Acta Chemica Scandinavica B 32 (1978) 313—316

Anodic Cyanation of Stilbenes in Emulsion Systems with the Aid of Phase Transfer Agents

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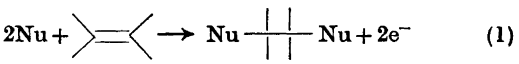
The anodic cyanation of *trans*-stilbene and *trans-p-p'*-dimethoxystilbene has been carried out on platinum electrodes in an emulsion system containing substrate, aqueous sodium cyanide, dichloromethane and tetrabutylammonium sulfate. On cyanation, *trans*-stilbene gave substitution of both olefinic and aromatic protons, addition and cyanodimerisation products, while *trans-p,p'*-dimethoxystilbene gave mainly products resulting from substitution of olefinic protons. Efforts to cyanate 1,1-diphenylethylene gave trace amounts of cyano-substituted products, whereas no cyanation was observed at all with indene as substrate.

Numerous cases of anodic 1,2-addition of acetate,[1–6] methoxide [7–10] or fluoride ion [11,12] (eqn. 1) across a carbon-to-carbon double bond are known,



$$2Nu + \rangle\!=\!\langle \longrightarrow Nu\text{—}\overset{|}{C}\text{—}\overset{|}{C}\text{—}Nu + 2e^- \qquad (1)$$

Nu: OAc^-, OMe^-, F^-

whereas the corresponding reaction with cyanide ion to our knowledge has not yet been realized. This contrasts strongly with the fact that anodic 1,4-addition of cyanide ion across the double bond system of aromatic rings is entirely feasible, as has been shown for 1,2,3,5-tetraphenylpyrrole,[13] 4,4'-dibutoxybiphenyl,[14] and 9,10-dialkylanthracenes.[15]

In our earlier studies [16,17] of anodic cyanation of aromatic substrates we have used two-phase systems with great advantage. One of the favorable factors seems to be the enhanced reactivity of cyanide ion toward radical cations and/or cations in the organic phase used, dichloromethane, compared to the commonly employed solvents (methanol [18–24] and acetonitrile,[15,22,25]). With this in mind, we have performed anodic cyanation of a few moderately activated monoolefins in a two-phase system with dichloromethane as the organic component, and have indeed been able to accomplish 1,2-addition of cyanide ion to *trans*-stilbene.

RESULTS AND DISCUSSION

The two-phase electrolyses were performed as described previously,[14,16,17] using *trans*-stilbene, *trans-p,p'*-dimethoxystilbene, 1,1-diphenylethylene and indene.

trans-*Stilbene*. The products *4* – *8* (see Scheme 1) were formed in the anodic cyanation of *trans*-stilbene. The yields at different current densities are given in Table 1. Besides the given products a substantial amount of tar was formed in the reaction. The yield of the desired addition product (*4*) was slightly better at the lower current density. The yields given for the 50 mmol run were isolated yields, where products *4*, *6* and *8* were isolated with column chromatography while *7* precipitated from an acetone solution of the tarry residue. In order to determine a crude value of the DL/*meso* ratio of *4* (see Table 1) the isolated product had to be recrystallized from ethanol to separate the two forms. Determination of the ratio by GLC was impossible, probably due to isomerisation in the injector chamber. The formation of the products *4* – *8* can be rationalized by the reaction sequence given in Scheme 1. The addition product *4* is formed *via* attack of a cyanide ion

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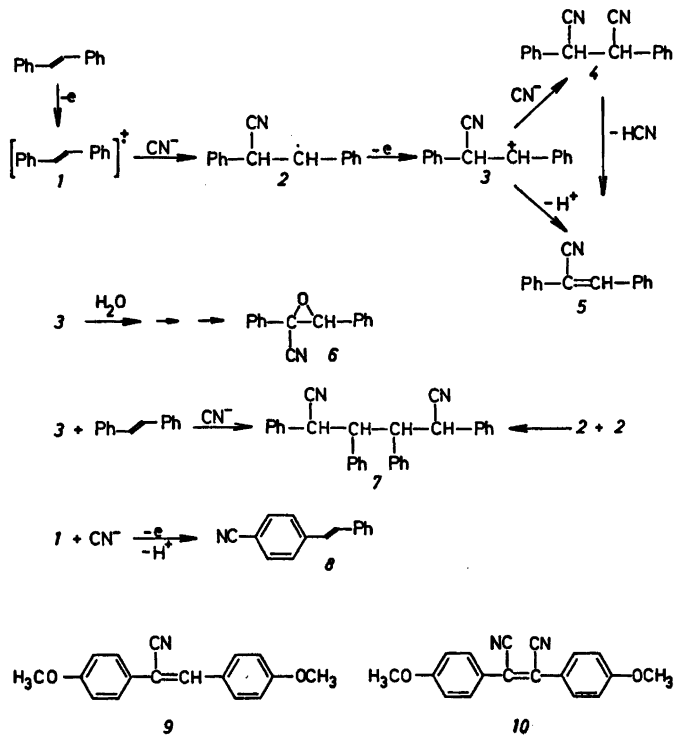
Table 1. Anodic cyanation of stilbenes.

