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Electrocatalytic dehalogenation of α-bromoketones in the presence of Cp_2TiCl_2

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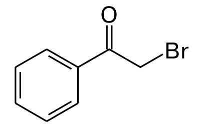
Processes of direct and electrocatalytic (in the presence of electrochemically reduced Cp_2TiCl_2) reduction of three α-bromoketones containing the $C(sp^3)$—Br or $C(sp^2)$—Br bond, *viz.*, 2-bromo- and 2,6-dibromo-4,4-dimethylcyclohexa-2,5-dien-1-ones and α-bromoacetophenone, were studied by cyclic voltammetry and preparative electrolysis. In all cases, the dissociative electron transfer proceeds *via* the concerted mechanism. Preparative electrolysis of these α-bromoketones in the presence of Cp_2TiCl_2 affords the reductive debromination products in 40—80% yield at low cathodic potentials (–0.85 V *vs.* Ag/AgCl/KCl). In the case of 2,6-dibromo-4,4-dimethylcyclohexa-2,5-dien-1-one in the potentiostatic regime, only one bromine atom can be eliminated selectively.

Key words: electrochemical reduction, α-bromoketones, electrocatalytic reactions, mediator catalysis, titanocene dichloride.

In most cases, the direct electrochemical reduction of alkyl and vinyl halides occurs at rather high negative potentials[1] and, therefore, the dehalogenation of complicated polyfunctional compounds is usually nonselective. The use of non-direct electrocatalytic reduction (mediator redox catalysis) makes it possible to decrease considerably the potential of the reaction, which can be substantial for selectivity of the process.

It is known[2] that in the nature many dehalogenation processes proceed *via* the reduction mechanism involving the catalysts containing the compounds of Co,[3,4] Ni,[5—7] Cu,[8] and other metals. We have previously shown[9,10] that the electrochemically reduced titanocene dichloride (Cp_2TiCl_2) can serve as a catalyst for the reductive dehalogenation of benzylic halides, whereas aryl halides usually undergo no dehalogenation. The present work continues these studies and is devoted to the elucidation of the applicability of this approach to cleavage of the C—Hal bond of other types. α-Bromoketones containing the $C(sp^3)$—Br or $C(sp^2)$—Br bond, which is activated by the adjacent carbonyl group, namely, α-bromoacetophenone (**1**), 2,6-dibromo- (**2**) and 2-bromo-4,4-dimethylcyclohexa-2,5-dien-1-one (**3**), were chosen as objects for the study. The latter two compounds are of special interest, because they represent the structural fragment of discorhabdine molecules C and E (**4** and **5**, respectively), which are present in the *Lafrunculia* sea sponge. It is known[11] that the antimicrobial properties of natural discorhabdines are due to the ability of the C—Hal bond to cleave. This cleavage proceeds presumably *via* the reduction mechanism. Therefore, it was interesting to reveal whether the electrocatalytic dehalogenation of similar compounds is possible in the presence of the electrochemically reduced titanocene dichloride and whether this process is a model of reactions involving discorhabdines in the nature or not.



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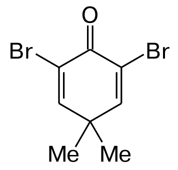

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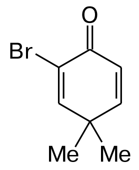

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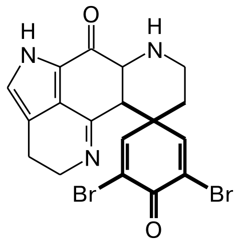

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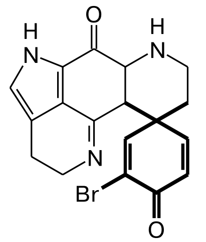

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Experimental

Cyclic voltammograms (CV curves) were recorded using an IPC-Win potentiostat at the stationary Pt electrode (d = 5 mm) against Bu_4NBF_4 in anhydrous organic solvents (THF, MeCN) at 20 °C in a special electrochemical cell switched on according

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to the three-electrode scheme. The potential sweep (υ) was varied from 50 to 500 mV s^{-1}. Electrolyses were carried out using a P-5827M potentiostat in a divided 10-mL electrolytic cell; the working electrode was a graphite tissue 1×1 cm^2 in size mounted on a Pt wire. In all cases, the counter Pt electrode and the Ag/AgCl/KCl(sat.) reference electrode (potential –0.47 V (in MeCN) *vs.* Fc/Fc^+) were used. The potential peak values were recalculated taking into account ohmic losses.

