Electrochemical study of the sequence of reductive dehalogenation of 2-bromo-5-dibromomethyl-4-dichloromethyl-4-methylcyclohexa-2,5-dien-1-one and its analogs

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The electrochemical behavior of a series of halogen-containing cyclohexa-2,5-dien-1-ones at the glassy-carbon electrode in DMF was studied. The reductive dehalogenation of 2-bromo-5-dibromomethyl-4-dichloromethyl-4-methylcyclohexa-2,5-dien-1-one first results in the elimination of the carbonylallylic bromine atoms, then the carbonylic bromine atom is eliminated, and finally, the neopentylic chlorine atoms are eliminated.

Key words: cyclohexadienones, electrochemical reductive dehalogenation.

Electrochemical reduction (ER) of organic halides containing halogen atoms of different nature is one of the best studied areas of organic electrochemistry.[1—3] Presently, the ER of halogen-containing compounds is in progress.[4—8] This is associated with contamination of the environment with halogen-containing organic compounds, which get into the organism of haematherms and exert hepatotoxic and carcinogenic effects.[4] From the viewpoint of ecology, the most appropriate technology for the degradation of halogen-containing compounds in the environment is the use of microorganisms that produce enzymes of the cytochrome group operating *via* the redox mechanism. These enzymes, being present in both eukaryotic and prokaryotic cells, are polyfunctional and induce catabolism in numerous organic compounds.[5] Cytochromes P450 of animals and man have been shown[4,6—8] to dehalogenate in steps polyhalogen-containing hydrocarbons to less halogenated molecules, in particular, CCl_4 is dehalogenated to methane. Many halogen-containing drugs, for instance, halothane, diclofenac, itraconazole, clonazepam, and isoflurane, undergo the same reductive dehalogenation in the human organism.[9]

It is known[10] that halogen-containing dienones are used in the synthesis of several therapeutical preparations, and the recent studies showed that brominated dienones are natural pharmacophores. Bioactive amide of 2-(3-bromo-1-hydroxy-4-oxocyclo-2,5-dien-1-yl)acetic acid brominated at the dienone ring was isolated from a sponge of the *Aplisina fistularis* species.[11,12] A sponge of the *Latrunculia* species produces the previously unknown type of pentacyclic molecules, *viz.*, discorhabdins, containing the brominated dienone fragment due to which they possess high bioactivity and a wide spectrum of action. It is most likely that metabolites appeared due to catabolism are responsible for these properties of discorhabdins.[13,14]

An approach modeling dehalogenation processes of these pharmacophores can be the ER of their structural analogs, namely, halogen-containing cyclohexadienones, which were objects of our study. As the basic compound we chose 2-bromo-5-dibromomethyl-4-dichloromethyl-cyclohexa-2,5-dien-1-one (**1**) containing the Br and Cl atoms in different blocks of the molecule, which makes it possible to determine the sequence of dehalogenation in this molecule and also to predict this sequence for more complex halogen-containing compounds.

Results and Discussion

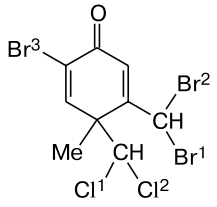
Molecule **1** contains three groups of halogen atoms of different nature: two neopentylic geminal chlorine atoms (Cl^1 and Cl^2), two carbonylallylic geminal bromine atoms (Br^1 and Br^2), and one α-carbonylvinylic bromine atom (Br^3). Based on published data,[1,2] we can be sure to a certain extent that one of the two geminal allylic Br atoms should be eliminated first at the least negative potentials. It remains unclear what C—Hal will be cleaved in the second step. Numerous experimental data show that the reduction is facilitated by the following factors: first, the element effect (the C—Br bond is reduced more easily that the C—Cl bond); second, the presence of the second halogen atom in the geminal position; third, the type of the carbon atom (allylic > alkylic > vinylic) to which halogen is bonded. However, it is unknown which of these factors predominates in each particular case. Therefore, it

† Deceased.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 9, pp. 1558—1564, September, 2006.

1066-5285/06/5509-1617

is very difficult to conclude unambiguously about the sequence elimination of halogen atoms during the reduction of compound **1**.



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Electrochemical study of compounds **1—11** was carried out by the methods of cyclic voltammetry (CV) and rotating disk electrode (RDE) at the glassy-carbon (GC) electrode in DMF solutions in the presence of Bu_4NClO_4. The results are presented in Table 1, and the cyclic voltammograms are shown in Figs 1—3. The sequence of reductive elimination of the halogen atoms in compound **1** can reliably be established by labor-consuming preparative electrolysis. Our approach for the identification of ER intermediates is the analysis and comparison of the obtained electrochemical data for cyclohexadienone **1**, less halogenated compounds **2—5** and **7**, and compounds **9** and **11** containing no halogen atoms. The latter can potentially be intermediate or final products of the reduction of ketone **1**.

