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1,7-Dimethyl-1,7-dichloromethyl-5 ,8-ethenodecalin-3-ene-2,6-dione. Structure, Bromination, Electrochemistry

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Abstract—The structures of 1,7-dimethyl-1,7-bis(dichloromethyl)-5,8-ethenodecalin-3-ene-2,6-dione, the dimer of 6-methyl-6-dichloromethyl-cyclohexa-2,4-dien-1-one, and of products of its bromination were established by XRD analysis. The dependence of composition of the products of bromination on the ratio of reactants was established. Electrochemical reduction of the dione and its bromine-containing derivatives was studied.

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The analysis of published data indicates that decalin-2,6-dione is present as a structural fragment in many organic compounds of both synthetic and natural origin. These compounds are used in the synthesis of drugs and in modern technologies. The decalindione structure forms the basic block of a number of compounds isolated from natural products widely used in traditional medicine.

Decalindiones have been used in the synthesis of lipophilic ganglion blocking agents. The biological activity of the quaternary ammonium diiodide salts of cis-2,6-di(*N*-trimethylammonium)-*cis*(*trans*)-decalin is similar to the activity to the benzohexonium drug used in medicine [1]. The decalin-2,6-dione is a structural unit of the intermediate compounds necessary for the synthesis of anticancer drug 2,8-diaminochrizene [2].

Noteworthy is the application of the substituted decalin-2,6-diones as intermediate in the synthesis of helical structures that can be used as asymmetric catalysts or liquid crystals. Due to their twisted nonplanar π-electron system helicanes have spiral chirality [3]. The decalin-2,6-dione is an important structural element in the composition of the components for producing nanotubes [4], in the synthesis of cage structures like pentacyclotetradeca-10,12-diene-2,6-diones [5].

Natural ethenedecaline structures are dimeric *o*-quinoid systems. A distinctive structural feature of these dimers is the presence of the ethylene bridge between the C^5 and C^8 atoms, and a carbon–carbon double bonds between the atoms C^3 and C^4 of the etheno-decaline frame. Such dimers containing different substituents are found in many natural products of different biosynthetic origin possessing substantial biological activity [6–17].

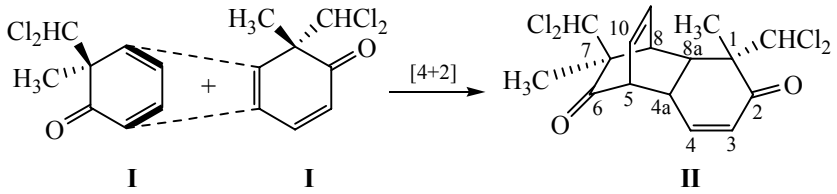
Among the synthetic approaches to the design of dimeric structures the oxidation of 3-(2-hydroxy-phenyl)propionic acid should be noted resulting in 1,7-di(spirooxacyclopentyl)-5,8-ethenodecalin-3-ene-2,6-dione [18].

Cyclohexa-2,4-dien-1-ones with various substituents in the position 6 were shown to enter readily in the cyclodimerization [19–21]. The cyclodimerization of 6-dichloromethyl-6-methylcyclohexa-2,4-dien-1-one was mentioned briefly in [20, 22].

The purpose of this study was to establish the structure of the 6-dichloromethyl-6-methylcyclohexa-2,4-dien-1-one dimer, to study its reaction with bromine and the electrochemical reduction of the products of bromination.

