Electrochemical Reduction of 3-Chloro-2-cycloalkenones

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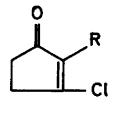
Previously[1] aryl 2-chlorovinyl ketones (*4*) (RAr–CO–CH=CHCl) have been investigated electrochemically; the major products were diaroylbutenes and diaroylbutadienes, formed by dimerization of a primarily formed radical or through an ionic mechanism. The reduction of 2-chloro-2-cyclohexenones (*5*) at a mercury cathode in acetonitrile at the first wave[2] has been found to yield the cyclohexenones.

Substituted 2-cycloalkenones (*3*) are of interest in the synthesis of many compounds; one way of obtaining *3* is to reduce 3-chloro-2-cycloalkenones (*1*). As reducing agents, zinc,[3] zinc/potassium iodide[4] and a zinc-silver alloy,[5] have been employed.

The electrochemical reduction of *1* to *3* might be an attractive alternative to the known methods; the results of an electroanalytical and preparative investigation of *1* are reported below. In the investigation are included 2-alkyl-3-chlorocyclopent-2-en-1-ones (*6a–6g*), 3-chloro-5,5-dimethylcyclohex-2-en-1-one (*7*) and the mercury compound (*8*) obtained from *7*.



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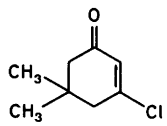

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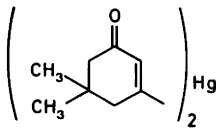

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a R=CH_3 *d* R=C_4H_9 *f* R=C_6H_{13}
b R=C_2H_5 *e* R=C_5H_{11} *g* R=C_7H_{15}
c R=C_3H_7

Results and discussion. Cyclic voltammetry of *7* in *N*,*N*-dimethylformamide (DMF) containing tetrabutylammonium iodide (TBAI) shows two waves, 7A and 7B; the first one is irreversible at the scan rates (v) investigated (0.04 to 1000 V s^{-1}); dE_p (d log v)$^{-1}$ = −51 mV, which indicates a rather slow rate of the heterogeneous charge transfer. Wave 7B is also irreversible with dE_p (d log v)$^{-1}$ = −57 mV. As 7B corresponds to the reduction of *3* and the relative height of 7A and 7B does not change with v the chemical reactions following the charge transfer step of 7A must be rather fast. The voltammetric behaviour of *7* is not influenced by the addition of carbon dioxide, which also points to a fast follow-up reaction.

8 behaves similarly to *7*, the second wave of *8* falling at the same potential as 7B. At 400 mV s^{-1} the difference in peak potentials between 7A and 7B is 370 mV whereas it is 170 mV between the two peaks of *8*. No indication of the formation of *8* is seen on the voltammograms of *7*.

Cyclic voltammetry of *6a–6g* in aprotic and in protic media (pH < 7) exhibits also two irreversible waves; the second peak grows on addition of the corresponding cyclopentenone. The peak potentials of *6a–6g* are quite similar; in DMF/0.1 M tetraethylammonium perchlorate $E_1 = -1.94 \pm 0.01$ V and $E_2 = -2.34 \pm 0.02$ V *vs.* SCE; in a Testal buffer pH 1, $E_1 = -0.70 \pm 0.02$ V, and $E_2 = -1.13 \pm 0.05$ V *vs.* SCE. The peak potentials of *6* are dependent on pH in a way similar to that observed in α-halogenated carbonyl compounds.[6–8]

At the dropping mercury electrode (DME) *7* shows at pH < 7 in 50 % aqueous ethanolic solution a two-electron wave followed by a one-electron wave; the half-wave potentials are pH-dependent, but as the first wave is deformed by a pronounced maximum the determination of the half-wave potential is unsatisfactory. The maximum can be suppressed by Triton-100, but the wave is still somewhat deformed. The pH-dependence of the waves can be explained by a kinetically controlled preprotonation of the carbonyl group. At pH > 7 the two waves merge.

The polarography of *8* is similar to *7*, but the first wave is a one-electron wave and is shifted about 80 mV to more negative values compared to *7*. The maximum and the second wave is found at the same potentials as for *7*. The data are in accordance with the assumption that *8* is formed as an intermediate at the dropping mercury electrode in protic media.

Coulometric measurements of *6a* at the potential of the first wave gave in acid solution $n = 2$ F mol^{-1}, whereas $n = 1.3$ F mol^{-1} was found in DMF. The low n in DMF is not due to the formation of a dimer, as it would be a conjugated diketone reducible at the potential employed. A formation

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of a mercury compound or a polymerization might explain the results; a hydrogen atom abstraction might also occur.[11,12] *7* forms, a.o., some mercury compounds during preparative reduction in DMF.