For all compounds of the studied series, the number of added electrons (n) can reliably be determined in experiments using RDE only for the first step. However, for the second step this is possible only for some compounds containing one type of halogen atoms. To determine the n value for the reduction of complex compounds, n was first determined for compounds **9** and **11** containing no halogen atoms, and then the behavior of more halogenated compounds was studied. This provides the full pattern of the ER of pentahalogenated ketone **1**. This approach has been used earlier to determine the sequence of reductive debromination of bromine-substituted anisoles,[15] benzenes,[16] and some [2.2]paracyclophanes.[17]

None of compounds **1—11** is oxidized under the experimental conditions at the GC electrode, which allows us to judge about the nature of the eliminated halogen atoms from the reoxidation peaks of the halide ions observed in the anodic region upon the potential reverse after the corresponding cathodic peaks.

Table 1. Reduction potentials[a] of compounds **1—11** measured by CV (*vs.* Ag|AgCl|KCl (sat.)) at the GC electrode in DMF in the presence of 0.05 *M* Bu_4NClO_4

Compound	E_{pc}	$E_{1/2}$
	V	
1	−0.80/+0.84[b]; −0.98/+0.84[b]; −1.48/+0.84[b]; −1.59/+1.11[c]; −2.56	−0.83 (2)
2	−0.95/0.88[b];−1.47/0.86[b]; −1.58/1.10[c]; −2.62	−0.90 (2); −1.47[d]
3	−1.48/+0.92[b];−1.59/+1.12[c]; −2.42	−1.53(4); −2.42[d]
4	−1.56/+1.27[c]; −2.43	−1.52 (2); −2.42(1)
5	−1.37/+0.86[b]; −1.53/1.17[c]; −2.47	−1.30 (2); −1.54(2)
6	−1.53/+0.84[b]; −1.59/0.84[b]; −2.54	−1.57 (2); −2.54[d]
7	−1.61/+0.86[b]; −1.92/−1.82	−1.61(2); −2.03(1)
8	−0.83/0.86[b]; −0.93/0.86[b]; −1.49/0.86[b]; −1.55/0.86[b]; −2.21; −2.56	−0.80 (2)
9	−1.92/−1.82	−1.90 (1)
10	−1.26/1.15[c]; −1.49	−1.19 (2); −1.50[d]
11	−2.03; −2.51	−2.02 (1); −2.62 (1)

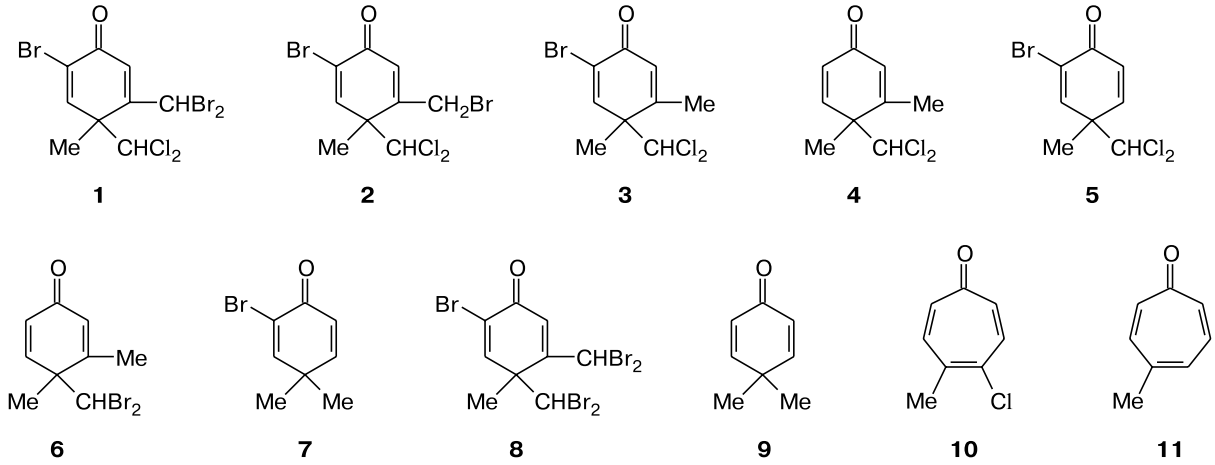
[a] E_{pc} are the potentials of cathodic peaks (200 mV s^{-1})/potentials of inverse peaks; $E_{1/2}$ are the potentials of half-waves measured by the RDE method (2800 rpm) (the number of electrons determined by comparison with the height of the one-electron oxidation wave of ferrocene is given in parentheses).

