ELECTROCHEMICAL CYCLIZATION. CATHODIC REDUCTION OF SOME BIS-ACTIVATED OLEFINS

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ABSTRACT. — The electrohydrocyclization of three bis-activated olefins, two aliphatic and one disubstituted by phenyl groups, has been studied in acetonitrile by polarography, cyclic voltammetry, coulometry and preparative scale electrolysis as a function of the concentration of water in the medium. Cyclization is shown to play a minor role in the substituted compound and attention is focused on the mechanism of hydrogenation of the double bonds. For the two aliphatic bis-olefins, the experimental results obtained at low water concentration provide evidence for a mechanism involving the cyclization of the initial anion-radical by radical attack on the unreduced double bond. When the water content is raised a radical-radical coupling in the bis-anion-radical appears to compete with the preceding mechanism. These conclusions are discussed in connection with previous findings concerning the mechanism of the electrohydrodimerization of activated olefins.

In the preceding articles of this series 1 - 3 the diagnostic criteria for mechanism determination of fast electrohydrocyclization (EHC) processes were established for linear sweep voltammetry (LSV) and Convolution Potential Sweep Voltammetry. They were applied to the elucidation of the reduction mechanism of 1,3 dibenzoyl-propane \( \Phi - C - (\text{CH}_2)_3 - C - \Phi \) in which it was shown that the five-membered cyclic product is formed almost quantitatively when the acidity of the medium is kept constant by continuous acid addition or when the electrolysis is carried out in the presence of a lithium salt. It was concluded that the cyclization step involves the internal radical-radical coupling of the di-ketyl di-anion rather than a cyclization at the level of the initial ketyl-anion. The di-ketyl di-anion was shown to derive from electron solution transfer (disproportionation) of the initial ketyl-anion.

The EHC of bis-activated olefins 4 - 7 has been shown to be a valuable synthetic reaction, giving rise to high yields of product especially for five and six-membered rings. The mechanism proposed for aliphatic bis-olefins activated by ester or nitrile groups, based on polarographic studies in dimethylformamide \( 6 \) (DMF) involves a one-electron reduction of one of the activated olefinic groups (1), the anionic attack of the resulting anion-radical on the other olefinic moiety (2) and further one-electron reduction at the electrode of the cyclized anion-radical thus formed (3) followed by protonation of the cyclized di-anion by residual water (4) according to the following scheme:

\[
\begin{align*}
\text{C}_6\text{H}_5 & + \text{CH}_2 = \text{CH} - \text{COOC}_2\text{H}_5, \\
\text{C}_6\text{H}_{11} & + 2\text{H}_2\text{O} \rightarrow \text{C}_6\text{H}_{11} + 2\text{OH}^-
\end{align*}
\]

(A) \( \text{CH}_2 \) \( 4 \)

In the present study it soon became apparent that the amount of water present in the medium, acetonitrile (ACN) and DME with tetrabutylammonium perchlorate exerts a strong influence, not only on the nature and yields of the reduction products but also on the mechanism of the cyclization process. It is the purpose of the present paper to report these observations together with the result of polarographic and cyclic voltammetry investigations in an attempt to further discuss the mechanism of EHC. Three activated olefins, the formulas of which are shown below were studied in this connection. Two of them, \( B \) and \( C \), were taken in the series previously investigated by Baizer and coworkers 4, 6.

\[
\begin{align*}
\text{C}_6\text{H}_5 & + \text{CH}_2 = \text{CH} - \text{COOC}_2\text{H}_5, \\
\text{CH}_2 \text{H}_2 & + \text{CH}_2 \text{H}_2
\end{align*}
\]

Diethyl-1,7 diene, 2,7-diphenyl sebacate
Experimental

The electronic apparatus, cell and electrodes used for polarography and cyclic voltammetry (CV) have been previously described 5. The reference electrode used was either the Ag/0.01 M AgNO₃ couple in ACN or the aqueous saturated calomel electrode in DMF.

