148. Influence of the Water Content of the Solvent on the Product Distribution in the Electrohydrodimerization of 2-Cyclohexenones[1][2]

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Summary

The product distribution of compounds **2**, **3** and **4** formed in the electrohydrodimerization (EHD) of **1** was determined as function of the water content of the solvent (CH_3CN). The presence of water favours the formation of the glycols **4** and reduces the relative amounts of 1,6-diketones **2** and hydroxyketones **3**, as determined by GC./MS.-analysis.

We recently presented [1] preliminary results of cyclovoltammetric studies on the EHD of several alkyl-substituted 2-cyclohexenones **1**. We had determined the lifetimes of the radical anions formed and had suggested from this analysis, that in acetonitrile the hydrodimers **2**–**4** were formed *via* reaction of the radical anion **A** with the substrate in a 'radical-substrate coupling reaction' (path *b*), rather than by coupling of two radical anions (path *a*). In presence of proton donors the neutral radical **AH** would be formed, the dimerization of this species then giving the same products **2**–**4** (path *c* in *Scheme 1*).

The fact that the hydrodimers **2**–**4** are obtained *via* two different reaction paths (*b* and *c* in *Scheme 1*) led us to investigate the variation of the product ratio as function of the water content of the solvent, as increasing amounts of water should favour path *c* over path *b*. Furthermore, the EHD-reaction would gain in preparative utility if products **2**, **3** and **4** could be obtained selectively just in varying the experimental conditions. Compounds **1a**–**1d** were thus electrolized in acetonitrile containing 0–5% (*v*/*v*) water and TBAFB (tetrabutylammonium fluoroborate) as electrolyte. For the hydrodimers of enones **1a**–**1c**, combined GC./MS.-analysis was used to determine the structure and the ratio of products. As no satisfactory GC.-conditions were found to avoid the decomposition of **3d**, the mixture **2d**/**3d**/**4d** was resolved by ^{1}H-NMR. spectroscopy and chromatography on SiO_2.

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[1] Graduate-Diploma Thesis (*J.P.S.*), University of Geneva, 1979.

[2] Reported at the 4th EUCHEM Conference on Organic Electrochemistry at Rodez (France), May 1980.

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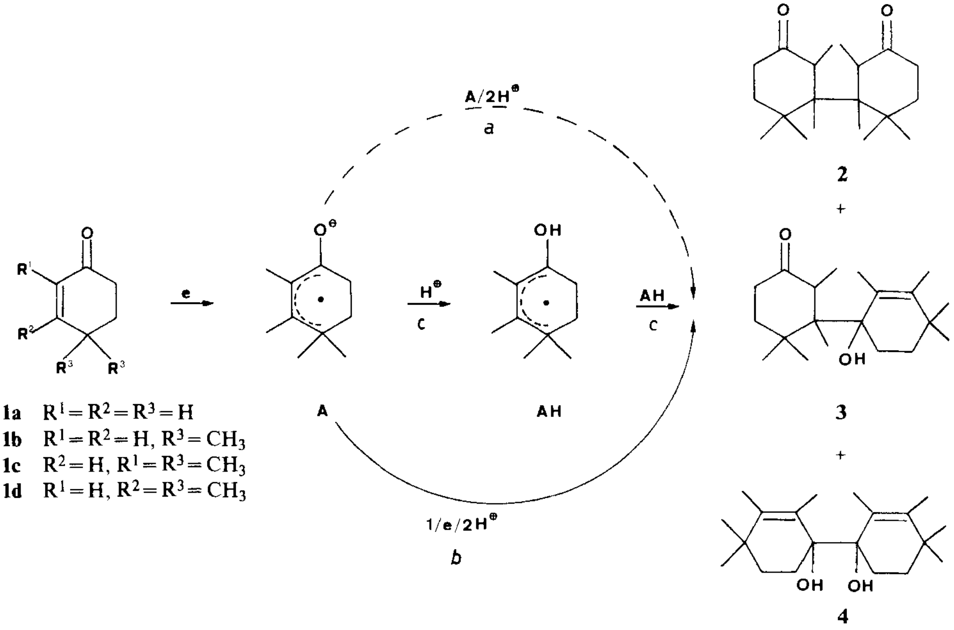
Scheme 1