LC-MS analysis was carried out on a Finnigan MAT SSQ 7000 instrument (ionization energy 70 eV) equipped with an HP-5 (30 m) capillary silicone column.

Acetonitrile (pure grade) was stirred for 12 h over CaH_2, distilled, then refluxed for 2 h over P_2O_5, and distilled again collecting the fraction with b.p. 81—82 °C (760 Torr); THF (pure grade) was stirred over KOH, then distilled from $LiAlH_4$, and stored over sodium benzophenoneketyl. The freshly distilled portion of the solvent was used in each entry.

Preparative electrolysis was performed in an appropriate solvent in the potentiostatic regime at the reduction potential of Cp_2TiCl_2 (–0.85 V) and the concentration of Cp_2TiCl_2 and organic halide equal to 3 and 7—10 mmol L^{-1}, respectively. The electrolysis course was monitored using a digital amperometer from a change in the current. After the end of electrolysis ($Q \approx 2$ F per 1 mole of organic halide), the solvent was evaporated *in vacuo* (~100 Torr) and the reaction products were extracted with ether and examined using GLC and LC-MS analyses. The yields and efficiencies were determined as based on the starting halide.

Debromination of 2-bromo-4,4-dimethylcyclohexa-2,5-dien-1-one (3). ***A.*** Titanocene dichloride (7.5 mg, $3\cdot10^{-5}$ mol) was dissolved in THF (10 mL), and Bu_4NBF_4 (380 mg, 10^{-4} mol) and bromoketone **3** (13.8 mg, $7\cdot10^{-5}$ mol) were added. Preparative electrolysis was carried out using the general procedure at a potential of –0.85 V (*vs.* Ag/AgCl/KCl) and stopped after 15.9 C electricity (2.35 F per 1 mole of the starting bromoketone) passed through the solution. The yield of 4,4-dimethylcyclohexa-2,5-dien-1-one was 33%, and the efficiency was 28%. MS, *m/z*: 122 $[M]^+$, 107 $[M^+ - Me]$, 92 $[M^+ - 2\ Me]$, 64 $[M^+ - 2\ Me - CO]$. The fraction of the unreacted bromide **3** was ~65%.

B. The experiment was carried out analogously but a solution of Bu_4NBF_4 (190 mg, $5\cdot10^{-5}$ mol) in MeCN was used as the supporting electrolyte. For an electric charge of 14.2 C (2.1 F per 1 mole of the initial bromoketone), the yield of 4,4-dimethylcyclohexa-2,5-dien-1-one was 38% and the efficiency was 36%.

Debromination of 2,6-dibromo-4,4-dimethylcyclohexa-2,5-dien-1-one (2). ***A.*** Titanocene dichloride (7.5 mg, $3\cdot10^{-5}$ mmol) was dissolved in THF (10 mL), and Bu_4NBF_4 (380 mg, 10^{-4} mol) and dibromoketone **2** (22.5 mg, $8\cdot10^{-5}$ mol) were added. Preparative electrolysis was carried out according to the general procedure at a potential of –0.85 V (*vs.* Ag/AgCl/KCl) and stopped after 15.5 C of electricity (2.05 F per 1 mole of the initial dibromoketone) passed through the solution. The yield of 2-bromo-4,4-dimethylcyclohexa-2,5-dien-1-one was 52%, and the efficiency was 51%. MS, *m/z*: 200 $[M]^+$, 121 $[M^+ - Br]$, 106 $[M^+ - Br - Me]$, 91 $[M^+ - Br - 2\ Me]$, 63 $[M^+ - Br - 2\ Me - CO]$. The fraction of the unreacted dibromide **2** was ~40%.

B. The experiment was carried out similarly, but a solution of Bu_4NBF_4 (190 mg, $5\cdot10^{-5}$ mol) in MeCN was used as the supporting electrolyte. For 17.9 C of electricity (2.3 F per 1 mole of the starting dibromoketone) passed through the solution, the yield of 2-bromo-4,4-dimethylcyclohexa-2,5-dien-1-one was 82% and the efficiency was 71%.

Debromination of α-bromoacetophenone (1). Titanocene dichloride (7.5 mg, $3\cdot10^{-5}$ mol) was dissolved in MeCN (10 mL), and Bu_4NBF_4 (190 mg, $5\cdot10^{-5}$ mol) and α-bromoacetophenone (**1**) (19.8 mg, 10^{-4} mol) were added. Preparative electrolysis was carried out according to the general procedure at a potential of –0.85 V (*vs.* Ag/AgCl/KCl) and stopped after 21.4 C of electricity (2.2 F per 1 mole of the initial bromoketone) passed through the solution. The yield of acetophenone was 54%, and the efficiency was 49%. The fraction of the starting bromoketone **1** was 5%. The reaction mixture also contained the trans-halogenation product: α-chloroacetophenone (35%).