Coulometry in DMF at a potential at the crest of the second peak of *6a* gave $n=2.1$ F mol^{-1}; α,β-unsaturated ketones are in general reduced in a one-electron reaction in aprotic media.[9,10]

Preparative reduction in methanolic sulfuric acid (0.1 M) at mercury, lead or zinc cathodes of *6a*–*6g* gives the corresponding alkylcyclopent-2-enones in good material yield; the current yield is about 80 % at mercury and lead but about 30 % at zinc electrodes; the latter has a lower hydrogen overvoltage and a certain hydrogen evolution can be expected.

Reduction of *7* in 0.5 M hydrochloric acid containing 20 % ethanol gave bis(5,5-dimethyl-3-ketocyclohex-1-enyl) mercury (*8*) as the main product (85 %) together with minor amounts of the cyclohexenone, $n=1$ F mol^{-1}. *8* precipitates during the electrolysis and is thus protected against further reduction.

Mercury compounds have been reported during reduction at mercury cathodes of different types of compounds, *e.g.* ketones[13] and different kinds of halides.[14–17]

Mercury compounds are also formed during the reduction of *6a*–*6g* in protic media. From electrolyses of these compounds in 50 % aqueous methanolic buffers pH 4–7 mercury compounds (*9*) analogous to *8* can be isolated, and a plot of the concentration of *6* against the electricity consumption reveals that the reduction begins as a one-electron reaction, but ends as a two-electron reduction (Fig. 1), indicating the intermediary formation of a dimeric product (*9*).

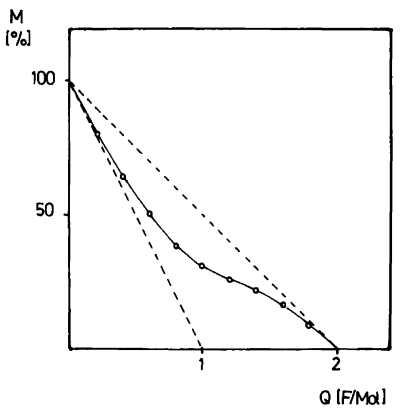

Fig. 1. Concentration (in % of initial concentration) of 3-chloro-2-methylcyclopent-2-enone (*6a*) in dependence of the electricity consumption during an electrolysis at a mercury cathode in 0.1 M methanolic sulfuric acid.

The results from both polarographic and preparative experiments suggest that mercury compounds are formed as intermediates from vinylogous acid chlorides (*6* and *7*) in protic media at DME and the stirred mercury pool electrode; at the HMD electrode no evidence is found of the formation of mercury compounds neither in DMF nor in aqueous–methanolic buffers. It seems as if a continuous renewal of the surface favours the formation of mercury compounds. At a stationary electrode the primarily formed radicals might react with the surface with the formation of a layer which is further reduced or which prevents the formation of *8* and *9*.

Organometallic compounds were not detected during the reduction of *6* at lead or zinc electrodes. Organolead or especially organozinc compounds are more reactive than the corresponding mercury compounds; furthermore, the tendency to form organometallic compounds seems less at a solid electrode.

In conclusion, the electrochemical removal of chlorine from 3-chloro-cycloalk-2-enones is found to be an attractive alternative to the traditional chemical reductions; lead and mercury have been found to be suitable electrode materials and from cyclic voltrammetric data glassay carbon should also be well-suited for preparative purposes.

Experimental. The apparatus has been described elsewhere.[1] The compounds *6a*–*6g* and *7* were prepared from the corresponding 1,3-diketones by means of phosphorus trichloride.[4]

Electrolysis of 2-alkyl-3-chlorocyclopent-en-1-ones. *6* (5 g) was reduced at −0.80 to −0.85 V *vs.* SCE in 0.1 M methanolic sulfuric acid; the anolyte was aqueous 0.1 M sulfuric acid. The proton activity in the catholyte was held constant by addition of sulfuric acid. The current density was 10 mA cm^{-2} at the beginning of the electrolysis and decreased to 0.1 mA cm^{-2} at the end. The catholyte was then added to 100 ml of water and extracted several times with diethyl ether, which was washed with an aqueous solution of sodium bicarbonate and dried over calcium chloride. The diethyl ether was evaporated and the residue distilled *in vacuo*. yields at different electrodes and the data are given below.

2-Methylcyclopent-2-enone: Yield: Hg 91 %, Pb 78 %, Zn 86 %, b.p.$_{10}$ 45–46 °C; IR (CCl_4, cm^{-1}): 1700, 1640. ^{1}H NMR (CCl_4): δ 1.66 (3 H, s); 2.27 (2 H, m); 2.46 (2 H, m); 7.28 (1 H, m). MS [*m/e* (% rel. int.)]: 96 (79), 81 (10), 68 (31), 67 (100), 53 (53), 39 (53).