1a $R^1 = R^2 = R^3 = H$
1b $R^1 = R^2 = H, R^3 = CH_3$
1c $R^2 = H, R^1 = R^3 = CH_3$
1d $R^1 = H, R^2 = R^3 = CH_3$

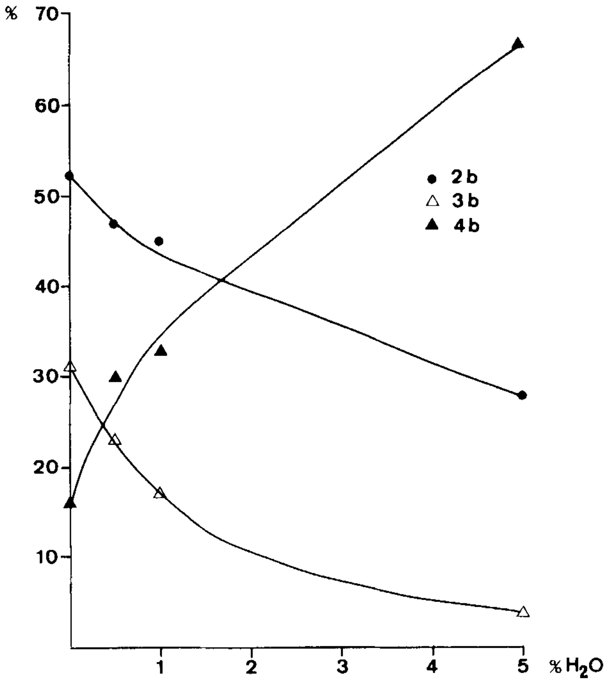


Figure. *Variation of product distribution of hydrodimers* **2b–4b** *with the water content* (v/v) *of the solvent*

Table 1. *Relative product distribution of hydrodimers*[a]) **2**, **3** *and* **4** *in the electrolysis of* **1** (2.10^{-1} M in CH_3CN) vs. *water content* (error: ± 5%)

	1a[b])			**1b**[b])			**1c**[b])			**1d**[c])		
	2a	**3a**	**4a**	**2b**	**3b**	**4b**	**2c**	**3c**	**4c**	**2d**	**3d**	**4d**
0% H_2O	97	-	-	52	31	16	10	40	50	10	60	30
5% H_2O	95	-	-	28	4	67	-	10	90	-	45	50

[a]) Mixture of diastereoisomers. [b]) From GC. [c]) From ^1H-NMR.

The results obtained are given in details for **1b** in the *Figure* to demonstrate the trend of product variation due to water content, and are summarized for the four compounds studied in *Table 1.*

The following MS.-criteria helped to establish the structures of the hydrodimers **2a**-**2c**, **3a**-**3c** and **4a**-**4c**. At the experimental GC.-conditions (see exper. part) the elution order of the isomeric hydrodimers was **4**, **2**, **3**. EI. mass spectra of the isomeric compounds **2** and **3** were qualitatively very similar. In one mixture, *e.g.* **2c**/**3c**/**4c**, the diketone **2c** was established by comparison of the GC./MS.-results of an authentic sample of **2c** prepared by the method described by *Dunoguès* [2].

In the EI.-mass spectra of all dimers the base peak at $m/z = M^{+}/2$ is produced by homolytic cleavage of the C,C-bond between the two cycles. Small but significant peaks are found at higher *m/z*-values. Compounds **2a**-**2c** and **3a**-**3c** show small molecular ion peaks (< 3% of base peak) while in the spectra of diols **4a**-**4c** molecular ion peaks are absent. Molecular ions of **2a**-**2c** and **3a**-**3c** lose only one neutral molecule of water. Those of **4a**-**4c** lose succesively two molecules of water resulting from the presence of two hydroxyl groups.