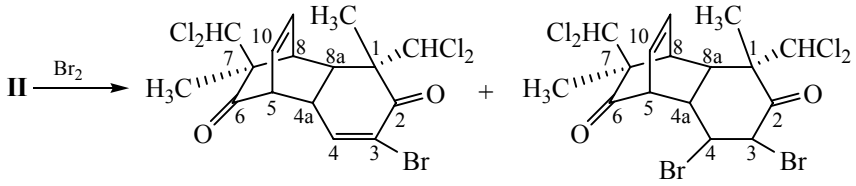
We found that 6-dichloromethyl-6-methylcyclo-hexyl-2,4-dien-1-one (**I**) on prolonged storage under-went autodimerization to form 1,7-dimethyl-1,7-bis-(dichloromethyl)-5,8-etenodecalin-3-ene-2,6-dione **II** [20, 22]. The dimerization of **I** proceeds as the Diels–Alder [4+2] cycloaddition, where one of the dienone molecules plays the role of a diene and the second one,

of a dienophile. In the dienophile the double bond is activated by the conjugation with electronegative fragment (C=C–C=O) [23]. The reaction affords the *endo*-adduct. The mechanism of the dimerization reaction of various *ortho*-quinoids has been discussed in detail [19, 21] and therefore needs no further consideration.



I **I** **II**

In this research we studied the bromination reaction of the dimer **II** and the dependence of the product composition on the ratio of reactants. At the ratio of **II:**Br_2 = 1:1 3-bromo-1,7-dimethyl-1,7-bis(dichloromethyl)-5,8-etenodecalin-3-ene-2,6-dione **III** and 3,4-dibromo-1,7-dimethyl-1,7-bis(dichloromethyl)-5,8-eteno-decalin-2,6-dione **IV** in the ratio ~ 1: 2 were isolated.

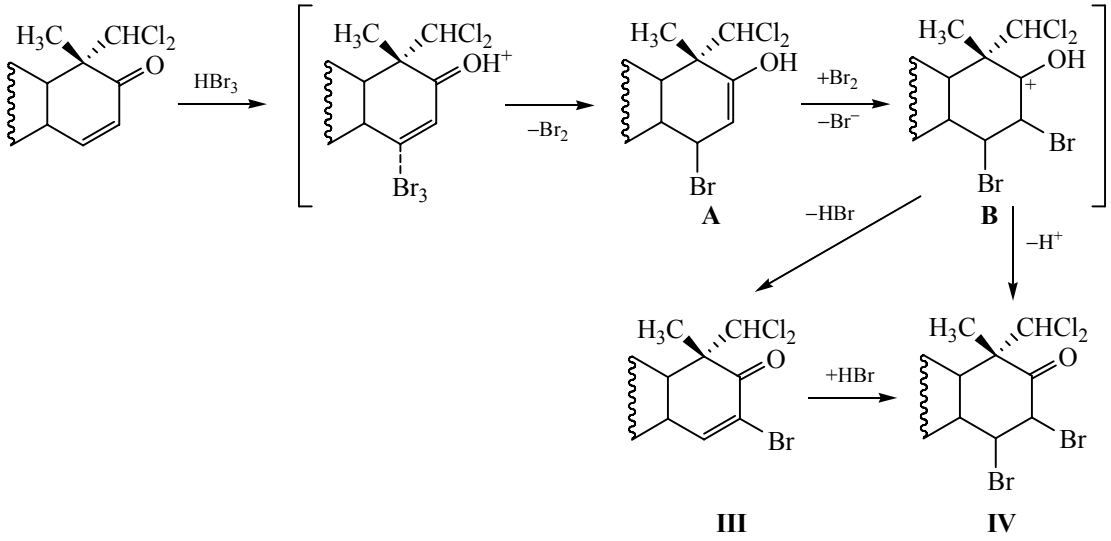


III **IV**

At the same time, at a large excess of bromine, **II:**Br_2 = 1:10, from the reaction mixture dibromo derivative **IV** was isolated in an almost quantitative yield. Note that non-conjugated, isolated ethylene bridge at C^9–C^{10} does not add bromine.

The assumed mechanism of bromination of the conjugated fragment of the dimer (the substrate of the Michael type) is shown below.