Preparative electrolyses were carried out in a H-type cell with ACN/0.2 M tetraethylammonium perchlorate background solution. After all the electroactive material has been consumed, the solution was decanted, the solvent removed and the resulting solution after neutralization with sodium carbonate extracted three times with ether. This ethereal solution was washed with water and dried over magnesium sulphate before the ether was removed leaving the crude product. This was further purified according to the specific material synthesized.

Coulometry was carried out in a cell of capacity 50 cm³, the mercury pool being approximately 20 cm³ in area. Small aliquots (0.05 cm³) were taken at regular intervals during the electrolysis, immediately neutralized with acetic acid and their organic content determined by g.l.c. A nine metre column of diameter 2 mm filled with 3 % OV 17 on Varaport S was employed for the majority of electrolyses.

CHEMICALS

ACN was purified by distillation over sodium hydride and has a water content of 0.1 %. The DMF employed for electrochemical use was distilled under vacuum. The water content was 0.3 %. The DMF employed for chemical preparations was rather drier; it was refluxed on Varaport 2. Preparative electrolyses were taken at regular intervals during the electrolysis, immediately neutralized with sodium carbonate extracted three times with ether. The resulting product was isolated under these conditions along with others.

bis-OLEFIN A AND REDUCTION PRODUCTS

The corresponding di-alcohol was prepared in a Reformatski reaction by the addition of ethyl bromoacetate and zinc to dibenzoylbutane. The alcohol was dehydrated by addition of phosphorus oxychloride and pyridine. The resulting product (Mpt 79-80°C) was recrystallised from ethanol. NMR indicated the presence of two olefinic protons.

NMR: sing. 2.7(5), multi. 4.0(1), suprim. quart. 5.8(2), wide multi. 6.5.8.5(4), trip. 8.7(3)

Mass spectrum (molecular mass: 406): 129, 115(877), 157(755), 123(755), 331(694), 142(612), 91(597), 29(571), 360(469), 286(469), 171(367), 103(350), 287(306), 190(286), 77(255), 259(224), 315(194), 406(163), 361(163).

This product is most probably a cis-trans isomer mixture.

The bis-olefin, on reduction with Raney nickel in ethanol, incorporated four hydrogens to give the corresponding saturated product. This was purified by distillation.

A partial hydrogenation of the bis-olefin, with an average of two hydrogens being incorporated gave a mixture of product. The fully hydrogenated product was obtained in a 25 % yield, 25 % of the starting bis-olefin remained unreacted and the remaining product corresponded approximately to a 50 % yield. This last product, although it was not found possible to efficiently separate it from the other two was most probably the linear demi-product, as further reduction of this product, at the same potential as that employed for reduction of the diolefin, gave the saturated product in a two electrons reaction.

Preparative electrolysis of A in aqueous acetoneitrile (20 % water) leads to the saturated product in a 4e reaction. It has, however, been shown that the same demi-product is an intermediate in this reaction.

In dry ACN—the pH of the solution being kept from becoming too alkaline by the addition of perchloric acid—the electrolysis led to a mixture of products. Preparative thin layer chromatography on a silicagel plate with a benzene/2 % ethanol eluant yielded a pure product (Mpt 148-50).

NMR: sing. 2.75(10), quart. 7.10(2), multi. 7.3(2), multi. 8.2(2), triplet 9.2 (3).

Mass spectrum: 273, 274(827), 362(792), 91(690), 316(672), 115(431), 128(396), 129(396), 184(379), 287(345), 239(310), 212(293), 77(276), 363(258), 317(224), 183(224), 105(207), 141, 143, 144(207), 208, 289(172); also: 374(69).