Results and Discussion

Direct electrochemical reduction (ER) of organic halides is a classical example of the dissociative electron transfer (DET) accompanied by the σ-bond cleavage. The DET is a convenient and chemically pure method for the generation of a reactive radical species due to the oxidation or reduction process. The DET reactions have first been considered theoretically.[12] To the present time, numerous electron-transfer reactions accompanied by the cleavage of the C—C, C—O, O—O, C—Hal, and C—S σ-bonds, as well as σ-bonds of other types (see, *e.g.*, Refs 13 and 14 and literature cited therein). The dissociative electron transfer from the donor to acceptor can be inter- or intramolecular and proceed *via* the concerted or two-step mechanism.

$$RX + e \rightleftharpoons R^{\cdot} + X^{-}\ \text{(concerted)}$$

$$RX + e \rightleftharpoons RX^{\cdot -} \rightleftharpoons R^{\cdot} + X^{-}\ \text{(stepwise)}$$

This or another mechanism occurs due to the sum of many factors,[15] the most important of which are the driving force and the internal activation barrier ($\Delta G_0{}^{\neq}$). The latter includes such parameters as the energies of bond reorganization and dissociation. The driving force is established by the comparison of the standard potentials for the concerted and stepwise mechanisms. The direction of the process depends on both the substrate nature and external factors, *e.g.*, temperature or potential.[13] The existence of the radical anion, whose lifetime is longer than the period of bond vibration (~10^{-13} s), is a necessary but not sufficient pre-requisite for the stepwise mechanism to occur. In addition to two opposite mechanisms, there are boundary situations due to which distinctions between the concerted and stepwise mechanisms become not so unambiguous. A problem arises how to determine the criterion for the occurrence of the process *via* this or another mechanism. For instance, it was shown[13] that a possible criterion can be the electrochemical transfer coefficient α calculated from the experimental data. The both mechanisms are characterized by the linear dependence of the α value on the potential and, therefore, the nonlinear region in the plot indicates that the mechanism has changed. As a rule, for the concerted mechanism controlled by the slow step of heterogeneous electron transfer $\alpha < 0.5$ (E_p is more negative than E^0), whereas for the stepwise mechanism $\alpha > 0.5$ (E_p is less negative than E^0).[15]

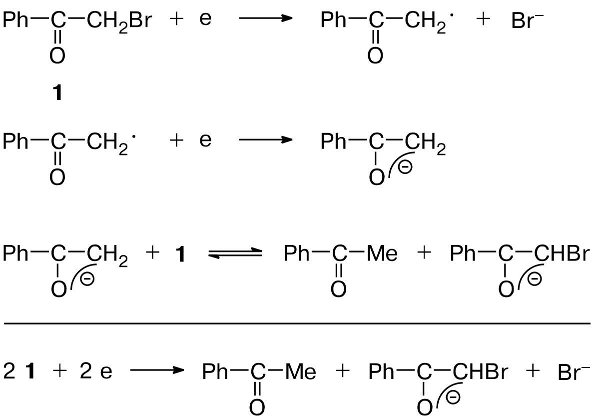
For substituted benzylic halides, the stepwise mechanism of ER occurs only in the case of the 4-nitro-substituted derivative ($\alpha > 0.5$); for other compounds of this series (CN-, OMe-substituted), the mechanism is most likely concerted.[15] The special properties of the 4-nitrosubstituted substrates were also found[16] when the ER of a series of substituted peroxy benzoates proceeding with the O—O bond cleavage were studied. It turned out that the stepwise mechanism was observed only for $4\text{-}NO_2C_6H_4CO_3Bu^t$, whereas the unsubstituted peroxides exhibit the purely concerted DET process; for the 4-COMe-, 3-NO_2-, and 4-CN-substituted derivatives, the transition from the stepwise to concerted mechanism was found with the shift of the applied potential to the region of less negative values. It is shown[17] in the case of substituted α-halogen- and α-benzoyloxyacetophenones that for the good leaving group (Br^- anion) the mechanism is determined by the reactivity of the radical anion formed. In the case of the electron-withdrawing substituents in the benzene ring (NO_2), the process proceeds *via* the stepwise mechanism ($\alpha > 0.5$), whereas the electron-donating substituents (OMe) are characterized by the concerted mechanism of the reaction ($\alpha < 0.5$). When the substrate contains the poorly leaving group (F, PhCOO), the process proceeds *via* the stepwise mechanism regardless of the nature of the substituent in the aromatic ring.