As seen, the nucleophilic addition of bromine at the C^3–C^4 bond of the dimer **II** may occur with the assistance of the hydrogen tribromide HBr_3 which is always present as an impurity in molecular bromine. The HBr_3 trace initiates the bromine 1,4-addition to the conjugated Michael system C=C–C=O with the formation of enol **A.** The electrophilic bromine addition to the activated double bond of the formed enol gives intermediate **B** stabilized further by either elimination of HBr with the formation of vinyl bromide **III**, or splitting off a proton from the OH group, which leads to the formation of dibromo derivative **IV**. In turn, the monobromide **III** is capable



III **IV**

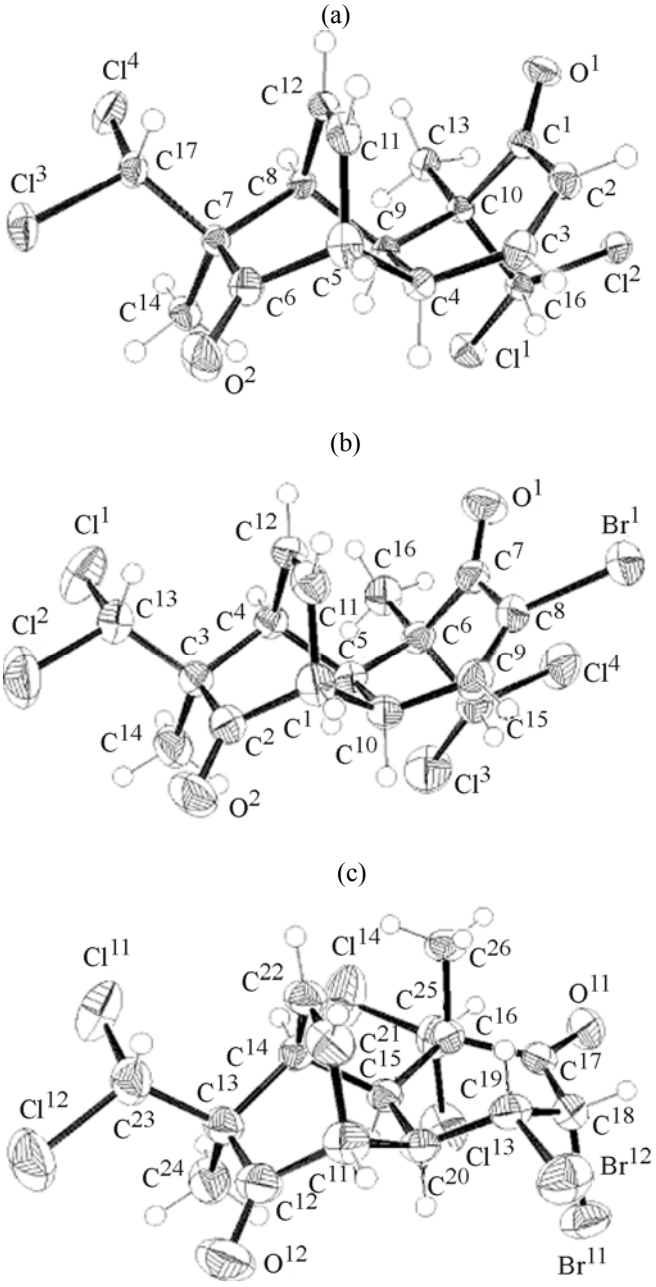


Fig. 1. Molecular structures of compounds (a) **II,** (b) **III,** and (c) **IV.** For **IV** one of the two independent molecules in the crystallographic cell is shown.

of attaching an HBr molecule, and this process dominates when Br_2 is taken in excess [24].

The structure of compounds **II–IV** was established from the data of XRD study and ^{1}H, ^{13}C–{^{1}H} NMR spectroscopy. Molecular structures of compounds **II–IV** with crystallographic numbering of atoms are shown in Fig. 1. In the case of compound **IV** the crystal unit cell contains two independent molecules with similar parameters. The non-conjugated fragment C^{4a}–C^5–C^6–C^7–C^8–C^{8a} in the molecules of all three compounds adopts a *boat* conformation. The second fragment, C^1–C^2–C^3–C^4–C^{4a}–C^{8a}, in **II** and **III** is in distorted *semi-chair* conformation with the C^1 atom deviated significantly from the C^9–C^{10} bridge. A similar steric structure of the framework was found in related structures of natural compounds of the diterpenoid series [17, 25]. In **IV**, the brominated fragment adopts a *boat* conformation. Two of the bromine atoms in **IV** are in cisoid conformation with the torsion angle 67.4(3)° (average over the two independent molecules in the cell).