These results are consistent with the formula:

\[
\begin{align*}
&\text{CH} = \text{CH} - \text{COOC}_2 \text{H}_5 \\
&\text{CH} = \text{CH} - \text{COOC}_2 \text{H}_5 \\
&\text{CH} = \text{CH} - \text{COOC}_2 \text{H}_5 \\
&\text{CH} = \text{CH} - \text{COOC}_2 \text{H}_5
\end{align*}
\]

This compounds would result from cyclization followed by Claisen elimination of an ethoxy group. It is clear from the NMR that one ester group has been lost; only one signal (quartet/triplet) from the ethoxy group can be noted. If we disregard the m/e peak at 374, which is fairly small and might be due to an impurity, the peak at 362 would be the peak of mass; the loss of OC₂H₅ giving rise to the 317 peak. The main peak at 273/274 are also easily explainable on this basis. The NMR signal (quartet/triplet) of the ethoxy group occurs at abnormally high field which can be explained by shielding from the two benzene rings.

bis-OLEFINS B AND C AND REDUCTION PRODUCTS

The two bis-olefins were synthesized according to Anderson et al 5. However the dibromo compound was prepared according to an alternative method, also described in the literature 10. The NMR and mass spectra are compatible with the expected structures. Both products were isolated as mixtures of two isomers in an approximate ratio of 4:1.

The preparative electrolyses of the cyclic products were carried out in 20 % H₂O/ACN. The appropriate bis-olefin (0.04 moles) was continuously added over a period of some 15 hours. The electrolyte was maintained neutral by the addition of acetic acid. After removal of the solvent water was added, the pH adjusted to neutrality and the solution extracted several times with ether. After drying over MgSO₄, the solvent was removed, leaving the crude cyclic product (yield based on starting material: 90 %). This was further purified by fractional distillation. The two cyclic compounds were characterized by mass spectrometry and NMR. A mixture of trans and cis isomers were obtained in agreement with previous results 6, 5.

Other products were isolated when the preparative scale electrolyses were carried out in dry ACN with high concentrations of starting material (0.5 M). In the case of the starting material B only one new product was isolated under these conditions along with the cyclic compounds.

NMR: Trip. 2.95(1), quart. 5.75(4), multi. 7.3-8.3(9), trip. 8.7 (6).

Mass spectrum: 194(826), 138(783), 195(522), 79(522), 88(478), 93(435), 152(304), 167(261), 123(132); also: 240(19), 241(4).

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These data are in agreement with this product being the 3-ethylcarboxy cyclohex-2-ene 1 ethylacetate:

\[
\text{COOC}_2\text{H}_3
\]
\[
\text{CH}_2\text{--COOC}_2\text{H}_3
\]

In the case of C two very similar compounds, probably isomers, were noted. The yield of the most abundant one increases with a reduction of the basicity of medium. A reasonably pure sample of this isomer (85-90 %) was obtained during fast electrolysis in a coulometric cell at a concentration of 0.1 M.

NMR: Mult. 2.9-3.3 (1), doub. 4.05, 4.3 (1), double quartet (4), mult + double trip. 7.7-8.7 (10).

Mass spectrum: 29, 180(623), 106(434), 81 (415), 55 (396), 93 (358), 135 (340), 134 (311), 79 (292), 121 (292); also: 160 (132), 208 (132), 209 (113).

These data indicate the following structure:

\[
\text{CH=CH--COOC}_2\text{H}_3
\]
\[
\text{0--CH, coo~·,H,}
\]

**Bis-olefin A. Results and discussion**

**POLAROGRAPHY AND CYCLIC VOLTAMMETRY**

The simplest cyclic voltammograms are obtained in dry DMF. At 10 V.s\(^{-1}\) a first broad and reversible wave is observed followed by a narrower irreversible peak (Fig. 1). At low sweep rates the first wave is less reversible, complete reversibility being reached at about 0.3 V.s\(^{-1}\). Addition of small amount of water induces positive shifts of both waves, with that of the second one dominating, thus resulting in a coalescence of the two waves. Before coalescence is reached and intermediate wave appears between the first two. As the water concentration and/or the sweep rate decrease, this intermediate wave gradually coalesces with the first wave until a higher wave is obtained (Fig. 2).

Similar effects are observed in polarography as shown on Figure 3. It is noted, in particular, that two well separated waves of approximately equal height are observed in dry DMF.