[b] Oxidation with Br^-.

[c] Oxidation with Cl^-.

[d] The number of electrons cannot be determined because of deep current decreases in the polarization curves.

The compounds under study exhibited only two-electron steps of reductive elimination of halogen atoms that can proceed *via* different mechanisms.[1,2] Two-electron



1 **2** **3** **4** **5**

6 **7** **8** **9** **10** **11**

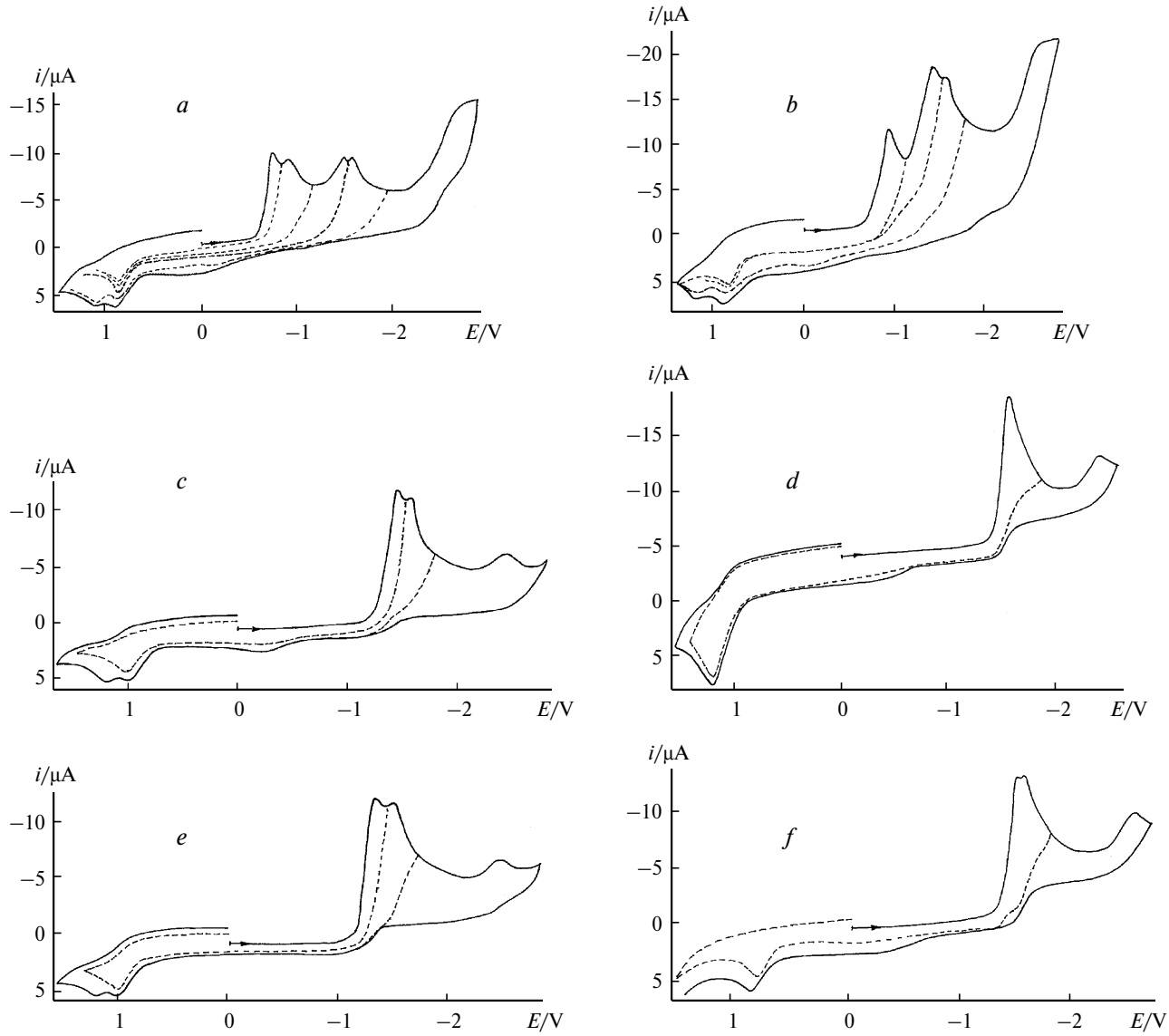


Fig. 1. Cyclic voltammograms of cyclohexadienones **1—6** (*a—f*, respectively) (10^{-3} mol L^{-1}, DMF, 0.1 *M* Bu_4NClO_4) at the GC electrode. Dashed lines are reverse scans after the corresponding cathodic peaks.