The ^{1}H NMR spectra of all three compounds **II–IV** contain sets of multiplets that with good accuracy can be analyzed as a first order spin systems. The application of the Lorentz–Gauss weighting function to improve the resolution of multiplets makes it possible to measure the coupling constants with up to 0.1 Hz accuracy (including long-range $^4J_{HH}$ 0.9 and 0.5 Hz) and thus a complete assignment of signals in these spectra can be achieved. The fact that the brominated ring C^1–C^2–C^3–C^4–C^{4a}–C^{8a} of the bromine derivatives **III** and **IV** induces the greatest changes in the parameters of ^{1}H and ^{13}C NMR spectra compared to initial compound **II**, while for the rest of the molecule these changes are minimal, facilitates the assignment.

It should be noted that in keeping with the known Karplus relationship the values of vicinal spin-spin coupling constants are in good correlation with the torsion angles between the corresponding protons measured by XRD (Fig. 2).Therewith the $^3J_{HH}$ values for the protons at the bonds C^{sp2}–C^{sp3} are regularly smaller than for the protons at the C^{sp3}–C^{sp3} bonds. This agreement between the XRD and NMR data indicates that the prevailing conformations of the rings in the decalindione framework of compounds **II–IV** in solution are identical to those found in crystals.

Compounds **II–IV** were studied by cyclic voltammetry and rotating disk electrode in DMF solution with a glassy carbon electrode in the presence of 0.1 M of Bu_4NClO_4 as a background electrolyte. The potentials of electrochemical oxidation and reduction (Table 1) were measured relative to Ag | AgCl | KCl (sat). The cyclic voltammograms obtained are shown in Fig. 3.

Compounds **II–IV,** like the previously studied derivatives of 4-halomethyl- and 4-dihalomethyl-4-methylcyclohexyl-2,5-dien-1-ones and 6-dihalo-