The DET mechanism in electrocatalytic processes is studied much more poorly. It has recently been shown[18] that the electrocatalytic reduction of several benzylic halides in the presence of $[Ni^I(salen)]^-$ (salen is *N*,*N*´-bis(salicylidene)-1,2-diaminoethane) proceeds *via* the mechanism of inner-sphere DET. It has been mentioned earlier[9,10,18] that the coordination of Ti^{III} with the substrate plays an important role in the electrocatalytic reduction of benzylic halides in the presence of titanocene dichloride. For nitrobenzyl halides, the process begins from the coordination of Ti^{III} at the NO_2 group of organic halide, is accompanied by the primary electron transfer to its π*-orbital (localized on the NO_2 group and aromatic ring), and is followed by the intramolecular electron transfer to the σ*-orbital of the C—Hal bond resulting in its cleavage.[10] In the case of unsubstituted benzyl halides, the coordination of Ti^{III} to the halogen atom (Cl, Br) is accompanied by the concerted electron transfer to the σ*-orbital of the C—Hal bond and cleavage of the latter.[10,19]

In the present work, we compared the processes of direct and electrocatalytic (in the presence of Cp_2TiCl_2) reduction of **1—3** containing the $C(sp^3)$—Br and $C(sp^2)$—Br bonds activated by the adjacent carbonyl group. These reactions are classified as processes with DET.

Direct electrochemical reduction of bromoketones 1—3. Two one-electron redox transitions can be observed in the CV curves of the direct ER of α-bromoacetophenone (**1**). The first one-electron peak ($E_1 = -1.18$ V) is related to the fast elimination of the bromide ion, which is oxidized during the reverse scan at a potential of 0.9 V. The second peak is attributed to the reduction of the carbonyl group ($E_2 = -1.75$ V). The data obtained agree well with published data.[17] The direct electrochemical reduction of compound **1** can be presented by Scheme 1.[17]

Scheme 1



The presence of a sufficiently acidic α-proton in the molecule of compound **1** induces autoprotolysis, due to which the number of consumed electrons becomes equal to two per two substrate molecules. Thus, formally one-electron reduction is observed, although the *ece*-process occurs.

Different methods are known for the estimation of the electrochemical transfer coefficient from the voltammetric data

$$\alpha = 1.85RT/[F(E_{p/2} - E_p)],$$
$$dE_p/d(\log\upsilon) = 1.15RT/\alpha F,$$

where $E_{p/2}$ is the potential at the half of the peak current value, and F is the Faraday constant (96 500 C mol^{-1}).

The electrochemical transfer coefficient α calculated from the difference $E_p - E_{p/2}$ (see Ref. 20) for compound **1** is equal to 0.17. The estimate based on the E_p—logυ plot gives a similar value ($\alpha = 0.19$). This indicates that halogen is eliminated *via* the concerted mechanism, which agrees with published data.[19]

The electrochemical reduction of bromocyclohexadienes has not been studied earlier. In the case of 2,6-dibromo-4,4-dimethylcyclohexa-2,5-dien-1-one (**2**),

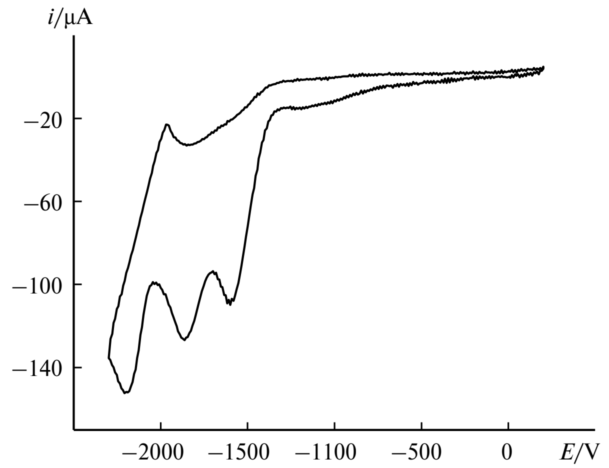
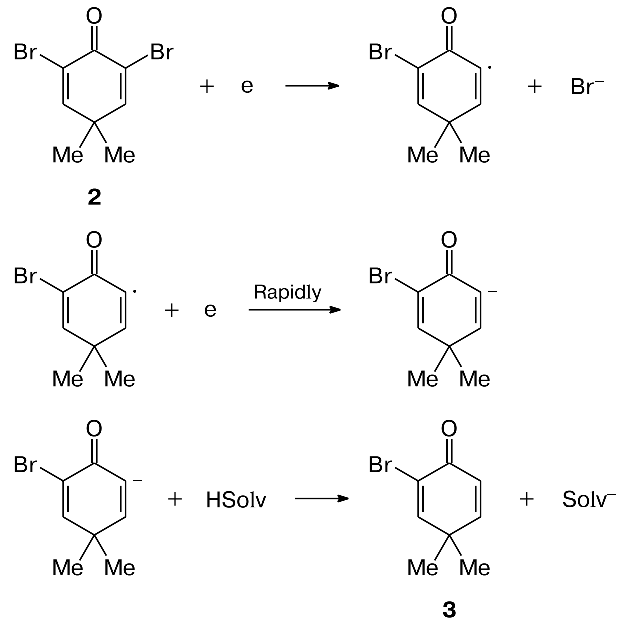