Compounds **2a**-**2c** and **3a**-**3c** exhibit the mass spectral fragmentation pattern of cyclic ketones, giving peaks corresponding to ions **x**, **x'** and **y** *(Scheme 2).*
Ions **x** and **y** are completely absent in the spectra of the hydrodimers **4a**-**4c**.

The mixture **2c**/**3c**/**4c** was also studied by chemical ionization GC./CI./MS.-analysis using CH_4 as reagent gas. The CI.-mass spectra were much simpler than the corresponding EI.-mass spectra *(Table 2).*

Scheme 2

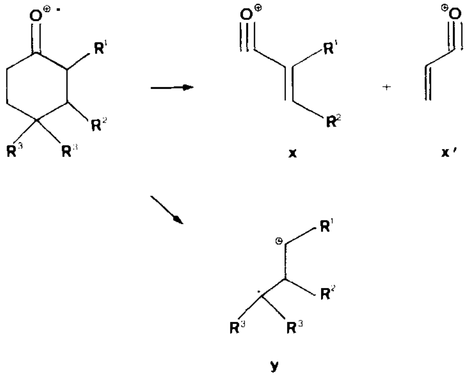


Table 2. *CI.-mass spectra* (*CH_4 as reagent gas*) *of the mixture* **2c/3c/4c** (intensities in % of base peak)

	MH^+	$MH-H_2O^+$	$MH-2H_2O^+$	$M/2^+$
4c	0	100	12	84
2c	100	37	0	11
3c	100	73	3	12

These results show better than EI.-mass spectra the differences between the three isomeric compounds with regard to the loss of one or two molecules of water from the protonated molecular ions. As it would be expected, the quasi-molecular ions of **4c** are very unstable and lose one and two molecules of water. The quasi-molecular ions of **2c** are much more stable and lose only one molecule of water. Compound **3c** shows an intermediate behaviour.

As already mentioned, hydrodimer **3d** decomposed partially under the GC.-conditions used. Therefore, **2d/3d/4d** were separated by chromatography (SiO_2/CH_2Cl_2). The relative amounts of **3d** and **4d** could be seen directly from the ^{1}H-NMR.-spectrum of the mixture as the olefinic protons of these compounds exhibit different chemical shift in $CDCl_3$ ($\delta = 5.50$ ppm for **4d** and 5.75 ppm for **3d**). The overall yield of dimeric products increases from 50% in the absence of water to about 80% in CH_3CN/water 95:5.

It can be seen from these results that less 1,6-diketones **2** and hydroxyketones **3** and more glycols **4** are formed with increasing water content of the solvent.

These results can be reasonably explained with the mechanistic features described in *Scheme 1*. In the absence of water the radical anion **A** will react with enone **1** preferentially *via* C(3),C(3′)-bonding; with increasing steric hindrance due to the methyl groups on C(4),C(2) and C(3) C(3),C(1′)-bonding leading to **3** becomes competitive [3] [4]. In adding water **A** will be trapped to give radical **AH**, which dimerizes *via* C(3),C(3′)-, C(3),C(1′)- and C(1),C(1′)-bonding, the first two reactions becoming less important with increasing alkyl substitution (**1a**→**1d**). It is interesting to note that for **1c** this dimerization of **AH** leads selectively to one diastereomeric glycol **4c**, probably the *meso*-form, which can be expected to be more stable on steric reasons than the corresponding DL-form [5]. Similar stereoselective pinacol formation have also been observed in the EHD of tetrahydro-3(2H)-phenanthrones [6]. The fact, that in the presence of water less polymeric material is formed, is readily explained in assuming that the polymer-forming step is the reaction of the new radical anion formed from **A** and **1** with a further molecule **1**. This reaction becomes less probable if **A** reacts with water to **AH**.