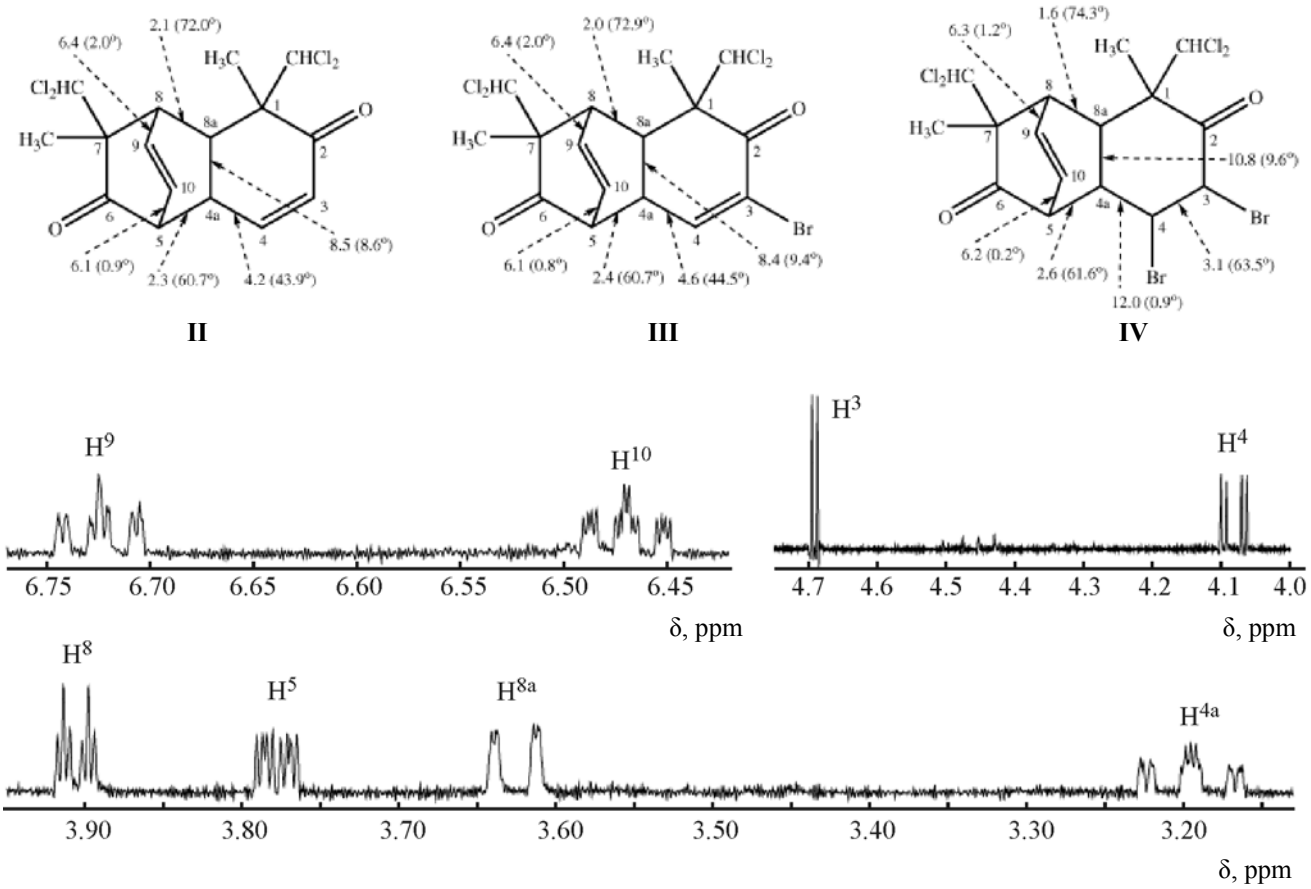
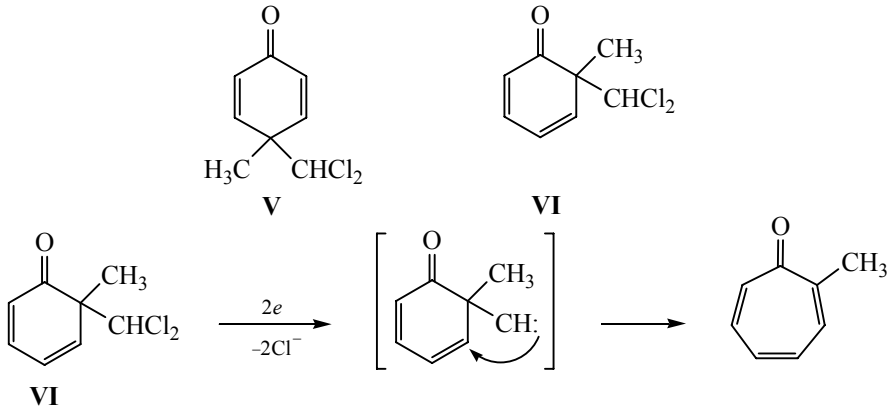


Fig. 2. ^{1}H NMR spectrum of compound **IV** (Lorentz–Gauss apodization).

methyl-6-methylcyclohexyl-2,4-dien-1-ones [26–28], are not oxidized at a potential below ~ +1.5 V, which makes it possible to establish the nature of a leaving halogen atoms from the peaks of reoxidation of halide ions observed in the anodic region at the reverse potential scan after appropriate cathodic peaks.

