148. Electrochemical Reduction of Cyclohex-2-enones

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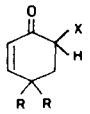
Summary

The electrochemical reduction of the cyclohex-2-enones **1a–1e** (mercury cathode, CH_3CN, Bu_4NBF_4) was studied by means of cyclic voltammetry, d.c. polarography, coulometry and chemical product analysis. Compounds **1a–1c** give a mixture of the hydrodimers **4** and **5** *via* formation of the radical anion **2** by an irreversible one electron transfer, followed by protonation and dimerization of the allylic radical **3**. The 6-halocyclohex-2-enones **1d** and **1e** exhibit two distinct reduction waves. The first corresponds to an irreversible two electron transfer with formation of the halide anion and the enolate anion **6** which gives **1b** by protonation. The second wave corresponds to a *quasi*-reversible one electron transfer to **6** to afford the radical dianion **7** (*Scheme 2*).

The electrochemical reduction of α,β-unsaturated ketones in general [1] [2] and of cyclohex-2-enones in particular [3–5] has been investigated by several research groups. Although the mechanism for this reaction in aqueous systems seems to be well understood [6] [7], less is known about it in nonaqueous media.

We now report results on a comparative study of the electrochemical reduction of the cyclohex-2-enones **1a–1e** (*Scheme 1*) in acetonitrile by cyclic voltammetry, d.c. polarography, coulometry and chemical analysis. In order to correlate reliably the experimental data of the controlled potential electrolyses for identification of the reaction products with those of the mechanistic studies, all experiments were run under as similar conditions as possible. This implies that the conditions were far from being optimal for preparative electrolyses as reflected in the modest yields of isolated products.

Scheme 1



a) R = X = H
b) R = CH_3 ; X = H
c) R = X = CH_3
d) R = CH_3 ; X = F
e) R = CH_3 ; X = Cl

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Two distinct behaviours were observed for **1a–1c** on the one hand and for **1d** and **1e** on the other. For the mechanistic descriptions the results obtained with compounds **1b** and **1e** can be regarded as representative.

Two cyclic voltammograms are shown in *Figure 1*. In acetonitrile containing 0.5 mol/l tetrabutylammoniumfluoroborate (TBAFB), **1b** exhibits one cathodic peak, while for the reduction of **1e** two cathodic peaks are observed. The results of the cyclic voltammetry studies are summarized in *Table 1*. It can be deduced that the reduction of **1a–1c** proceeds by an irreversible electron transfer while the reduction of **1d–1e** proceeds by two separate electron transfers, the first being irreversible and the second *quasi*-reversible[3]). In all cases the electron transfer is followed by a chemical reaction (EC).

The polarographic half-wave potentiels ($E_{1/2}$) and the transfer coefficients α are summarized in *Table 2*. The dependence of $E_{1/2}$ on the substituent X reflects the electron-donating or withdrawing properties of the group vicinal to the C=O bond.

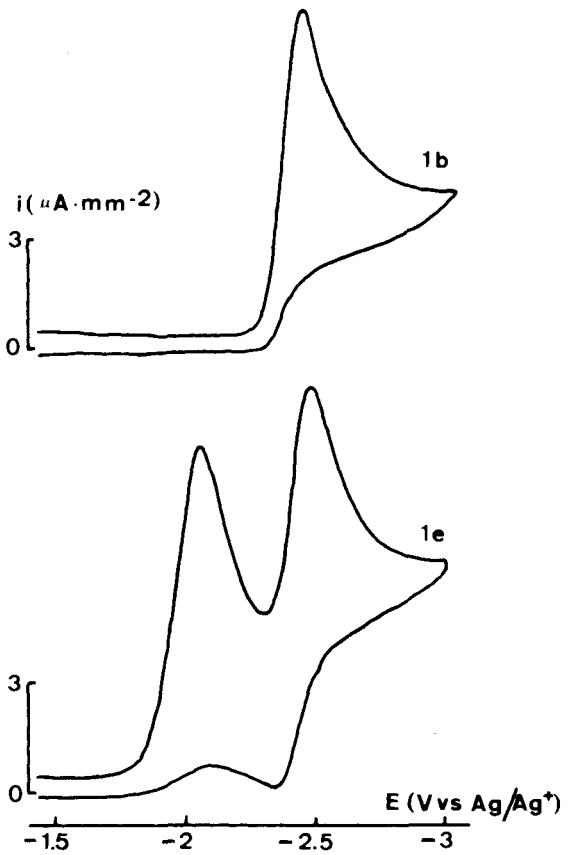


Fig. 1. *Cyclic voltammogram of* **1b** *and* **1e** *(10^{-3} M in CH_3CN). Scan rate = 500 mV · sec^{-1}*

[3]) As seen from the variation of E_{pc}–E_{pa} with the scan rate.