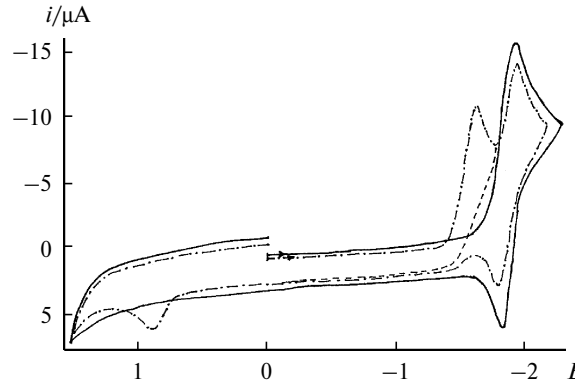


Fig. 2. Cyclic voltammograms of cyclohexadienones **7** (dashed line) and **9** (solid line) (10^{-3} mol L^{-1}, DMF, 0.1 *M* Bu_4NClO_4) at the GC electrode.

one-step reduction involving protons (Scheme 1, Eq. (2)), whose donors can be DMF and tetraalkylammonium cations,[1,2] is possible for monohalides. The same mechanism is especially characteristic of the reduction of *gem*-polyhalosubstituted compounds to form less halogenated compounds or hydrocarbons (see Scheme 1).

Scheme 1

$$RCHX_2 + 2\,e^- + H^+ \longrightarrow RCH_2X + X^- \quad (1)$$

$$RCH_2X + 2\,e^- + H^+ \longrightarrow RMe + X^- \quad (2)$$

However, some geminal dihalides undergo two-electron reductive elimination in one step involving no protons (Scheme 2).[1,2]

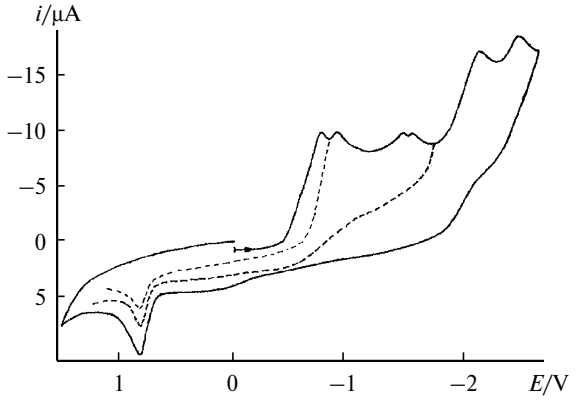
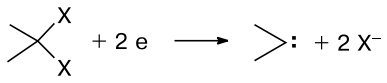


Fig. 3. Cyclic voltammogram of cyclohexadienone **8** (10^{-3} mol L^{-1}, DMF, 0.1 *M* Bu_4NClO_4) at the GC electrode. Dashed line indicates reverse scans after the corresponding cathodic peaks.

Scheme 2

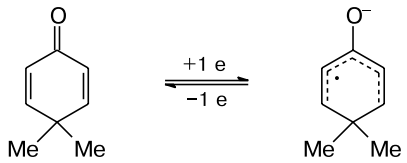


Probably, occurrence of this or another mechanism depends primarily on the structure of the compound subjected to ER.

The CV data for compound **1** show that the first redox process corresponds to the one-step two-electron reductive elimination of one Br atom in the form of a bromide ion, because its reverse scan contains the peak of its reoxidation, and then a proton is added to form hexadienone **2** as an intermediate product (see Fig. 1, *a*). The second reduction peak corresponds to the elimination of the Br atom from the bromomethyl group that formed, which follows from comparison of the potentials of compounds **1** and **2**. For compound **2** containing only one carbonylallylic Br atom, the potential of the first reduction peak is close to the potential of the second peak for compound **1** and the potential of the second peak is close to the potential of the first peak of ER of hexadienone **3** (see Fig. 1, *a*—*c*, Table 1). Therefore, compounds **2** and **3** are intermediates in the ER of compound **1**. Evidently, the first two reduction steps of compound **1** do not touch the neopentyl geminal Cl atoms, because the reverse scan contains no oxidation peaks of chloride ions.

To answer the question about the sequence of reductive elimination of the carbonylvinylic Br atom and geminal neopentylic Cl atoms, we studied compounds **4** and **7** (compound **4** contains only two geminal neopentyl Cl atoms, and compound **7** contains the carbonylvinylic Br atom only) and compound **9** containing no halogen atoms. The voltammetric curve obtained by the ER of the latter (see Table 1 and Fig. 2) exhibits the one-electron reversible reduction leading to the stable radical anion. This radical anion undergoes no further reduction under the experimental conditions (Scheme 3, see Fig. 2).