Fig. 1. CV curve of a solution of 2,6-dibromo-4,4-dimethylcyclohexa-2,5-dien-1-one (**2**) in MeCN (1 mmol L^{-1}) against 0.05 *M* Bu_4NBF_4 (Pt electrode, υ = 100 mV s^{-1}, *vs.* Ag/AgCl/KCl).

the former two peaks (E_1 = −1.48 V, E_2 = −1.72 V) are irreversible and correspond to the consecutive elimination of the bromine atoms, and the most negative peak (E_3 = −2.04 V) is reversible to the reduction of 4,4-dimethylcyclohexadienone (Fig. 1). The obtained value is well consistent with the data in Ref. 21, where the DET reactions of spiro[2.5]octa-4,7-dien-6-one accompanied by the C—C bond cleavage were studied.

The sequence of the ER steps of 2,6-dibromo-4,4-dimethylcyclohexa-2,5-dien-1-one (**2**) is shown in Scheme 2. Since the initial molecule of compound **2** contains no acidic protons, the two-electron reduction occurs, unlike that for α-bromoacetophenone (**1**). Traces of water present in the solvent can be a source of protons.

Scheme 2



HSolv is solvent

The CV curve for 2-bromo-4,4-dimethylcyclohexa-2,5-dien-1-one (**3**) contains by one peak less; however, in other respects it resembles the curve for dibromocyclohexadienone **2**. The observed values of potentials of the reduction peaks are E_1 = −1.65 V and E_2 = −2.02 V.

As it is known, the C(sp^2)—Br bond is substantially stronger than the C(sp^3)—Br bond. However, even with an increase in the sweep to 500 mV s^{-1} we could not detect the peak of radical anion re-oxidation in the CV curve, which indicates its low stability. The bromide ion is a good leaving group and, therefore, even the presence of the strong electron-withdrawing carbonyl group does not result in the formation of a stable radical anion.

The α coefficient for dibromocyclohexadienone **2** calculated from the data presented in Fig. 2 is equal to 0.25. The estimate by the $E_p - E_{p/2}$ difference (at the sweep 500 mV s^{-1}) gives α = 0.29. This implies that the concerted DET mechanism also occurs in this case.

Electrocatalytic reduction of compounds 1—3 in the presence of titanocene dichloride. The electrocatalytic reduction of organic halides by transition metal complexes was studied[22] much more poorly than the direct ER, because the presence of a catalyst affects strongly the character of DET. The ER processes using the complexes of Ni (see Ref. 17 and literature cited therein), Co,[23,24] Ti^{III},[9,10] Cu,[8] Ag,[25] and other metals. Unfortunately, the mechanisms of reactions that occur are not always studied in detail.

In the present work, we chose Cp_2TiCl_2 as the catalyst. Its electrochemical behavior has been studied in rather detail.[19,26—32] Titanocene dichloride is reduced to Ti^{III} at a potential of −0.85 V (*vs.* Ag/AgCl/KCl) at the Pt electrode in THF, while in MeCN it is reduced at a potential of −0.8 V to form species of three types: $[Cp_2TiCl_2]^{\bullet-}$,

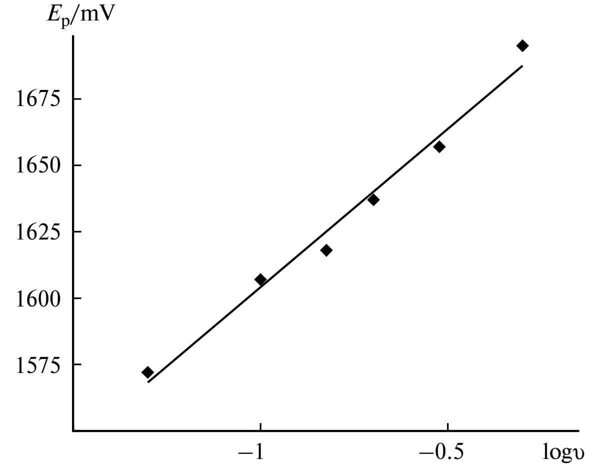


Fig. 2. Reduction potential of dibromoketone **2** (E_p) as a function of the potential sweep (logυ) (correlation coefficient 0.9828).