The cathodic branch of the voltammetric curves of compounds **II**–**IV** includes a strong peak corresponding to a reductive cleavage of the halide ion and a low-intensity peak in the far cathodic region (–2.30 to –2.36 V). But on the curve of dione **II** containing two dichlormethyl groups there is only one four-electron peak corresponding to the simultaneous reductive cleavage of the four chloride ions, and at the reverse scan a peak of reoxidation of chloride ions (E = +1.02 V) is observed in the anode region. Previously we have shown [28] that the geminal neopentyl dihalide (in particular, 4/6-dichloromethyl-4/6-methylcyclohexa-2,5/2,4-dien-1-ones **V** and **VI**) suffered a



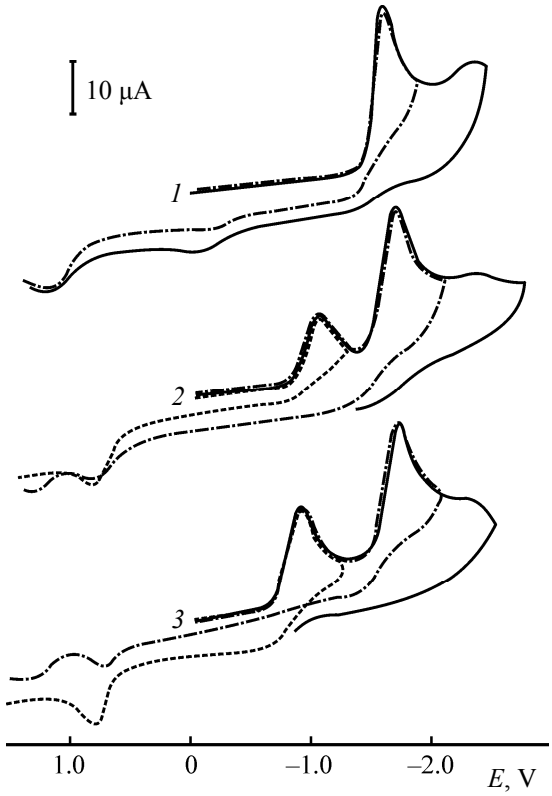


Fig. 3. Cyclic voltammograms of compounds (*1*) **II**, (*2*) **III**, and (*3*) **IV**.

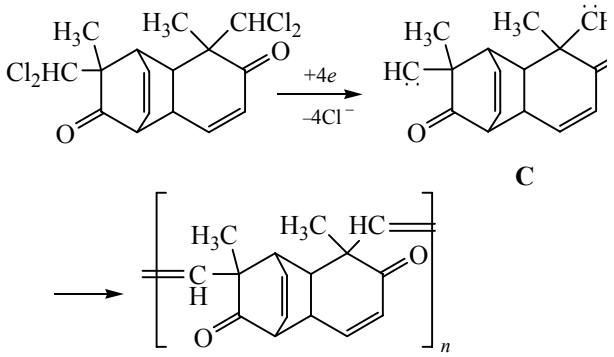
one-stage two-electron reductive elimination with the formation of a carbene, which further was rearranged with the ring expansion to form the corresponding tropone.

Compound **II** contains two dichloromethyl groups reduced simultaneously, which should lead to the formation of the intermediate with two carbenoid sites (**C**)**.** Unlike compound **V**, this intermediate subsequently polymerizes, and the polymer product **D** is deposited on the electrode forming a non-conducting film on the surface, which explains the low intensity of

Table 1. Reduction potentials of compounds **II–V** (DMF, 10^{-3} M)

Comp. no.	E_{pc}, V[a]
II	–1.64/1.07,[b] –2.30
III	–1.02/0.82,[c] 1.67/–1.26,[b] –2.36
IV	–0.94/0.81,[c] –1.66/–1.23,[b] –2.32
V	–1.29/1.03, 1.16,[b] 1.53/–1.47, –2.43

[a] E_{pc} are the potentials of cathode peaks (200 mV s^{-1}). [b] Reoxidation of Cl^-. [c] Reoxidation of Br^-.



C

the following cathodic peaks in the voltammograms of the compounds **II–IV**.

