internal (β-phenyl) nucleophiles for the positively charged carbon atom in this intermediate (Scheme 3, pathways *a* and *b*).

Higher reactivity of the external nucleophiles compared to that of the internal nucleophile is favorable for the formation of 1,2-dimethoxy-1,2-diphenylethane (**3a**) (pathway *b*), while the formation of the rearrangement product, diphenylacetaldehyde dimethyl acetal (**2a**) (pathway *a*), is suppressed, and *vise versa*. The former situation is realized when stilbene **1** undergoes electrooxidation in MeOH in the presence of sodium methoxide as the supporting electrolyte; in this case, the reaction

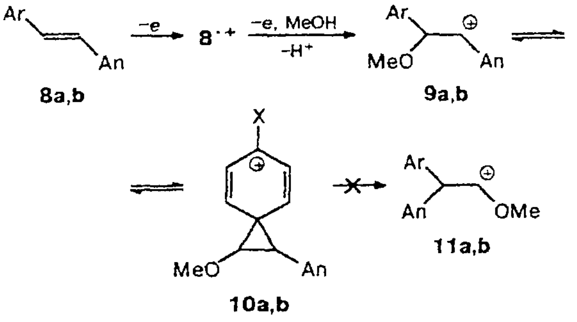
Scheme 3



follows[5] only pathway *b*. According to our results, the latter situation occurs when electrolysis of **1** is carried out in a medium less nucleophilic than MeOH, or in EtOH at an elevated temperature.

It is noteworthy that the direct anodic oxidation of 4-methoxy- (**8a**) and 4,4′-dimethoxystilbene (**8b**) in alcohols in the presence of KF or Bu_4NBF_4 does not induce their rearrangement into dialkyl acetals of anisylphenyl- and dianisylacetaldehydes, but, instead, leads to a complex mixture of products. This difference between the electrochemical behaviors of methoxy-substituted stilbenes **8** and compound **1** is apparently due to the fact that 1-anisyl-2-phenyl- and 1,2-dianisyl-2-methoxyethyl cations **9** (resulting from methanolysis and subsequent electrooxidation of the radical cations derived from stilbenes **8**) are unable to undergo rearrangement to give 2-anisyl-2-phenyl- (**11a**) and 2,2-dianisyl-1-methoxyethyl cations (**11b**) *via* arenonium ions **10** under the conditions used (Scheme 4).

Scheme 4



a: Ar = Ph, X = H
b: Ar = An, X = MeO

In our opinion, this is due to the fact that cations **9** are thermodynamically more stable than ions **10** and **11**.

Experimental

^{1}H and ^{13}C NMR spectra were recorded on Bruker WM-250 and Bruker AM-300 spectrometers in $CDCl_3$ using tetramethylsilane as the internal standard. Mass spectra were recorded on a Varian MAT-311A mass spectrometer (EI, 70 eV). GLC analysis was carried out using a Varian 3700 chromatograph (flame ionization detector, 2000×3 mm glass columns, 5% XE-60 on Chromaton N-AW 100/120 as the stationary phase). Column chromatography was carried out using silica gel L 40/100 mm. Commercial *trans*-stilbene (**1**) of the "pure" grade was used. 4-Methoxystilbene (**8a**) was prepared by condensation of $PhCH_2MgCl$ with anisaldehyde followed by dehydration of the resulting alcohol.[10] 4,4′-Dimethoxystilbene (**8b**) was synthesized from $BrCH_2CH(OEt)_2$ and anisole.[11] Methanol was dried by distillation over magnesium methoxide.

Anodic oxidation of stilbenes (general procedure). Electrooxidation was carried out under galvanostatic conditions in the undivided cell described previously;[4] the conditions of the electrolysis are listed in Table 1. Methanol was evaporated from the resulting electrolysate, the residue was extracted with $CHCl_3$ (2×15 mL), and the extract was analyzed by GLC and concentrated. The products were isolated from the residue by chromatography (using a hexane—ethyl acetate (0—2%) mixture as the eluent) (see Table 1).

Diphenylacetaldehyde dimethyl acetal (2a).[12] ^{1}H NMR, δ: 3.46 (s, 6 H); 4.41 (d, 1 H, *J* = 8.7 Hz); 5.17 (d, 1 H, *J* = 8.7 Hz); 7.30—7.52 (m, 10 H). ^{13}C NMR, δ: 54.01, 54.55, 106.45, 126.46, 128.36, 128.71, 141.14. MS, *m/z* (I_{rel} (%)): 242 $[M]^+$ (0.2), 241 (0.2), 211 (30), 167 (51), 165 (53), 121 (85), 75 (100).

Diphenylacetaldehyde diethyl acetal (2b).[13] ^{1}H NMR, δ: 1.13 (t, 6 H); 3.61 (m, 4 H); 4.29 (d, 1 H, *J* = 8.6 Hz); 5.13 (d, 1 H, *J* = 8.6 Hz); 7.10—7.42 (m, 10 H). ^{13}C NMR, δ: 15.12, 55.38, 62.42, 104.80, 126.26, 128.15, 128.94, 141.38.

1,2-Dimethoxy-1,2-diphenylethane (3a),[5,14] **a mixture of *dl*- and *meso*-diastereomers (72 : 28).** MS, *m/z* (I_{rel} (%)): 242 $[M]^+$ (2), 211 (13), 180 (15), 179 (17), 178 (18), 165 (17), 121 (100), 105 (55), 91 (60). ***dl*-3a**: m.p. 93—95 °C. ^{1}H NMR, δ: 3.27 (s, 6 H); 4.31 (s, 2 H); 6.95—7.30 (m, 10 H). ^{13}C NMR, δ: 57.16, 87.72, 127.64, 127.81, 128.08, 138.26. ***meso*-3a**: m.p. 138—139 °C. ^{1}H NMR, δ: 3.18 (s, 6 H); 4.31 (s, 2 H); 7.25 (m, 10 H). ^{13}C NMR, δ: 57.16, 87.01, 127.64, 127.81, 128.08, 138.59.

1,2-Diethoxy-1,2-diphenylethane (3b).[14,15] The stereochemistry was not determined. ^{1}H NMR, δ: 1.24 (t, 6 H); 3.51 (q, 4 H); 4.50 (s, 2 H); 7.10—7.50 (m, 10 H). ^{13}C NMR, δ: 15.18, 64.95, 85.78, 127.26, 127.62, 127.73, 139.50.

Diphenylmethyl methyl ether (4a).[16] ^{1}H NMR, δ: 3.42 (s, 3 H); 5.28 (s, 1 H); 7.25—7.42 (m, 10 H). ^{13}C NMR, δ: 57.12, 85.54, 127.06, 127.59, 128.53, 142.23. MS, *m/z* (I_{rel} (%)): 198 $[M]^+$ (80), 197 (20), 167 (92), 166 (51), 121 (100), 105 (48), 77 (45).

Diphenylmethyl ethyl ether (4b).[17] ^{1}H NMR, δ: 1.36 (t, 3 H); 3.62 (q, 2 H); 5.43 (s, 1 H); 7.20—7.62 (m, 10 H).

Benzaldehyde dimethyl and diethyl acetals (5a,b) were identical to those obtained previously.[4]

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Received May 19, 1997