Scheme 3



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The CV curve for compound **7** shows distinctly the reoxidation of the bromide ion at E_{pa} = 0.86 V in the anodic region upon potential reverse after the potential of the first reduction peak was achieved (E_{pc} = −1.61 V). It follows from this that the first step in this case is the two-electron reductive elimination of the bromide ion. Then a proton is added to form compound **9** (see Scheme 1, Eq. (2)). The formation of compound **9** is additionally confirmed by the retention of reversibility of the second one-electron reduction peak of compound **7**, whose potential coincides with that of ER of compound **9** (see Fig. 2 and Table 1).

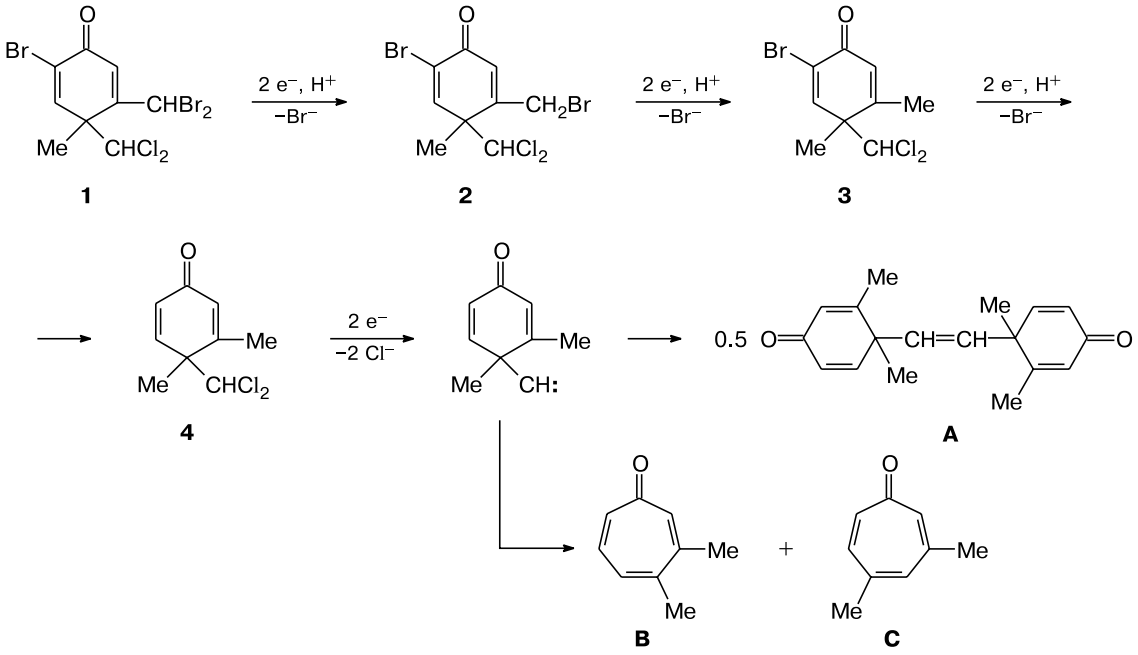
The first step of ER of compound **4** is the two-electron elimination of the chloride ions, which is indicated by the reoxidation peak of the chloride ion at E_{pa} = 1.27 V (see Fig. 1, *d*). The height of the first wave (see Table 1) and the intensity of the reoxidation peak assume the simultaneous reductive elimination of two chloride ions (see Scheme 1, Eq. (2)) followed by the dimerization of carbene (Scheme 4) and the formation of product **A**, as described earlier,[2] or by ring expansion leading to compounds **B** and **C** (see Ref. 18). Note that the subsequent ER of ketone **4** is one-electron and occurs when a strongly negative potential (−2.43 V) is achieved. Therefore, it can be assumed with high probability that this step corresponds to the reduction of one of the three possible products of the first step, namely, **A***, **B**, or **C****, rather than of neoalkyl chloride.

More negative reduction potentials of these products compared to that of 4-methyltropone **11** (see Table 1) are caused, most likely, by the second donor methyl group in them, which results in the cathodic shift. For compound **6**, the cathodic branch of the CV curve shows a similar pat-

* The dimer similar to **A** was synthesized by the treatment of 4-methyl-4-trichloromethylcyclohexa-2,5-dien-1-one $(PPh_3)_4Ni$ with a benzene—DMF mixture.[19] The electrochemical formation of compounds of type **A** by carbene dimerization during the reduction of geminal dihalides has been described[2] (p. 280).