The voltammogram of monobromo-derivative **III** (Fig. 3) has an additional peak compared with voltammogram of **II**, at $\delta_C = -1.02$ V, corresponding to the two-electron reductive elimination of bromide anion, as confirmed by the presence of the peak of Br^- oxidation (E = 0.82 V) at the reverse potential scan after reaching the potential of the first cathodic peak. Subsequent peaks in the cathodic region are identical to those observed on the curves of compound **II.**

At the electrochemical reduction of dibromide **IV**, like that of monobromide **III**, first spliting off of both the bromide ions occurs simultaneously at a potential –0.94 V. After the first reduction peak, the cathodic branch of the curve reproduces the pattern of electrochemical reduction of dione **II.** This suggests that dione **II** is formed in the first stage of electroreduction of both monobromide **III** and dibromide **IV.**

Dione **II** formed in the first stage does not prevent reoxidation of the resulting bromide ions. However**,** the intensity of the reoxidation peaks of the chloride ions formed at the reduction of compounds **II–IV** are significantly lower than expected, and the peaks of bromides **III** and **IV** are shifted to the anodic region. This fact is also due to the formation of a non-conducting polymer on the surface at the polymerization of the bis-carbene **D** after reaching the potential necessary for the reductive cleavage of chloride ions (–1.64 to –1.67 V).

Thus, the electroreduction of 1,7-dimethyl-1,7-dichloromethyl-5,8-ethenodecalin-3-ene-2,6-dione **II** results in the simultaneous reductive cleavage of the four chlorine atoms in the two dichloromethyl groups with similar electronic environment. The carbenoid

intermediate formed polymerizes on the electrode surface.

The electrochemical reduction of bromine-containing derivatives (**III**, **IV**) initially leads to the elimination of the bromine atoms, therewith both vicinal bromine atoms of the dibromo derivative **IV** split off at the same potential. The reductive debromination of halides **III**, **IV** results in the formation of dione **II.**

EXPERIMENTAL

The ^{1}H and ^{13}C–{^{1}H} NMR spectra were recorded on a Bruker Avance-400 spectrometer (at 400 and 100 MHz respectively) at 23°C, solvent $CDCl_3$. The chemical shifts are given relative to TMS (^{1}H) and $CDCl_3$ (δ_C = 77 ppm). The numbering of atoms of compounds **II**–**IV** is shown in Figs. 1 and 2. The IR spectra were recorded on a UR-20 spectrophotometer from mulls in mineral oil, UV spectra, on a Specord M-40 spectrophotometer from solutions in ethanol.

The reaction progress was monitored using thin layer chromatography on Silufol UV-254 plates. For preparative separation of mixtures of the reaction products column chromatography was used (carrier Silicagel L 40/100, column diameter 2 cm, height of the adsorbent bed 15 cm, eluent benzene).

For electrochemical studies an IPC-Pro M potentiostat was used, working electrode was glassy carbon disc (d = 2 mm), supporting electrolyte was 0.1 M solution of Bu_4NClO_4 in DMF, reference electrode was Ag/AgCl/KCl (sat), auxiliary electrode was platinum plate. Potentials are given with *iR*-compensation. In the study by cyclic voltammetry the potential sweep rate was 200 mV s^{-1}, in the study by RDE 20 mV s^{-1}. Potentials are given with *iR*-compensation. The surface of the working electrode was polished with alumina powder, particle size less than 10 μ (Sigma–Aldrich). All the measurements were performed in an atmosphere of dry argon, the samples were dissolved in a pre-deaerated solvent. DMF pure grade was purified by stirring over freshly calcined K_2CO_3 for 4 days followed by vacuum distillation initially over P_2O_5 and then over anhydrous $CuSO_4$.

Initial 6-dichloromethyl-4-methylcyclohexyl-2,4-dien-1-one (**I**) was prepared according to [29], its NMR spectra were identical with those given in [28].