Table 1. *Voltammographic data* (E_p; $i_p \cdot v^{-1/2}$) *for* **1a–1e** (10^{-3} M in CH_3CN). *Peak potentials in Volt* vs *Ag/Ag*$^+$

Compound	Scan rate in mV · s^{-1}				
	20	50	100	500	1000
1a	−2.42; 0.42	−2.43; 0.41	−2.46; 0.41	−2.48; 0.38	−2.52; 0.30
1b	−2.37; 0.39	−2.39; 0.40	−2.40; 0.38	−2.45; 0.36	−2.47; 0.33
1c	−2.45; 0.38	−2.46; 0.38	−2.47; 0.35	−2.49; 0.32	−2.50; 0.31
1d	−2.05; 0.42	−2.06; 0.42	−2.07; 0.40	−2.11; 0.39	−2.15; 0.36
	−2.39; 0.24	−2.40; 0.23	−2.41; 0.22	−2.42; 0.20	−2.44; 0.17
1e	−1.97; 0.42	−1.98; 0.40	−2.00; 0.38	−2.05; 0.37	−2.07; 0.31
	−2.42; 0.24	−2.43; 0.25	−2.44; 0.29	−2.47; 0.29	−2.49; 0.24

Table 2. *Half-wave potentials and transfer coefficients* ([enone] = 2.10^{-4} M)

Compound	$E_{1/2}$ (V *vs* Ag/Ag$^+$)[a])	α[b])
1a	−2.380 (± 0.005)	0.51
1b	−2.368	0.55
1c	−2.458	0.56
1d	−2.032; −2.505	0.25; 0.75
1e	−1.958; −2.508	0.22; 0.75

[a]) From d.c. polarography.
[b]) From cyclic voltammetry.

With increasing concentration of **1a–1c** the corresponding $E_{1/2}$-values become less negative[4]), a common feature for dimerization reactions.

The number of electrons exchanged for each of these steps was determined by coulometry at controlled potentials. As the product mixtures were often difficult to analyse quantitatively, the decrease in enone concentration relative to an internal standard was monitored by GC. The results for **1b** and **1e** are shown in *Figure 2*. Compounds **1a–1c** are thus reduced by a one electron transfer, a mechanism also proposed by other authors although the value of n had not been determined [4] [5] [8]. In contrast, the first reduction wave of the 6-halocyclohex-2-enones **1d** and **1e** corresponds to a two electron transfer. A value of $n = 2$ had been determined for the reduction of 2-chlorocyclohexanone to cyclohexanone in an aqueous medium [9] but no further reduction wave was observed. Finally the second reduction wave for **1d** and **1e** corresponds to a one electron transfer.

Electrochemical reduction of cyclohex-2-enone (**1a**) in aqueous acetonitrile gives a mixture of the *meso*- and racemic diketones **4a** and the hydroxyketone **5a** [4]. In the reduction of **1a–1c** similar products **4** and **5** were obtained and identified by comparison with products of known structure obtained by chemical reduction [10–12]. In contrast, the reduction of **1d** and **1e** at −2.05 V (corresponding to the first reduction wave) leads to the selective formation of 4,4-dimethylcyclohex-2-enone (**1b**) by

[4]) As an example, $E_{1/2}$ for **1b** varied between −2.458 and −2.414 V in the concentration range 2.10^{-4} M–5.10^{-3} M.