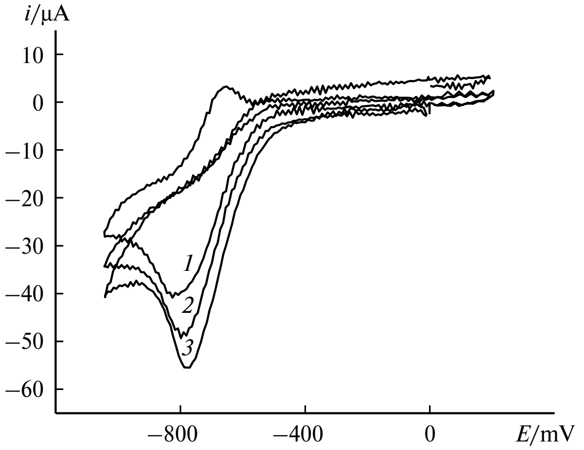


Fig. 3. CV curves for Cp_2TiCl_2 (*1*) and Cp_2TiCl_2 with an additive of 0.5 (*2*) and 1 mmol L^{-1} (*3*) bromoketone **3** (THF, 0.05 *M* Bu_4NBF_4, υ = 100 mV s^{-1}, Pt electrode, *vs.* Ag/AgCl/KCl).

Cp_2TiCl, and $[Cp_2TiCl]_2$, whose relative yield depends on the concentration of the starting Cp_2TiCl_2.[30] The introduction of Cp_2TiCl_2 into the reaction mixture makes it possible to decrease considerably the reduction potential of haloketones **1**—**3**. The change in the character of Cp_2TiCl_2 reduction and Ti^{III} re-oxidation in the presence of 2-bromo-4,4-dimethylcyclohexa-2,5-dien-1-one (**3**) is shown in Fig. 3. As it is seen, the addition of bromide **3** results in the successive increase in the cathodic current of Cp_2TiCl_2 reduction and the disappearance of the peak of Ti^{III} re-oxidation, indicating the catalytic process.

An analogous situation is observed in the case of compound **2**: the successive increase in the cathodic current of Cp_2TiCl_2 reduction and the disappearance of the peak of Ti^{III} re-oxidation.

It can be seen from the comparison of the reduction potentials of compounds **2** and **3** that dibromosubstituted derivative **2** is reduced by 0.17 V more positively than monobromide **3**. The difference of potentials between the reduction peaks of these compounds and Cp_2TiCl_2 is 0.48 and 0.65 V, respectively. Since the electrochemical gap for the dibromosubstituted derivative is smaller, it can be expected that the electron transfer would be faster in this case. The preparative electrolysis data for compounds **2** and **3** in the presence of Cp_2TiCl_2 confirm this assumption. The yield of the debromination product is much higher in the case of the dibromosubstituted derivative (Table 1).

As indicated by the preparative electrolysis data, the mediator ER process allows one to eliminate selectively only one bromine atom in ketone **2**. The halogen atom in product **3** begins to eliminate to a noticeable extent only after the complete consumption of dibromide **2**, because the reaction rate is substantially higher in the latter case.