In ACN, the polarographic and CV characteristics are of the same type. In dry ACN, the first wave is however less reversible than in dry DMF. The first polarographic wave is higher, relatively to the second wave, in dry ACN than in dry DMF and the waves coalesce completely for moderate water addition, 7.5 % (Fig. 4). On the whole the system behaves in dry ACN as in DMF with a higher water content.

CV of the demi-product shows two waves, with the first partially reversible and the second irreversible, located in the same potential ranges as the waves of the starting bis-olefin.
C. P. ANDRIEUX, D. J. BROWN AND J. M. SAVÉANT

Table 1. — Electrolysis of bis-olefin A in ACN with LiClO₄, 0.1 M.

<table>
<thead>
<tr>
<th>Electron consumption per molecule</th>
<th>Percentage starting material</th>
<th>Intermediate products (*)</th>
<th>Final saturated product (**)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>100%</td>
<td>I</td>
<td>I</td>
</tr>
<tr>
<td>1</td>
<td>51.2%</td>
<td>40.5</td>
<td>2.1</td>
</tr>
<tr>
<td>2.2</td>
<td>5.1%</td>
<td>72.7</td>
<td>5.0</td>
</tr>
<tr>
<td>3.2</td>
<td>1.8%</td>
<td>41.3</td>
<td>1.8</td>
</tr>
<tr>
<td>4.0</td>
<td>0.6%</td>
<td>0.6</td>
<td>98.0</td>
</tr>
</tbody>
</table>

(*) Two isomers, presumably cis and trans, are detected by g.l.c.
(**) Linear saturated product corresponding to a 4 electron reduction of the starting material

DISCUSSION

In dry DMF the reduction leads to the mono-anion radical and the bis-anion radical which are stable in the CV time scale in two closely spaced steps. On this basis it can be stated that the height of the two polarographic waves in dry DMF corresponds to two electrons per mole each. From the shape of the CV wave it can be estimated 11 that the standard potential separation is about 100 mV. This value is larger than that which was determined for the analog bis (p-nitro-phenyl) compound (46 mV) 12. This can be interpreted by noting that in the present case the charges are less delocalized so that the coulombic repulsion for a given configuration of the di-anion is larger. The disproportionation equilibrium constant of the anion radical into the di-anion and the parent bis-olefin can then be estimated as about 2.10⁻².

Cyclization appears as a minor pathway in the overall reduction of bis-olefin A. A cyclized product is obtained only when the water concentration is very low, i.e., when electrolysis leading to hydrogenation has consumed enough of the initially present water in "dry" ACN. As soon as water or Li⁺ is added the reaction shifts toward hydrogenation first of one and then of two double bonds. This can be related to (i) the steric hindrance to cyclization, (ii) the coulombic repulsion against cyclization, (iii) the relatively high basicity of the anion-radical which favors hydrogenation, as discussed in the closely related problem of competition between dimerization and hydrogenation 13, 14.

The second and the third parameters can be reasonably considered as stronger here in the case of di-benzoyl propane ⁴ leading to a diminished tendency toward cyclization and to an increased, hydrogenation. The main aspects of the reaction mechanism can be
ELECTROCHEMICAL CYCLIZATION

depicted as show below (A: Ph-C=CH-CO₂C₂H₅
(:(CH₂)₄)

\[ \begin{align*}
A^- & \rightarrow \rightarrow \rightarrow A'^- \\
-1.83 \text{ V} & \rightarrow -1.93 \text{ V} \\
2A'^- & \rightarrow \rightarrow A^- + \rightarrow A'^- \\
\text{Claisen elimination product} & \\
A'^- H₂O & \rightarrow \rightarrow \rightarrow A^- H₂O \rightarrow \rightarrow A^- H₂O \rightarrow \rightarrow A^- \\
\text{intermediate wave} & \\
A'^- H₂O & \rightarrow \rightarrow \rightarrow A^- H₂O \rightarrow \rightarrow A^- H₂O \rightarrow \rightarrow A^- H₂O \rightarrow \rightarrow A^- H₂O \\
\text{2nd wave} & \\
A'^- & \rightarrow \rightarrow \rightarrow A^- \\
\text{2nd wave} & \\
\end{align*} \]

The cyclization reaction has been written as a radical-radical coupling involving the bis (anion-radical) in analogy to in the reaction sequence for dibenzoyl propane ². There may however be competition with a cyclization processus involving the initial anion-radical. The extent of the cyclization process is not important enough to allow a further investigation of this problem.

