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Direct and Indirect Electrolysis of 1,2-Dihalo-1,2-diphenylethanes

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1,2-Dihalo-1,2-diphenylethanes (*meso* and *d,l*) have been reduced in *N,N*-dimethylformamide at a mercury cathode and indirectly by means of electrolytically generated anion radicals to a mixture of *cis*- and *trans*-stilbene. The ratio of *cis*- to *trans*-stilbene was found to depend on the kind and concentration of the supporting electrolyte; the *cis*/*trans* ratio increases with the size and concentration of the cation. These results were interpreted as being caused by ion-pairing between the cation and an anionic intermediate.

Several investigations [1,2] on the electrolysis of *vic*-dihalides have shown that a reductive elimination of the halogen atoms is the usual reduction route; the stereochemistry of the electrolytic reductive elimination [3] of the *d,l*- and *meso*-1,2-dibromo-1,2-diphenylethanes in *N,N*-dimethylformamide (DMF) has been investigated, and *trans*-stilbene was reported to be the only product obtained.

Sodium naphthalene reacts with *vic*-dihalides to give olefins in high yield.[4] The stereochemistry of the dehalogenation of *erythro*- and *threo*-2,3-dibromo-3-methylpentanes by sodium naphthalene in 1,2-dimethoxyethane (DME) [5] and of 2,3-dihalobutanes [6] under similar conditions has been reported; in the latter investigation [6] CIDNP was used to demonstrate the occurrence of radicals during the reaction.

In this investigation comparison is made between the stereochemical results from direct and indirect electrolytic reduction of *d,l*- and *meso*-1,2-dibromo-1,2-diphenylethane (*d,l*- and *meso-1*) and *d,l*- and *meso*-1,2-dichloro-1,2-diphenylethane (*d,l*- and *meso-2*) in DMF; the mechanism is further illuminated by varying the supporting electrolyte which might influence the degree of ion-pairing during the reaction, if anionic species were intermediates.

RESULTS

Direct electrochemical reduction of *meso-1* in DMF/TBABr gave *trans*-stilbene (*trans-3*) with no detectable (NMR, GLC) *cis*-stilbene (*cis-3*) in the product, in agreement with published results.[3]

Table 1. Relative yield of *cis*- and *trans*-stilbene in the electrochemical reduction of *d,l*-1,2-dibromo-1,2-diphenylethane in DMF containing different supporting electrolytes.

Supporting electrolyte	Concentration/M	*cis-3*/*trans-3*
$(CH_3)_4NBF_4$	0.20	0.47 ± 0.04
$(C_2H_5)_4NBr$	0.10	0.45 ± 0.04
$(C_2H_5)_4NClO_4$	0.11	0.56 ± 0.05
$LiClO_4$	0.10	0.52 ± 0.05
LiBr	0.10	0.56 ± 0.05
$(C_4H_9)_4NBr$	0.10	0.79 ± 0.06
$(C_4H_9)_4NBF_4$	0.1	0.89 ± 0.06
$(C_2H_5)_4NBr$ $(C_4H_9)_4NBr$	0.01 0.10	0.82 ± 0.06
$(C_8H_{17})_4NBr$	0.1	1.27 ± 0.06

Table 2. Relative yield of *cis*- and *trans*-stilbene in the electrochemical reduction of *d,l*-1,2-dibromo-1,2-diphenylethane in DMF containing different concentrations of supporting electrolyte.

Supporting electrolyte	Concentration/M	*cis-3*/*trans-3*
LiBr	0.012	0.18 ± 0.03
LiBr	0.10	0.56 ± 0.05
LiBr	0.58	0.79 ± 0.06
$(C_4H_9)_4NBr$	0.010	0.37 ± 0.04
$(C_4H_9)_4NBr$	0.10	0.79 ± 0.06
$(C_4H_9)_4NBr$	0.30	0.96 ± 0.06

In DMF with different supporting electrolytes *d,l-1* gave a mixture of *cis-* and *trans-3* at variance with previous results;[3] the product distribution depended on the nature and concentration of the supporting electrolyte. In Table 1 is given the relative yields of *cis-* and *trans-3*. No other products than the stilbenes were detected. In Table 2 is shown the influence of the concentration of supporting electrolyte on the relative yields of *cis-* and *trans-3*.