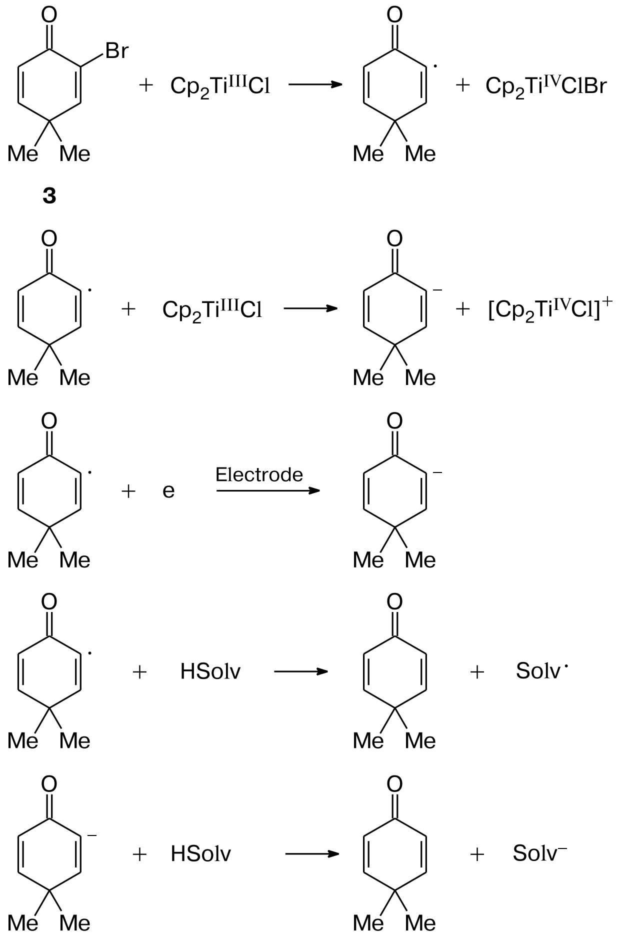
Table 1. Results of potentiostatic electrolysis of α-bromoketones **1**—**3** (C = 10 mmol L^{-1}) in the presence of Cp_2TiCl_2 (C_0 = 3 mmol L^{-1}, E = −0.85 V *vs.* Ag/AgCl/KCl)

α-Bromoketone	Solvent	Debromination product (%)	
		yield	efficiency
1	MeCN	54	49
2	MeCN	82*	71*
2	THF	52*	51*
3	MeCN	38	36
3	THF	33	28

* For the monodehalogenation product.

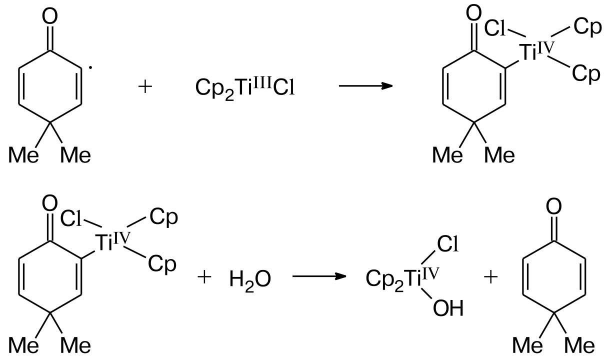
Based on the CV and preparative electrolysis data, the presumable mechanism of electrocatalytic conversion can be presented by Scheme 3.

Scheme 3



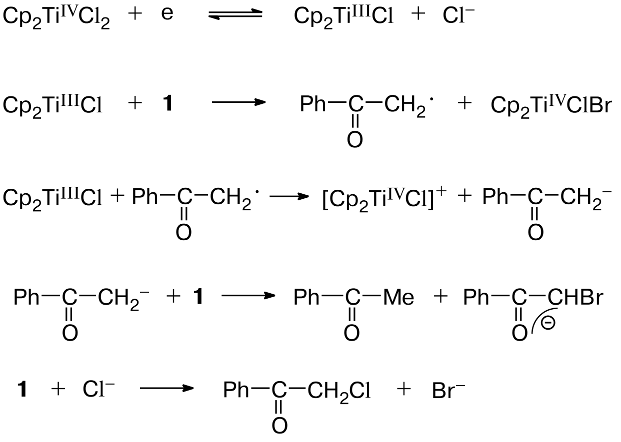
Although the Ti^{III} complexes are strong reducing agents, a possibility of the parallel process of interaction of paramagnetic $Cp_2Ti^{III}Cl$ with organic radicals to form an organotitanium compound cannot be excluded (Scheme 4). However, when the reaction products are isolated from the reaction mixture, the complex formed can decompose to yield the same dehalogenation product.

Scheme 4



Electrocatalytic debromination can be carried out for compound **1** as well. When the latter is added to a solution containing Cp_2TiCl_2, the CV curve exhibits an increase in the peak corresponding to the reduction of Ti^{IV} to Ti^{III} and a decrease in the peak of Ti^{III} re-oxidation, which is characteristic of the catalytic process. The preparative electrolysis under these conditions gave acetophenone in 54% yield (see Table 1). The assumed mechanism of redox catalysis can be presented by Scheme 5. Principally, a possibility of the formation of organotitanium intermediates (see Scheme 4) of the type $PhC(O)CH_2TiCp_2Cl$ or $PhC(=CH_2)OTiCp_2Cl$ cannot be excluded.