The intermediate wave can be assigned to the second reduction step of the demi-product. Thus water addition in DMF results in the enhancement of the first wave due to the occurrence at the same, potential of the first reduction step of the demi-product. Addition of water induces a positive shift of the second wave of the demi-product due to the acceleration of the neutralization of the di-anion of this compound, until complete merging with the first wave. Lowering of the sweep rate in CV has a similar effect which shows that the second reduction step of the demi-product is kinetically controlled by the neutralization of its di-anion.

That the second wave of the demi-product shifts more readily upon water addition than the second wave of the starting bis-olefin can be explained by the very fact that water induces the formation of the demi-product from the initial anion-radical of the bis-olefin. Indeed, this formation results in the disapperance of the bis (anion radical) the rate of which increases with the water concentration. Thus the addition of water induces two opposite effects for the processes occuring on the second wave i. e.: (i) acceleration of a preceding reaction which induces a negative potential shift (ii) acceleration of a following reaction (neutralization of the tri and quadranions) which induces a positive potential shift. Even if this last effect is finally dominant, this accounts for the advancement of the second wave being less than in the case of the demi-product.

**Bis-olefins B and C. Results and discussion**

**POLAROGRAPHY AND CYCLIC VOLTAMMETRY**

In the polarography of B and C in dry ACN two indistinct waves are observed (Fig. 5 and 6). The total height of the waves is equivalent to two electrons on comparison with bis-olefin A. Addition of water induces a positive shift of both waves, the shift of the second wave being larger than that of the first one. The total height remains approximately constant and the second wave increases slightly at the expense of the first one. Cyclic voltammetry shows that in both cases the two waves are irreversible at any sweep rate.

**Figure 5.** - Polarography of bis-olefin B (4 mM) in ACN. Water addition (a): 0 %, (b): 10 %.

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The cyclic isomers of the bis-olefins B and C formed upon internal Michael reaction show a polarographic wave slightly more negative than that of the starting material.

Coulometry and preparative scale electrolyses

The results of coulometric determinations and preparative scale electrolysis for several amounts of water added are given in Table II (B) and III (C). For 20% H₂O, the yields are in good agreement with previous determinations made in similar conditions. The most abundant isomer I has been assigned as the trans isomer on the basis of refractive index determinations.

As the percentage of water is lowered, two effects are noticeable: (i) the number of electrons required for the production of a molecule of cyclic product (8th column) decreases passing from a value of about 1.6 at 20% H₂O to 1 at low water concentrations in both cases; (ii) the appearance of another product identified as an isomer of the starting material resulting from an internal Michael reaction as described in the experimental part. Concomitantly, the number of electrons required for the reduction of one molecule of the initial bis-olefin (7th column) decreases steeply, reaching values as low as 0.4-0.3.

Also, as the water content is lowered, the ratio isomer I/isomer II increases slightly but distinctly in the case of B (from 3 to 4 between 20% and 0% water addition) and decreases in the case of C (from 2.4 to 1.6 between 20% and 0% water addition).

Electrolyses were also carried out in the presence of deuterium oxide instead of water. The yields in di-, mono- and non-deuterated cyclic products are given in Table IV in the case of B, together with the number of electrons per molecule of cyclic product formed, the percentage of deuterium incorporation was derived from the M-45 peak in mass spectroscopy. It is seen that the same decrease as with water is observed for the last figure as the D₂O content is lowered. On the other hand, it can be noted that although the minimal concentration of D₂O is several times the concentration of residual water, raising the D₂O concentration results in increased yield of mono and then di-deuterated product, this last compound being largely dominant in 20% D₂O.