** Tropones similar to **B** and **C** have been synthesized previously by the reduction of 4-dibromomethyl-4-methyl-2,5-cyclohexa-2,5-dien-1-one with zinc in DMF.[18]

Scheme 4



tern but the first ER peak is bifurcated, which indicates, probably, that the elimination of the bromide ions is incompletely synchronous compared to that of the chloride ions (see Fig. 3). A similar assumption has been advanced previously.[1,2] The elimination of the Br atom in the first step of ER of compound **6** can also be judged from the reoxidation peak of the bromide ions in the anodic region. It is noteworthy that the potentials of the first reduction peaks of compounds **4** and **6** almost coincide (see Table 1 and Fig. 1, *d*, *f*). Thus, the "heteroelement effect" [1,2] is absent in this case. Due to this effect substituted 4-dibromomethylhexadienone **6** should be reduced earlier than its dichloromethyl analog **4**. A similar regularity is also observed for the ER of ketone **8**: the potential corresponding to the reductive elimination of its neopentylic geminal Br atoms is close to the elimination potentials of the neopentylic Cl atoms characteristic of the ER of compounds **1—5** (see Table 1 and Figs 1, *a—e* and 3). Therefore, neither the nature or the presence of substituents in the dienone system affect the easiness of reductive elimination of the neopentylic halogen atoms in the substrates under study.

The key moment for the determination of the morphology of the CV curves of ketone **1** was to reveal the sequence of steps of halogen elimination during the ER of compound **5**. The structure of ketone **5** represents a superposition of compounds **4** and **7**. However, the reductive elimination of the carbonylvinylic Br atom in bromodienone **7** occurs at the potential value close to that observed for the elimination of the neopentylic Cl atoms in molecule **4**. Therefore, for ketone **5** it is difficult to establish *a priori* which of the halogen atoms undergoes reductive elimination at a lower potential.

On the one hand, the alkylic (especially geminal) halogen atoms are eliminated more easily than the vinylic halogen atoms. On the other hand, first, the electron-withdrawing carbonyl group is situated in the α-position to the Br atom; second, the Cl atoms are at the C atom of the neopentyl type and their reactivity to nucleophilic reactants is lowered.[20] In addition, in the general case the Br atom is eliminated more easily than the Cl atom. In the case considered, only the reoxidation peak of the bromide ion at E_{pa} = 0.86 V after the first ER peak of compound **5** suggests that in this molecule the Br atom is primarily eliminated (at the potential by 0.16 V "less cathodic" that the elimination potential of the geminal Cl atoms (see Fig. 1, *e* and Table 1)).

Unlike hexadienone **5**, the presence of the methyl group in position 5 of compound **3** exerts no effect on the potential of ER of the 4-dichloromethyl group but impedes the reductive elimination the carbonylvinylic Br atom (see Table 1: E_{pc} = −1.48 and −1.37 V for compounds **3** and **5**, respectively). This results in bringing together the reduction peaks of the both halogen-containing fragments (see Fig. 1, *c* and Table 1). Simultaneously this fact is indirect evidence for the proposed sequence of ER of ketone **3**. Since the cathodic potentials of ER for ketone **1** coincide with the potentials of compound **3** beginning from the third one, we can conclude that the further steps of ER coincide.

Thus, the results of the present study suggest that halogen-containing cyclohexadienones are dehalogenated

under the ER conditions (GC electrode, DMF, Bu_4NClO_4) in steps following the sequence carbonylallylic Br atom—carbonylvinylic Br atom—neopentylic Cl atom.

Experimental

A PI-50-1.1 potentiostat connected to a PR-8 programmer was used for electrochemical studies. The working electrode was glassy-carbon (d = 2 mm), a 0.1 *M* solution of Bu_4NClO_4 in DMF was the background electrolyte, Ag/AgCl/KCl (sat.) was the reference electrode, and a platinum plate served as the auxiliary electrode. The potential sweep in CV and RDE studies was 200 and 20 mV s^{-1}, respectively. The potentials are presented with allowance for *iR*-compensation. The number of transferred electrons in redox processes was determined by comparison of the limiting current of the wave in RDE experiments with the current of one-electron oxidation of ferrocene taken in equal concentration.

All measurements were carried out in dry argon; samples were dissolved in the pre-deaerated solvent; DMF (purity grade) was purified by stirring over freshly calcined K_2CO_3 for 4 days followed by distillation *in vacuo* first over P_2O_5 and then over anhydrous $CuSO_4$.

The compounds used were synthesized according to described procedures. The physicochemical and spectral characteristics confirm their structures and correspond to published data.