2 differs from *1* in that both the *meso-* and the *d,l*-forms gave only *trans-3* on direct electrolytic reduction.

Indirect reduction of *d,l-1* by electrolytically generated chloranil anion radical gave a stilbene mixture containing 7 % *cis-3*, whereas indirect reduction by means of quinoxaline anion radical of *d,l-2* gave no detectable *cis-3*. The *meso*-forms gave only *trans-3*.

The absence of *cis-3* from the reduction of *d,l-2* could conceivably be due to instability of *cis-3* under the experimental conditions. In order to check this a solution of *cis-3* in DMF was allowed to be in contact for 10 h with a mercury electrode kept at a potential slightly more negative than that used for the reduction of *2*, but less negative than the reduction potential of *3*; no isomerisation of *cis-3* to *trans-3* was observed. This is in accordance with the results published recently [7,8] which show that the *cis/trans* isomerisation of *3* proceeds through the ion-pair of the dianion of *3* in THF and relatively slowly through the anion radicals of the *cis-* and *trans*-forms in HMPT.

DISCUSSION

The *meso*-forms of both *1* and *2* give *trans-3* in direct and indirect electrochemical reductions, as they do in chemical reductions.[9,10]

d,l-2 gives also *trans-3* on direct electrochemical reduction in DMF/TBAI and by using continuously electrogenerated quinoxaline anion radicals as reducing agents. In both cases a rotation around the central carbon-carbon bond must be allowed during the reaction unless a *syn*-elimination is assumed. There seems little reason to assume that *d,l-2* should react by a *syn*-elimination and *meso-2* by an *anti*-elimination.

d,l-1 gives a fair yield (32 – 56 %) of *cis-3* on electrochemical reduction, contrary to results reported previously.[3] The change in product distribution with the kind of supporting electrolyte, although not dramatic, (Table 1) is parallel to the change in effective size of the cation; the larger the cation the higher is the yield of *cis-3*.

The isolation of a fair yield of *cis-3* shows that there is not time enough during the reaction to establish a rotational equilibrium between the precursors leading to the two alkenes. The lower yield of *cis-3* obtained in the indirect electrolytic reduction is consistent with the larger time interval between the delivery of two electrons by one-electron carriers, such as anion radicals, compared to that in the direct reduction at the electrode.

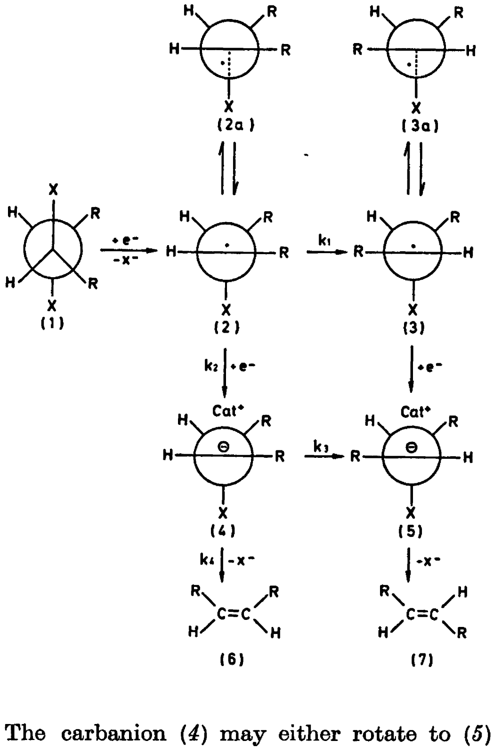
Different cations could influence the reaction by changing the proton availability in the double layer, the adsorption of the substrate to the electrode, the distance of closest approach of the substrate to the electrode, and the ion-pair formation with a carbanionic intermediate.