Discussion

As far as mechanism determination is concerned, the most important of the preceding observations is that the number of electrons required for forming a molecule of cyclic product tends toward 1 as the water content decreases. The only possible explanation of this fact seems to be that, under these conditions, the cyclization process occurs at the level of the mono-anion-radical by attack on the unreduced double bond and that the resulting cyclic anion radical abstracts an hydrogen atom from the solvent or the supporting electrolyte.

\[
\text{CH}_2\text{CN} \rightarrow \text{CH}_2\text{CN}^- + \text{H}^+.
\]

The resulting anion would then be neutralized by the strongest proton donnor present in the medium (water or starting material as will be discussed later). The protonation could however precede the H-atom abstraction instead. The assumption of an hydrogen...
Table II. — Electrolysis of bis-olefin B in ACN with various amounts of water added.

<table>
<thead>
<tr>
<th>Coulometric consumption</th>
<th>Cyclic product (%)</th>
<th>Remaining Michael product (%)</th>
<th>Number of electrons consumed</th>
<th>Number of electrons formed</th>
</tr>
</thead>
<tbody>
<tr>
<td>relative to initial concentration (F/M)</td>
<td>Cyclic product (%)</td>
<td>Remaining Michael product (%)</td>
<td>Number of electrons consumed</td>
<td>Number of electrons formed</td>
</tr>
<tr>
<td></td>
<td>Isomer I</td>
<td>Sum of isomers</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20 % H₂O, E = −2.30 V</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.20</td>
<td>10</td>
<td>15</td>
<td>82</td>
<td>97</td>
</tr>
<tr>
<td>0.36</td>
<td>18</td>
<td>25</td>
<td>73</td>
<td>98</td>
</tr>
<tr>
<td>0.55</td>
<td>29</td>
<td>41</td>
<td>58</td>
<td>99</td>
</tr>
<tr>
<td>0.80</td>
<td>40</td>
<td>54</td>
<td>45</td>
<td>99</td>
</tr>
<tr>
<td>1.05</td>
<td>48</td>
<td>68</td>
<td>31</td>
<td>99</td>
</tr>
<tr>
<td>1.3</td>
<td>60</td>
<td>79</td>
<td>17</td>
<td>96</td>
</tr>
<tr>
<td>1.6</td>
<td>67</td>
<td>89</td>
<td>6</td>
<td>95</td>
</tr>
<tr>
<td>1 % H₂O, E = −2.40 V</td>
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<td>0.1</td>
<td>7</td>
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<td>89</td>
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<td>0.2</td>
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<tr>
<td>0.3</td>
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<td>31</td>
<td>65</td>
<td>2</td>
</tr>
<tr>
<td>0.4</td>
<td>33</td>
<td>42</td>
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<td>3</td>
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<td>0.6</td>
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<tr>
<td>0.8</td>
<td>59</td>
<td>75</td>
<td>14</td>
<td>7</td>
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<tr>
<td>0.5 % H₂O, E = −2.41 V</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.1</td>
<td>7</td>
<td>9</td>
<td>12</td>
<td>1</td>
</tr>
<tr>
<td>0.2</td>
<td>13</td>
<td>19</td>
<td>82</td>
<td>2</td>
</tr>
<tr>
<td>0.35</td>
<td>23</td>
<td>31</td>
<td>69</td>
<td>3</td>
</tr>
<tr>
<td>0.55</td>
<td>36</td>
<td>46</td>
<td>42</td>
<td>10</td>
</tr>
<tr>
<td>0 % H₂O, E = −2.48 V</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
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<td>0.1</td>
<td>8</td>
<td>11</td>
<td>90</td>
<td>2</td>
</tr>
<tr>
<td>0.2</td>
<td>14</td>
<td>19</td>
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<tr>
<td>0.3</td>
<td>19</td>
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<tr>
<td>0.4</td>
<td>23</td>
<td>27</td>
<td>8</td>
<td>57</td>
</tr>
</tbody>
</table>

atom abstraction from the solvent is reinforced by the results of the deuteration experiments, assuming, as seems reasonable, that the solvent is a better H atoms donor than water and a poorer acid. The fate of the resulting solvent radical \( \text{CH}_2\text{CN} \) is not known. No succinonitrile has been detected in the electrolysis products. However further reaction of the radical may lead to other products which could be ultimately transformed into amides which are not detectable by normal identification methods.