2-Bromo-5-dibromomethyl-4-dichloromethyl-4-methylcyclohexa-2,5-dien-1-one (1),[21] m.p. 187—188 °C. UV, λ_{max}/nm (logε): 257 (3.12). IR, ν/cm^{-1}: 1605, 1630, 1650. ^{1}H NMR, δ: 1.65 (s, 3 H, C(4)Me); 5.90 (s, 1 H, C(4)$CHCl_2$); 6.25 (s, 1 H, C(5)$CHBr_2$); 7.25 (s, 1 H, H(6)); 7.35 (s, 1 H, H(3)). ^{13}C—{^{1}H} NMR, δ: 22.62 (Me(4)); 31.14 (C(5)$CHBr_2$); 53.67 (C(4)); 74.44 (C(4)$CHCl_2$); 126.60 (C(2)); 134.23 (CH(6)); 147.13 (CH(3)); 158.90 (C(5)); 178.14 (C=O).

2-Bromo-5-bromomethyl-4-dichloromethyl-4-methylcyclohexa-2,5-dien-1-one (2),[21] m.p. 79—80 °C. UV, λ_{max}/nm (logε): 251 (3.74). IR, ν/cm^{-1}: 1610, 1665. ^{1}H NMR, δ: 1.62 (s, 3 H, C(4)Me); 4.12 (AB system, 2 H, C(5)CH_2Br, ^2J = 12.4 Hz); 5.99 (s, 1 H, C(4)$CHCl_2$); 6.70 (s, 1 H, H(6)); 7.48 (s, 1 H, H(3)). ^{13}C—{^{1}H} NMR, δ: 23.72 (Me(4)); 26.79 (C(5)CH_2Br); 54.07 (C(4)); 75.26 (C(4)$CHCl_2$); 126.67 (C(2)); 132.19 (CH(6)); 148.11 (CH(3)); 154.79 (C(5)); 178.02 (C=O).

2-Bromo-4,5-dimethyl-4-dichloromethyl-4-methylcyclohexa-2,5-dien-1-one (3),[21] m.p. 99—100 °C. UV, λ_{max}/nm (logε): 248 (4.158). IR, ν/cm^{-1}: 1610, 1640 sh, 1660. ^{1}H NMR, δ: 1.45 (s, 3 H, C(4)Me); 2.00 (d, 3 H, C(5)Me, ^3J = 1.3 Hz); 5.87 (s, 1 H, C(4)$CHCl_2$); 6.23 (q, 1 H, H(6), ^4J = 1.3 Hz); 7.53 (s, 1 H, H(3)). ^{13}C—{^{1}H} NMR, δ: 18.65 (C(5)Me); 23.54 (C(4)Me); 53.92 (C(4)); 75.42 (C(4)$CHCl_2$); 126.80 (C(2)); 128.10 (CH(6)); 148.01 (CH(3)); 158.24 (C(5)); 177.98 (C=O).

4-Dichloromethyl-3,4-dimethylcyclohexa-2,5-dien-1-one (4),[22] m.p. 98—100 °C. UV, λ_{max}/nm (logε): 231 (4.18). IR, ν/cm^{-1}: 1670. ^{1}H NMR, δ: 1.39 (s, 3 H, C(4)Me); 1.96 (s, 3 H, C(3)Me); 5.89 (s, 1 H, C(4)$CHCl_2$); 6.11 (s, 1 H, C(2)H); 6.37 (d, 1 H, C(6)H, ^3J = 10.1 Hz); 7.06 (d, 1 H, C(5)H, ^3J = 10.1 Hz). ^{13}C—{^{1}H} NMR, δ: 18.74 (C(3)Me); 23.58 (C(4)Me); 50.51 (C(4)); 76.00 (C(4)$CHCl_2$); 129.72, 130.90 (CH(2), CH(6)); 147.82 (CH(5)); 157.71 (C(3)); 185.06 (C=O).

2-Bromo-4-dichloromethyl-4-methylcyclohexa-2,5-dien-1-one (5),[21,23] m.p. 59—60 °C. UV, λ_{max}/nm (logε): 240 (4.30), 268 (3.67). IR, ν/cm^{-1}: 1600, 1640, 1660. ^{1}H NMR, δ: 1.54 (s, 3 H, C(4)Me); 5.76 (s, 1 H, C(4)$CHCl_2$); 6.51 (d, 1 H, H(6), ^3J = 10.1 Hz); 6.99 (dd, 1 H, H(5), ^3J = 10.1 Hz, ^4J = 2.9 Hz); 7.4 (d, 1 H, H(3), ^4J = 2.9 Hz). ^{13}C—{^{1}H} NMR, δ: 22.47 (C(4)Me); 51.63 (C(4)); 75.81 (C(4)$CHCl_2$); 126.75 (C(2)); 129.12 (CH(6)); 148.70, 148.81 (CH(3), CH(5)); 177.78 (C=O).