Scheme 5



$$\mathrm{Cp_2Ti^{IV}Cl_2} + e \rightleftharpoons \mathrm{Cp_2Ti^{III}Cl} + \mathrm{Cl^-}$$

$$\mathrm{Cp_2Ti^{III}Cl} + \mathbf{1} \longrightarrow \mathrm{Ph{-}\underset{\overset{\|}{O}}{C}{-}CH_2^{\cdot}} + \mathrm{Cp_2Ti^{IV}ClBr}$$

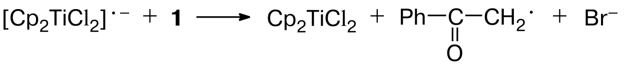
$$\mathrm{Cp_2Ti^{III}Cl} + \mathrm{Ph{-}\underset{\overset{\|}{O}}{C}{-}CH_2^{\cdot}} \longrightarrow [\mathrm{Cp_2Ti^{IV}Cl}]^+ + \mathrm{Ph{-}\underset{\overset{\|}{O}}{C}{-}CH_2^-}$$

$$\mathrm{Ph{-}\underset{\overset{\|}{O}}{C}{-}CH_2^-} + \mathbf{1} \longrightarrow \mathrm{Ph{-}\underset{\overset{\|}{O}}{C}{-}Me} + \mathrm{Ph{-}\underset{\overset{\|}{O}^{\ominus}}{C}{-}CHBr}$$

$$\mathbf{1} + \mathrm{Cl^-} \longrightarrow \mathrm{Ph{-}\underset{\overset{\|}{O}}{C}{-}CH_2Cl} + \mathrm{Br^-}$$

Since the solution of electrochemically reduced Cp_2TiCl_2 contains both $[Cp_2TiCl_2]^{\bullet-}$ and Cp_2TiCl or its dimer,[30] different forms of Ti^{III} can act as reducing agents. However, according to the estimate,[17] the standard potential for α-bromoacetophenone is $E^0(RBr/RBr^{\bullet-})$ = 1.76—2.01 V and, hence, the outer-sphere electron transfer from the coordinately saturated radical anion to organic halide (Scheme 6) is lowly probable.

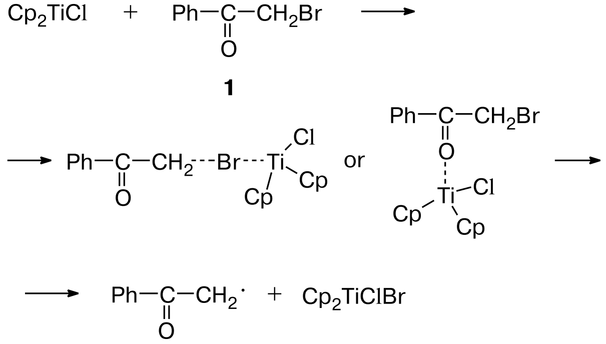
Scheme 6



$$[\mathrm{Cp_2TiCl_2}]^{\cdot -} + \mathbf{1} \longrightarrow \mathrm{Cp_2TiCl_2} + \mathrm{Ph{-}\underset{\overset{\|}{O}}{C}{-}CH_2^{\cdot}} + \mathrm{Br^-}$$

It can be assumed that the inner-sphere reaction rate is higher, especially if taking into account the high affinity of titanium to oxygen (Scheme 7).

Scheme 7



Thus, the data obtained indicate that the Cp_2TiCl_2/Cp_2TiCl redox system can serve as a catalyst for the reductive dehalogenation of α-haloketones. The reaction occurs at low cathodic potential (−0.85 V *vs.* Ag/AgCl/KCl(sat.)) and affords the target debromination products in a preparative yield (40—80%).

It should be mentioned in conclusion that dissociative electron transfer often occurs in the natural catalytic processes.[2,13,33] Intramolecular DET from the donor to acceptor in the natural systems occurs at rather long distances (>10 Å) and very rapidly (10^5 s^{-1}), although the driving force of such reactions is low, as a rule (only ~0.1 eV). This is probably achieved due to the geometry optimization of the reacting particles and a great role of the intramolecular interactions (for instance, hydrogen bonds) in a protein molecule. Our data indicate that bromoketones **2** and **3** containing the $C(sp^2)$—Br bond, which is activated by the adjacent electron-withdrawing group, easily undergo reductive dehalogenation at rather low (close to "biological") potential values. Perhaps, this process models the biological effect of natural discorhabdines C and E containing the fragments of the indicated ketones.

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