In the anion-radical the charge is mainly located on the ester group and the unpaired electron on the \( \beta \)-carbon. The coupling process is therefore more likely to be a neutral olefinic radical cyclization \(^{15}\) rather than a Michael type reaction.

There are two possibilities for the explanation of the increase of the number of electron required to form a molecule of cyclic product upon addition of water:

(i) acceleration of the reduction, at the electrode and/or in solution, of the cyclized anion radical, or its protonated form, competing more and more favorably with the H-atom abstraction reaction:
(ii) acceleration of the radical-radical internal coupling of the bis-anion radical by increasing the solvation of the two anion radical moieties and then decreasing the coulombic repulsion which normally inhibits coupling. This effect has been evidenced in radical-radical dimerisation of anion radicals (see, e. g., the reduction of acetophenone in ACN as a function of water addition [19]). The overall reaction scheme would then be, after the formation of the initial anion-radical, as follows:

\[
2 \overset{\cdot}{A}^{-} + 2 \overset{\cdot}{A}^{-} \rightarrow \overset{\cdot}{A}^{-} + \overset{\cdot}{A}^{-} + 2H_2O \rightarrow \overset{\cdot}{A}^{-} + \overset{\cdot}{A}^{-} + 2OH^-
\]
Table IV. — Electrolysis of bis-olefin B in ACN in the presence of deuterium oxide.

<table>
<thead>
<tr>
<th>Percentage Deuterium oxide (%)</th>
<th>Non deuterated product (%)</th>
<th>Mono-deuterated product (%)</th>
<th>Di-deuterated product (%)</th>
<th>Number of electrons per molecule of cyclic product formed</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>89</td>
<td>10</td>
<td>2</td>
<td>1.1</td>
</tr>
<tr>
<td>3</td>
<td>57</td>
<td>28</td>
<td>15</td>
<td>1.4</td>
</tr>
<tr>
<td>20</td>
<td>16</td>
<td>16</td>
<td>79</td>
<td>1.7</td>
</tr>
</tbody>
</table>

competing more and more favorably with:

\[
\text{cis} \quad \rightarrow \quad \text{cis} + (\text{CH}_3\text{CN}+\text{Bi}) \quad \rightarrow \quad \text{cis} + (\text{CH}_3\text{CN}+\text{B}^\cdot)
\]

upon water addition.

The second wave would then represent the same type of process occurring at the electrode

\[
\text{cis} \quad \rightarrow \quad \text{cis} + \text{H}_2\text{O} \quad \rightarrow \quad \text{cis} + \text{H}_2\text{O}^\cdot
\]

with its half-wave potential shifting toward positive value as the radical-radical cyclization speeds up.

The observed variations of the cis/trans ratio upon water addition seem to favor the second possibility. It has been noted previously that in the electrochemical cyclization of 1,3 dibenzoyl-propane only the cis-isomer is obtained. Since, in this case, cyclization involves the bis-anion-radical some kind of cooperative solvation of the two functions probably reduces the effect of the coulombic repulsion and steric hindrance which are larger than for the trans-isomer formation. In the case of bis-olefin B, the percentage of cis-isomer increases upon water addition. This is compatible with the second possibility whereas for the first one the replacement of the H-atom abstraction by a reduction would not change the stereochimistry of the final product since, at this stage, cyclization has already occurred. The situation is different in the case of C since cooperative solvation may lead to the trans-isomer.