Parker has recently reported results on derivative cyclic voltammetry kinetic data for the EHD of diethyl fumarate [7] and methyl cinnamate [8]. These reactions proceed *via* radical-substrate coupling and the author comments on the question of the radical-anion coupling mechanism takes place in any EHD reaction. Two important aspects should be taken into consideration in comparing the EHD reactions of activated olefins. The first one concerns the lifetime of the radical anion formed. With increasing stability of the radical anion (*i.e.* with better delocalization of the negative charge) the probability of radical anion dimerization increases as well. The second argument concerns the polarization of the C,C double bond of the olefine itself. Radical anions should react preferentially with polarised (*i.e.* mono- or 1,1-disubstituted) olefins. For these compounds, *e.g.* the 2-cyclohexenones, the radical-substrate mechanism will predominate. A final comment concerns the preparative utility of the EHD of 2-cyclohexenones. Glycols **4** are formed preferentially when water is added to the solvent during the electrolysis. As these glycols rearrange to 1,6-diketones **2** *via* a thermal [9] or catalyzed [10] oxy-*Cope* reaction, it is now easier to obtain each of the hydrodimers selectively.

We are grateful to Miss *Hélène Lartigue* for her technical assistance.

Experimental Part

Materials. 2-Cyclohexenone (**1a**, *Fluka*) was distilled before use. Compounds **1b** [11], **1c** [12] and **1d** [13] were synthesized following the literature. Acetonitrile was purified as in [14]. Tetrabutylammonium fluoroborate (TBAFB) was prepared according to [15].

Preparative electrolysis at controlled potential. A potentiostat (*Wenking PCA 72L*) was used. The electrolytic cell (*Metrohm* EA 840-20T) was equipped with a magnetic stirrer and a N_2 inlet and outlet. A mercury pool of 6.6 cm^2 surface area was used as working electrode, a Pt-anode as counter electrode and Ag/Ag^+ 10^{-2}M as reference electrode. The current quantity was determined with an integrator (*Amel 558*). About 3.10^{-3} mol **1** in 15 ml CH_3CN containing 0.5 mol/l TBAFB and 0 to 5% (*v/v*) H_2O were electrolyzed with 100% theoretical current amount at -2.05 V (**1a**), -2.29 V (**1b**), -2.42 V (**1c**) and -2.47 V (**1d**); mean current density was 16 mA/cm^2. The solvent was then evaporated and 20 ml ether added to the residue. The organic phase was filtered from electrolyte and polymeric material.

Product analysis. Gas chromatography was performed on a *Carlo Erba 2350* instrument on a 20 m × 0.33 mm SE-54 capillary column using a temperature programme between 60–250°; *n*-dodecane was used as internal standard for peak integration. Mass spectra after GC. separation were recorded on a *Finnigan 4023 GC-MS-computer*, the ionization energy being 70 eV. The source temperature was 250°. GC.-chemical ionization MS. was performed at the same conditions than GC./EI./MS., with a CH_4 pressure of 0.35 Torr. Hydrodimer mixture **2d**/**4d** was separated by column chromatography (SiO_2/CH_2Cl_2) and analyzed by ^1H-NMR.-spectroscopy on a *Varian A-60 instrument.* ($CDCl_3$, δ in ppm against TMS; **2d**: 2.50–1.50 (*m*, 12 H); 1.15 (*s*, 6 H); 0.90 (*s*, 6 H); **3d**: 5.75 (*s*, 1 H); 2.40–2.80 (*m*, 10 H + OH); 1.95 (*s*, 3 H); 1.10–0.90 (*s*, 15 H); **4d**: 5.50 (*s*, 2 H); 2.45 (2 OH); 1.70 (*s*, 6 H); 1.80–1.45 (*m*, 8 H); 1.02 (*s*, 6 H); 1.80–1.45 (*m*, 8 H); 1.02 (*s*, 6 H); 0.95 (*s*, 6 H).

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