4-Dibromomethyl-3,4-dimethylcyclohexa-2,5-dien-1-one (6),[21] m.p. 130 °C. UV, λ_{max}/nm (logε): 231 (4.18). IR, ν/cm^{-1}: 1670. ^{1}H NMR, δ: 1.47 (s, 3 H, C(4)Me); 2.03 (d, 3 H, C(3)Me, ^4J = 1.2 Hz); 5.87 (s, 1 H, C(4)$CHBr_2$); 6.19 (m, 1 H, H(2)); 6.46 (dd, 1 H, H(6), ^3J = 10.0 Hz, ^4J = 1.6 Hz); 7.18 (d, 1 H, H(5), ^3J = 10.0 Hz). ^{13}C—{^{1}H} NMR, δ: 18.73 (C(3)Me); 24.86 (C(4)Me); 49.77 (C(4)$CHBr_2$); 49.90 (C(4)); 129.63 (CH(2), CH(6)); 130.81 (CH(6), CH(2)); 149.49 (CH(5)); 157.80 (C(3)); 185.24 (C=O).

2-Bromo-4,4-dimethylcyclohexa-2,5-dien-1-one (7).[24] UV, λ_{max}/nm (logε): 240 (4.28). IR, ν/cm^{-1}: 1600, 1640, 1660. ^{1}H NMR, δ: 1.31 (s, 6 H, C(4)Me); 6.31 (d, 1 H, H(6), ^3J = 10.1 Hz); 6.88 (dd, 1 H, H(5), ^3J = 10.1 Hz, ^4J = 2.9 Hz); 7.31 (d, 1 H, H(3), ^3J = 2.9 Hz). ^{13}C—{^{1}H} NMR, δ: 26.40 (Me(4)); 41.72 (C(4)); 123.23 (C(2)); 125.64 (CH(6)); 156.82, 156.93 (CH(3), CH(5)); 178.94 (C=O).

2-Bromo-4,5-di(bromomethyl)-4-methylcyclohexa-2,5-dien-1-one (8),[21] m.p. 184 °C. UV, λ_{max}/nm (logε): 260 (4.01). IR, ν/cm^{-1}: 1610, 1630, 1650. ^{1}H NMR, δ: 1.68 (s, 3 H, C(4)Me); 5.81 (s, 1 H, C(4)$CHBr_2$); 6.22 (s, 1 H, C(5)$CHBr_2$); 7.28 (s, 1 H, C(6)); 7.40 (s, 1 H, C(3)). ^{13}C—{^{1}H} NMR, δ: 24.19 (Me(4)); 30.87 (C(5), $CHBr_2$); 46,65 (C(4), $CHBr_2$); 53.08 (C(4)); 126.50 (C(2)); 134.04 (CH(6)); 148.54 (CH(3)); 158.80 (C(5)); 178.22 (C=O).

4,4-Dimethylcyclohexa-2,5-dien-1-one (9).[25,26] UV, λ_{max}/nm (logε): 235 (4.06). IR, ν/cm^{-1}: 1630, 1665. ^{1}H NMR, δ: 1.18 (s, 6 H, C(4)Me); 6.14 (d, 2 H, H(2), H(6), ^3J = 10.1 Hz); 6.80 (d, 2 H, H(3), H(5), ^3J = 10.1 Hz). ^{13}C—{^{1}H} NMR, δ: 26.35 (Me(4)); 37.97 (C(4)); 126.92 (CH(2), CH(6)); 157.37 (CH(3), CH(5)); 186.41 (C=O).

5-Chloro-4-methylcyclohepta-2,4,6-trien-1-one (10),[27] m.p. 75 °C. UV, λ_{max}/nm (logε): 231 (4.23), 320 (3.89). ^{1}H NMR, δ: 2.33 (s, 3 H, Me); 6.72 (dd, 1 H(2), H(7), ^3J = 13.0 Hz, ^4J = 3.0 Hz); 6.78 (dd, 1 H(7), H(2), ^3J = 13.0 Hz, ^4J = 3.0 Hz); 6.96 (d, 1 H(3), ^3J = 13.0 Hz); 7.16 (d, 1 H(6), ^3J = 13.0 Hz). Mass spectrum (EI, 70 eV), m/z: 156, 154 $[M]^+$; 128, 126 $[M - CO]^+$; 91 $[M - CO - Cl]^+$.

4-Methylcyclohepta-2,4,6-trien-1-one (11).[28] IR, ν/cm^{-1}: 1590, 1640. ^{1}H NMR, δ: 2.27 (m, 3 H, ^4J = 1.3 Hz); 6.82—7.01 (m, 5 H). Mass spectrum (EI, 70 eV), m/z (I_{rel} (%)): 120 $[M]^+$ (32); 92 $[M - CO]^+$ (50); 91 $[M - CO - H]^+$ (100).

This work was financially supported by the Russian Foundation for Basic Research (Project No. 04-03-32845).

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Received May 5, 2006;
in revised form July 4, 2006