Protons are not important in the reaction, as no other products than *3* have been isolated. Protonation of any intermediates cannot compete with the elimination.

Adsorption of the substrate to the electrode competes with adsorption of cations. Adsorption of tetraalkylammonium ions to a mercury electrode in DMF at -0.9 V (SCE) is probably not very strong, but stronger for tetraethylammonium (TEA+) than for tetraoctylammonium (TOA+) ions. If adsorption was important, adsorbed *d,l-1* should be reduced to *cis-3*, contrary to what has been suggested.[3] The same *cis/trans* ratio is obtained by reduction of *d,l-1* at -0.9 V and at -1.9 V (SCE); at the latter potential TBA+ would be stronger adsorbed than at -0.9 V.

If differences in the closest approach of the substrate to the electrode were important, the half-wave potential of *d,l-1* would be expected to vary so the reduction would be easiest in the presence of Me_4N^+ (TMA+). This is not the case. Furthermore, reduction in the presence of 0.1 M TBA+ and 0.01 M TMA+ gave (Table 1) a *cis/trans* ratio close to that obtained in the presence of TBA+ alone. It has been shown [11] that even small concentrations of smaller quaternary cations displace larger cations from the electrode surface.

Change in the *cis/trans* ratio through differences in ion-pair formation could occur, if a carbanionic intermediate was formed as shown in the Scheme, and if the ions come close enough to each other to exert some influence on each other. The Scheme is analogous to that suggested for the reduction of 2,3-dichlorobutane by sodium naphthalene.[6] In the Scheme the intermediate (*4*) is depicted as a carbanion, although it might not be a fully developed carbanion.



The carbanion (*4*) may either rotate to (*5*) (k_3) or lose a bromide ion forming *cis*-stilbene (k_4). The Scheme must thus explain that the nature of the cation (Cat+) can influence the ratio k_3/k_4. It should be noted that a rapid inversion of the radical or the carbanion, or whether the radical is planar or not,[12,13] is of no consequence for the stereochemistry of the product; only a rotation around the central bond brings about a change. In the scheme it is assumed that the electron uptake takes place with the halogen atoms *anti*-periplanar, although such a conformation probably is not the most favoured one for the *d,l*-forms;[14] the difference in reduction potential for the *d,l*- and the *meso*-forms (*d,l-1*, −0.35 V, *vs.* SCE; *meso-1*, −0.18 V) may be related to differences in the probability of the *anti* periplanar conformation.

In DMF solvation of a large carbanion, such as a benzylic carbanion, is rather loose, and the same is the case for the large tetraalkylammonium ions; solvent separated ion-pairs are commonly found in DMF. A lithium ion is solvated rather firmly, and the effective radius of a solvated lithium ion lies between that of a tetraethylammonium ion and that of a tetrabutylammonium ion.

The cation in an ion-pair partly neutralizes the charge of the anion (and *vice versa*), and the closer the positive and the negative charge can be approached, the more effectively a neutralization can take place. The more effectively the negative charge of the carbanion is neutralized, the slower would the loss of halide ion be expected to occur.

Electrochemical reduction in the presence of an (effectively) small cation would thus be expected to give a product in which the stereochemical integrity would be lost to a higher degree than in the presence of a large cation, as a result of a diminishing of k_4 in the former case.

The Scheme is thus capable of explaining for *d,l,-1* the dependence of the product distribution on the size of the cation; the dependence on the concentration of supporting electrolyte could be explained by the formation at higher concentrations of electrolyte of larger aggregates (*e.g.* $Li^+\cdots Br^-\cdots Li^+$) which act as large cations.

d,l-2 gives *trans-3* on electrochemical reduction. The experimental evidence does not allow conclusions with respect to the different behaviour of the dibromide and the dichloride, but at least two factors could be suggested. The bridging of the radical (*2a*) could be less important for $X = Cl$ than for $X = Br$ which would result in a faster transformation of (*2*) into (*3*); furthermore, as chloride ion even in DMF usually is a poorer leaving group than bromide ion, k_4 would be lower for $X = Cl$ than for $X = Br$ with a more complete transformation of (*4*) into (*5*) as a result.