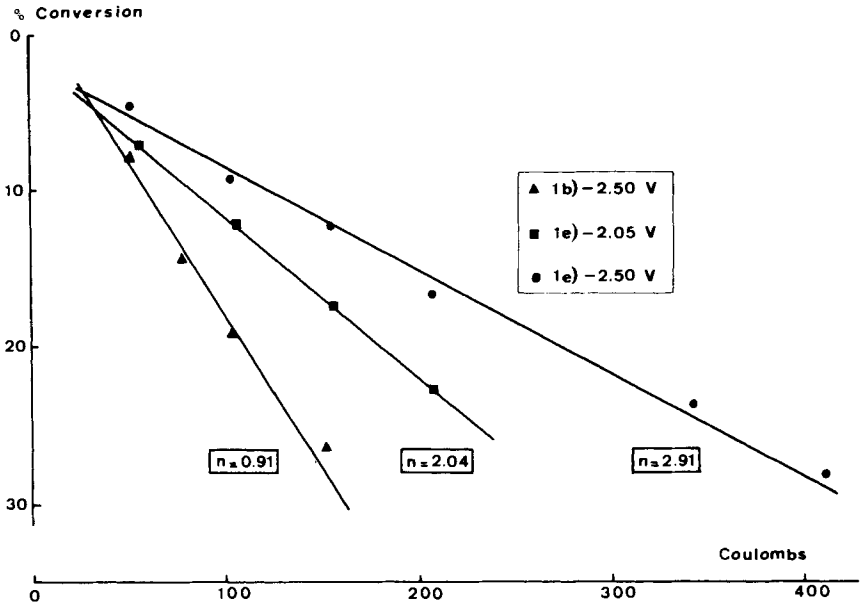


Fig. 2. *Current quantity* vs. *conversion of starting material. Reference electrode*: Ag/Ag^+

a cathodic substitution reaction [13] [14], while the reduction of the same compounds at −2.5 V gives a complex mixture of unidentified products. The yields of isolated products are summarized in *Table 3*.

On the basis of our results we propose the following reaction sequences (*Scheme 2*) for the electrochemical reduction of the cyclohexenones **1a**–**1e**.

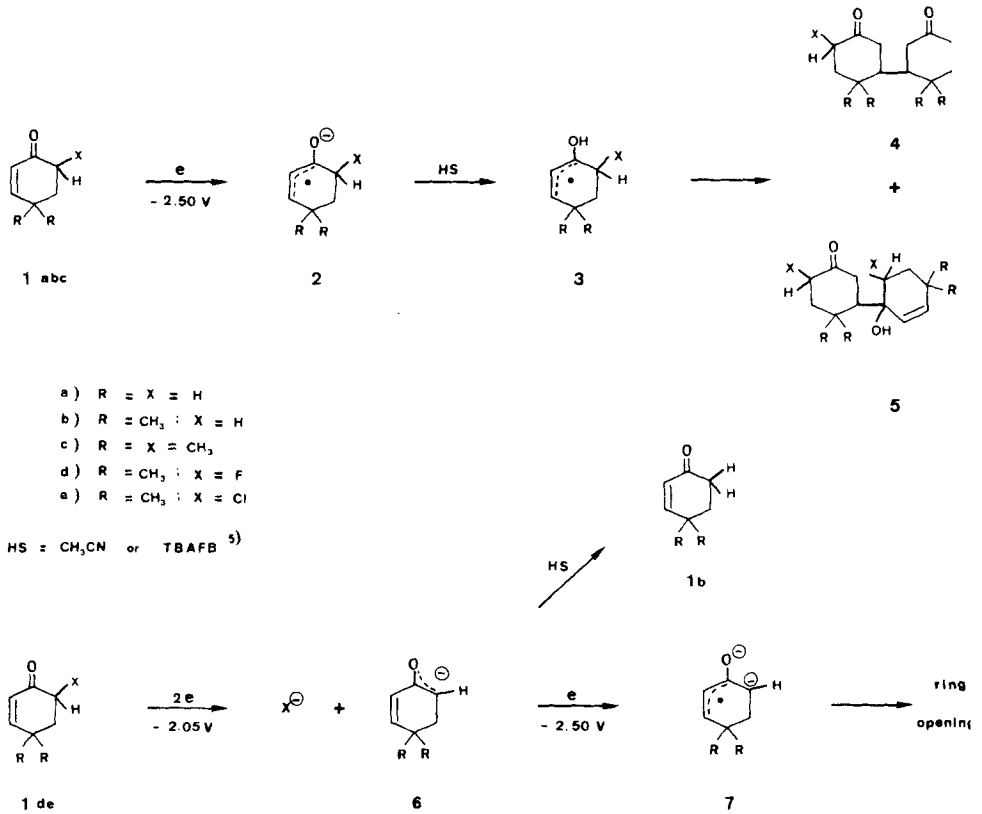
Some aspects of the reaction sequence for the 6-halocyclohex-2-enones deserve a more detailed analysis. First **1d** and **1e** do not give hydrodimers at low potentials as protonation of the anion radical **2** is much slower than the consecutive halide