On the other hand, the formation of internal Michael products at low water content can be explained by catalysis by strong bases, such as the cyclized anions, formed during the electrochemical reduction. This would lead in the case of bis-olefin B to:

\[
\begin{align*}
\text{CH}=&\text{CH} \quad \rightarrow \quad \text{CH}=&\text{CH} \\
\text{CH}=&\text{CH} \quad \rightarrow \quad \text{CH}=&\text{CH} \\
\text{CH}=&\text{CH} \quad \rightarrow \quad \text{CH}=&\text{CH}
\end{align*}
\]

and in the case of C:

\[
\begin{align*}
\text{CH}=&\text{CH} \quad \rightarrow \quad \text{CH}=&\text{CH} \\
\text{CH}=&\text{CH} \quad \rightarrow \quad \text{CH}=&\text{CH} \\
\text{CH}=&\text{CH} \quad \rightarrow \quad \text{CH}=&\text{CH}
\end{align*}
\]

Several other examples of Michael reactions catalyzed by electrogenerated bases have already been given. One of the main conclusions of the present work is that cyclization of the bis activated olefins occurs, at least partially, through a radical-double bond attack. On the other hand electro-hydrocyclization, is a particular case of electrohydrodimerization (EHD) corresponding to a large concentration of the starting material. It seems therefore worthwhile to compare the results of the present work to those obtained in previous mechanistic studies of the EHD of activated olefins. For this last reaction, the problem was to discriminate between three possible types of coupling: radical-radical (RRC), radical-substrate (RSC) and ion-substrate (ISC). The last possibility can be ruled out in a large number of cases, i.e. when a second wave exist leading to hydrogenation of the double bond through the intermediary of the di-anion. It has been shown that in the polarographic concentration range the coupling of activated olefins in solvents such as ACN and DMF is unambiguously of the RRC type in the case where the reduction rate does not depend on the amount of water present, i.e. in the case of conjugated molecules where the negative charge in the anion radical is largely delocalized. When delocalization is less, i.e. for the aliphatic mono-activated olefins the RRC mechanism also appears as the most probable in the millimolar concentration range. Mixed coupling experiments would lead to conclude that the RSC mechanism is operative at higher concentrations. However this is not actually
conclusive since in the mixed coupling the coupling step could be preceded by an electron transfer in solution and remain of the RRC type. Alternatively even if the coupling step is of the RSC type in the mixed reaction it might be that the RRC mechanism would be operative for the self-EHD of each olefin. One must however conceive the RRC and RSC mechanisms as competing sequences of reactions rather than excluding each other. Three main factors may influence this competition:

(i) The structure of the initial olefin; coulombic repulsion against RRC is small if the negative charge in the anion radical is largely delocalized.

(ii) Solvation of the anion radical. If, e. g., a large amount of water relative to the olefin concentration is present, specific solvation would again decrease the coulombic repulsion and thus favor the RRC reaction path.

(iii) Concentration of the starting material. Increasing the substrate concentration obviously accelerates the RRC reaction. The first effect is larger than the second as shown by analysis of the kinetics of each process in linear sweep voltammetry and stationary state voltammetry.\(^\text{14, 30, 31}\) (30 mV positive shift of the peak or half-wave potential per decade of concentration in the first case and 20 mV in the second case). The RSC mechanism is thus favored by a high concentration of the starting material and therefore also in an EHC reaction.

It has been shown recently\(^\text{32}\) that in the case of p-methyl-benzylidene-malonitrile, where the negative charge in the anion radical is largely delocalized, the mechanism of the EHD remains of the RRC type even at high concentrations (0.1 M). The results of the present study indicate that in the case of an aliphatic olefinic moiety, at what is equivalent to a high concentration (cyclization), the RRC and RSC mechanisms are competing the second reaction route being entirely predominant at low water concentrations.

Acknowledgment

The work was supported in part by the Délégation Générale à la Recherche Scientifique et Technique (Action Concertée : « Activation Selective en Chimie organique »).

NOTES AND REFERENCES

18. The rate of coupling in the EHC is therefore larger than in the EHD of a mono-olefin of similar structure in polarographic conditions (\(10^{-3} \text{ M}\)). This explain why the half-wave potential is markedly more positive in the first case than in the second\(^\text{9}\) without particular implication about the coupling mechanism.