2-Ethylcyclopent-2-enone: Hg 95 %, Pb 82 %, b.p.$_{10}$ 53–54 °C; IR (CCl_4, cm^{-1}): 1700, 1630. ^{1}H NMR (CCl_4): δ 1.00 (3 H, t); 2.08 (2 H, m);

2.21 (2 H, m); 2.48 (2 H, m); 7.18 (1 H, m). MS [*m/e* (%)]: 110 (56), 95 (28), 67 (100), 53 (23), 41 (30).

2-Propylcyclopent-2-enone: Hg 76 %, Pb 78 %, $b.p._{0.3}$ 48–49 °C; IR (CCl_4, cm^{-1}): 1690, 1620. ^1H NMR (CCl_4): δ 0.85 (3 H, t); 1.43 (2 H, m); 2.04 (2 H, m); 2.23 (2 H, m); 2.49 (2 H, m); 7.16 (1 H, m). MS [*m/e* (%)]: 124 (10), 109 (10), 96 (10), 67 (10), 27 (100).

2-Butylcyclopent-2-enone: Hg 96 %, Pb 86 %, $b.p._{0.4}$ 53–55 °C; IR (CCl_4, cm^{-1}): 1700, 1630. ^1H NMR (CCl_4): δ 0.88 (3 H, t); 1.34 (4 H, m); 2.06 (2 H, m); 2.21 (2 H, m); 2.48 (2 H, m); 7.14 (1 H, m). MS [*m/e* (%)]: 138 (99), 123 (36), 110 (66), 96 (100).

2-Pentylcyclopent-2-enone: Hg 85 %, Pb 87 %, $b.p._{0.1}$ 52–53 °C; IR (CCl_4, cm^{-1}): 1700, 1630. ^1H NMR (CCl_4): δ 0.83 (3 H, t); 1.26 (6 H, m); 2.06 (2 H, m); 2.19 (2 H, m); 2.48 (2 H, m); 7.16 (1 H, m). MS [*m/e* (%)]: 152 (50), 124 (29), 109 (36), 96 (76), 28 (100).

2-Hexylcyclopent-2-enone: Hg 77 %, Pb 95 %, $b.p._{0.2}$ 79–80 °C; IR (CCl_4, cm^{-1}): 1700, 1630. ^1H NMR (CCl_4): δ 0.84 (3 H, t); 1.26 (8 H, m); 2.06 (2 H, m); 2.20 (2 H, m); 2.47 (2 H, m); 7.12 (1 H, m). MS [*m/e* (%)]: 166 (52), 138 (33), 123 (29), 109 (29), 97 (100), 96 (40).

2-Heptylcyclopent-2-enone: Hg 85 %, Pb 92 %, $b.p._{0.07}$ 89–90 °C; IR (CCl_4, cm^{-1}): 1710, 1640. ^1H NMR (CCl_4): δ 0.81 (3 H, t); 1.27 (10 H, m); 2.05 (2 H, m); 2.20 (2 H, m); 2.47 (2 H, m); 7.13 (1 H, m). MS [*m/e* (%)]: 180 (29), 137 (27), 123 (24), 109 (25), 97 (100), 96 (78).

Reduction of 3-chloro-5,5-dimethylcyclohex-2-enone, 7. 7 (2 g) was reduced at a mercury pool electrode in 0.5 M hydrochloric acid containing 20 % ethanol at −0.7 V (SCE), $n = 1.0$ F mol^{-1}. During the reduction a white precipitate was formed. After the current had decreased to about 10 mA (0.3 mA cm^{-2}) the reaction was stopped, the precipitate (2.41 g, 85.5 %) collected and the filtrate extracted with diethyl ether. After drying, the solvent was evaporated leaving a residue (180 mg) which according to the ^1H NMR spectrum mainly consisted of 5,5-dimethylcyclohex-2-enone.

The precipitate, recrystallized from butanol, had m.p. 252–254 °C. It was proved to be bis(5,5-dimethyl-3-ketocyclohex-1-enyl) mercury from the spectral data. ^1H NMR ($CDCl_3$): δ 1.05 (6 H, s); 2.24 (2 H, s); 2.45 (2 H, d, J 2.1 Hz); 5.99 (1 H, t, J 2.1 Hz). The MS showed the characteristic Hg-isotope pattern at *m/e* Hg+246. IR spectrum [cm^{-1} (int.)]: 2900 (m), 1640 (vs), 1565 (m), 1292 (s), 1268 (s), 1245 (s), 1135 (m), 990 (m), 903 (m), 860 (m).

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