Table 3. *Yields of isolated products in preparative electrolyses of* **1a**–**1e** (5.10^{-3} mol in 15 ml CH_3CN containing 0.5 M TBAFB)

Compound	Potential V *vs* Ag/Ag^+	Product distribution
1a	−2.50	25% **4a**[a])
1b	−2.50	25% **4b**[a])+15% **5b**
1c	−2.50	27% **4c**[a])
1d	−2.05	18% **1b**
	−2.50	[b])
1e	−2.05	60% **1b**
	−2.50	[b])

[a]) Diastereomeric mixture, *cf.* [10–12].
[b]) Mixture of products, all of them < 5% yield.

Scheme 2



anion elimination. This event could take place either after the almost simultaneous transfer of the second electron or before, *i.e.* the formation of **6** would be due to the reduction of its corresponding radical. We tend to favour the first possibility due to the non-occurrence of any coupling-elimination for these compounds [13]. Furthermore it is interesting that no hydrodimers **4b** or **5b** are observed in the reduction of **1d** or **1e** at more negative potentials. This would imply that the radical dianion **7** is not diprotonated but reacts further, *e.g.* by ring opening. Other experiments for studying the step **6** → **7** under different conditions are necessary, as well as investigation of the behaviour of cyclohex-2-enones with different substitutions, such as 2- or 3-chloro-cyclohex-2-enones. Such studies are now in progress.

Experimental Part

Materials. – Cyclohex-2-enone (**1a**, *Fluka*) was distilled before use. **1b** [15], **1c** [16], **1d** [17] and **1e** [18] were synthesized following the literature. Acetonitrile was purified as in [19]. Tetrabutylammonium fluoroborate was prepared according to [20].

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5) *Cf.* p. 409 in [2].

Cyclic voltammetry and d.c. polarography. – 1. *Electronics.* A potentiostat (*Wenking PCA 72 L*), an electronic ramp generator (*Wenking WFG72*) and a potentiometric XY recorder were used.

2. *Cell and electrodes.* The electrolytic cell (*Metrohm EA 840-20-T*) was equipped with a magnetic stirrer and a N_2-inlet and outlet. The temperature was kept at 10°. The volume of the solutions was 15 ml. The concentration of the supporting electrolyte (TBAFB) was $5 \cdot 10^{-1}$ mol/l. All solutions were prepared and handled in a dry box. A Pt-anode was used as counter electrode and Ag/Ag^+ 10^{-2}M as reference electrode. For polarography the forced dropping time was 1.4 s at −2.2 V. For cyclic voltammetry a hanging mercury drop of 1.6 mm^2 surface area was employed as working electrode. The concentration range of **1** was 2.10^{-4}M–5.10^{-3}M.

Coulometry. – The same cell described above with a mercury pool of 6.6 cm^2 surface area as working electrode was used. The current quantity was determined with an *AMEL 558* integrator. The decrease in concentration of the cyclohexenones was monitored by GC. (5% SE 30, 160°) with an internal standard (triglyme for **1b** and diethyleneglycol diethylether for **1e**). Thus $5.3.10^{-3}$ mol **1** were electrolysed up to 20–30% conversion in 15 ml CH_3CN containing 0.5 mol/l TBAFB and 1 ml standard.

Preparative electrolyses at controlled potential and product analysis. – The same cell and electrode arrangement as described for the coulometry experiments were used. About 5.10^{-3} mol **1** in 15 ml CH_3CN containing 0.5 mol/l TBAFB were electrolysed with the amount of current necessary for 100% conversion. The solvent was evaporated and 20 ml ether were added to the residue. The ether solution was filtered and evaporated. The residue was then chromatographed on a column (50 g silicagel, benzene/ethyl acetate 2:1) and the fractions analysed by NMR., IR. and mass spectrometry.

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