If the Scheme is correct, a coupling during an indirect reduction between the anion radical and the radicals (*2*) or (*3*) could be expected. It has recently been shown,[15,16] however, that benzylic radicals are much less apt to couple with anion radicals than are aliphatic radicals. In a reduction of 1,2-dichloroethane with anthracene anion radical, however, a good yield of a mixture of 1,2-di(9,10-dihydroanthranyl-9)-ethane and 2-chloro-1-(9,10-dihydroanthranyl-9)ethane was obtained.[17]

EXPERIMENTAL

The electrochemical cell was an H-cell with two sintered-glass diaphragms separating the catholyte (65 ml) from the anolyte; the area of the mercury cathode was 15 cm^2. The catholyte was kept at ambient temperature by means of a water bath. For potential control a Juul 100 V/3 A potentiostat was used; a Varian A-60 spectrometer was used for the ^{1}H NMR measurements. All potentials are referred to the aqueous saturated calomel electrode (SCE).

Materials. The *d,l-* and *meso* stilbene dibromides (*d,l-1* and *meso-1*) were prepared from *cis-* and *trans-*stilbene, respectively, by bromination according to Buckles *et al.*[18] *d,l-1* was purified on a column of silica with $CHCl_3$ as eluent, m.p. 113 – 114 °C (ethanol); $E_{\frac{1}{2}}$ in DMF/0.1 M TEAP = – 0.35 V (aq. SCE). *meso-1*, m.p. 237 – 239 °C (ethanol); $E_{\frac{1}{2}}$ in DMF/0.1 M TEAP = – 0.18 V (aq. SCE).

The stilbene dichlorides (*2*) were prepared according to Buckles *et al.*[19] *d,l-2*, m.p. 89 – 90 °C light petroleum); $E_{\frac{1}{2}}$ in DMF/0.1 M TEAP = – 1.89 V (aq. SCE); *meso-2*, m.p. 189 – 190 °C (ethanol); $E_{\frac{1}{2}}$ in DMF/0.1 M TEAP = – 1.80 V (aq. SCE).

Reduction of stilbene dihalides. Stilbene dihalide (100 mg) was reduced at – 0.95 V (aq. SCE) for bromides or at – 1.9 V for the chlorides in 65 ml of DMF containing the appropriate supporting electrolyte, $n = 2$ F/mol. When the reduction was completed (3 – 6 h), the catholyte was diluted with 100 ml of water and extracted 3 times with doubly distilled light petroleum (b.p. 50 °C); the organic phase was washed twice with 4 N HCl and twice with water, dried ($CaCl_2$), and evaporated. The residue (yield 70 – 85 %) was analyzed by GLC and by ^{1}H NMR spectrometry using the relative intensities of the signals at δ 6.6 (*cis*-stilbene) and δ 7.1 (*trans*-stilbene) as a measure of the *cis/trans* ratio. All results reported are based on at least two reductions under the specified conditions; the reproducibility was good and the spread not greater than is inherent in the NMR measurements.

Indirect reduction of stilbene dihalides. Chloranil (50 mg) was reduced at – 0.15 V (SCE) in DMF/0.1 M TBAI in the presence of *d,l-1* (100 mg). When the reduction was completed, the reaction mixture was worked up as described above for the direct reduction; the traces of chloranil left did not influence the NMR measurements. For the indirect reduction of *d,l-2*, quinoxaline (68 mg, reduced at – 1.6 V (SCE) in DMF/0.1 M TBAI) was employed as electron transferring agent.

GLC. For the determination of the ratio *cis/3/trans-3* a 2.5 % FFAP-column was used, injection temperature 180 °C, column temperature 140 °C for 8 min, increasing (8 °C/min) to 200 °C.

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