Substrate (amount/mmol)	Current density/ mA cm^{-1}	Charge/F mol^{-1}	Product; Current yields/% [a]						
			4	*5*	*6*	*7*	*8*	*9*	*10*
Stilbene (10)	6.25	1	7	6	9	–	11 [b]		
Stilbene (10)	1.88	1	14	6	5	–	14 [b]		
Stilbene (50)	6.25	2	4 [c,d]	–	1 [c]	1 [c]	1 [c]		
p,p'-Dimethoxy-stilbene (10)	6.25	1						28	4 [b]

[a] Determined by GLC unless otherwise noted. [b] Unidentified products – 10 %. [c] Isolated yield. [d] DL/*meso* ratio 3/2.

on the radical cation *1* to form *2* which is further oxidized to the cation *3* that reacts with a cyanide ion to form *4*. No stereospecificity is evidenced in the formation of *4*. Product *5* can be formed in two ways, either by loss of a proton from the cation *3* or by elimination of hydrogen cyanide from *4*. The elimination reaction was shown to take place in the solvent/supporting electrolyte used in a blank experiment run overnight at room temperature. After work-up GLC analysis showed a *4*/*5* ratio of 47/53. Product *6* can be formed by attack of water on *3* followed by loss of the proton α to the cyano group and further oxidation to the corresponding cation which can cyclise to the epoxide *6*. The dicyanodimer *7* is probably formed by dimerisation of *1* or *2* or by attack of *3* on a substrate molecule to generate a dimeric cation that is trapped by cyanide ion. Product *8* is presumably the result of an attack



Scheme 1.

of cyanide ion on the aromatic nucleus of *1* (in the anodic cyanation of diphenylacetylene, this reaction mode is predominant [26]).

trans-p,p'-*Dimethoxystilbene*. Anodic cyanation of *trans-p,p'*-dimethoxystilbene gives *9* in 28 % current and 29 % material yield, and *10* in 4 % current yield. Apart from these compounds four others were detected by GLC in amounts estimated to be equivalent to about 10 % current yield. A substantial amount of tar was formed. No attempt to isolate these products was made. The reaction mixture contained no trace of the desired addition product, 2,3-bis(4-methoxyphenyl)succinonitrile. These results indicate that the loss of a proton from the intermediate analogous to *3* is much faster than the nucleophilic attack of a cyanide ion.

Attempted cyanation of 1,1-diphenylethylene gave trace amounts only of cyano-substituted product whereas no cyanation was observed at all with indene as substrate.

EXPERIMENTAL

General procedures were as described previously.[14]

Chemicals. Solvents, reagents and supporting electrolytes used in this work were commercially available reagent grade chemicals and were used without further purification.

Reference substances. The following substances were prepared according to literature methods: *4*,[27] *5*,[28] *9*,[29] *10*.[30,31] 2,3-Bis(*p*-methoxyphenyl)-succinonitrile was prepared according to the method used for *4*. M.p. 222–224 °C. Spectra were in accordance with the structure.

Electrolysis procedure. The equipment used has been described previously.[14,16,17] Substrate amounts, current densities and charge passed are given in Table 1. The electrolyte consisted of substrate, dichloromethane (230 ml), 1 M sodium cyanide (230 ml) and neutralized tetrabutylammonium hydrogen sulfate (20 mmol) dissolved in water (15 ml). A given amount of charge was passed at constant current. When the electrolysis was started the stirrer had to be turned on for a few seconds, then turned off and left for 30 s, and then turned on again. This procedure gave an increase in the potential drop over the cell from 4 V to 7–15 V. This behaviour may be due to a wetting phenomenon.

Work-up procedure for trans-*stilbene*. 1. The phases were separated and the organic phase was evaporated to dryness. The residue was taken up in ether and washed with water to remove remaining supporting eletrolyte. An internal standard was added and the yield was determined by GLC.

2. One experiment was carried out on a 50 mmol scale and was worked up according to the following procedure. The organic phase was separated and evaporated to dryness. The residue was boiled in ether which left a tarry mass insoluble. The tar was dissolved in acetone whereupon dimer *5* precipitated. The ether solution was chromatographed on silica with pentane/ether (9/1) as eluent.

The following substances were isolated: *4* in 4 % current yield. The DL and *meso* forms were separated by recrystallization from ethanol [32] yielding a DL/*meso* ratio of 3/2. *6* in 1 % current yield, *7* in 1 % current yield and *8* in 1 % current yield.

Work-up procedure for trans-p,p'-*dimethoxystilbene*. The two phases were separated and the organic phase was extracted three times with water. Internal standard was added and the yield was determined by GLC.

Acknowledgements. Financial support from the Swedish Natural Science Research Council (to L.E.) and the Royal Physiographic Society in Lund (to B.H.) is gratefully acknowledged.

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Received December 28, 1977.