Single crystals of compounds **II, III**, and **IV** were obtained by crystallization from a two-phase hexane/CH_2Cl_2 system. The XRD study of compounds **II**, **III** and **IV** was performed on an automatic diffractometer Bruker SMART II using MoK_α radiation (λ = 0.71073 Å, graphite monochromator). The structures were solved by the direct method and refined by the full-matrix anisotropic least-squares method with respect to F^2 for all non-hydrogen atoms [30]. In structure **II** all hydrogen atoms were found from the difference synthesis and refined in an isotropic approximation; in structures **III** and **IV** all hydrogen atoms were placed in calculated positions and refined according to the *rider* scheme. Crystallographic data, experimental details, and structure refinement are given in Table 2.

1,7-Dimethyl-1,7-bis(dichloromethyl)-5,8-ethenodecalin-3-ene-2,6-dione (II). Compound **II** formed in a quantitative yield at the prolonged (several months) keeping of **I** at room temperature in diffuse daylight. After reprecipitation of **II** with hexane from chloroform it was isolated in 95% yield, mp 186°C. UV spectrum: λ_{max} 205 nm (log ε 4.00), λ_{max} 233 nm (log ε 4.04), λ_{max} 317 nm (log ε 2.46). IR spectrum, ν, cm^{-1}: 1630, 1690, 1732. ^{1}H NMR spectrum, δ, ppm, *J,* Hz: 1.35 s (3H, Me); 1.41 s (3H, Me); 3.07 d.d [^{1}H, H^{8a,3}, J(H^{8a}–H^{4a}) = 8.5, ^3J(H^{8a}–H^8) = 2.1], 3.13 d.d.d [^{1}H, H^8, ^3J(H^8–H^9) = 6.4, ^3J(H^8–H^{8a}) = 2.1, ^4J(H^8–H^{10}) = 1.7], 3.24 d.d.d.d [^{1}H, H^{4a}, ^3J(H^{4a}–H^{8a}) = 8.5, ^3J(H^{4a}–H^4) = 4.2, ^3J(H^{4a}–H^5) = 2.3, ^4J(H^{4a}–H^3) = 1.8], 3.35 d.d.d [^{1}H, H^5, ^3J(H^5–H^{10}) = 6.1, ^3J(H^5–H^{4a}) = 2.3, ^4J(H^5–H^9) = 1.4], 5.74 s (^{1}H, CHCl), 5.80 s (^{1}H, $CHCl_2$), 4.6 d.d.d [^{1}H, H^{10}, ^3J(H^{10}–H^9) = 8.1, ^3J(H^{10}–H^5) = 6.1, ^4J(H^{10}–H^8) = 1.7], 6.7 d.d [^{1}H, H^3, ^3J(H^3–H^4) = 10.1, ^4J(H^3– H^{4a}) = 1.8], 6.43 d.d.d [^{1}H, H^9, ^3J(H^9–H^{10}) = 8.1, ^3J(H^9–H^8) = 6.4, ^4J(H^9–H^5) = 1.4], 6.47 d.d [^{1}H, H^4, ^3J(H^4–H^3) = 10.1, ^3J(H^4–H^{4a}) = 4.2). ^{13}C–{^{1}H} NMR spectrum, δ, ppm: 14.29, 15.49 (1,7-Me); 38.94, 39.89, 44.99, 53.60 (CH^{4a}, CH^5, CH^8, CH^{8a}), 55.16, 56.17 (C^1 , C^7), 76.68, 79.51 (1,7-$CHCl_2$), 128.97, 129.77 (CH^3 , CH^9), 133.92 (CH^{10}), 144.34 (CH^4), 196.23 (C^2), 206.51 (C^6). Found, %: C 50.16, H 4.20. $C^1{}_6H_{16}Cl_4O_2$. Calculated, %: C 50.26, H 4.18.

Reaction of II with molecular bromine (ratio of **II**:Br_2 = 1:1). A mixture of 0.191 g (0.5 mmol) of compound **II** and 0.080 g (0.5 mmol) of Br_2 in 5 ml of CH_2Cl_2 was kept in the dark for 48 h at 20°C.

The solvent was then evaporated, and the fuming oily residue was stirred with 1 g (12 mmol) of ZnO in 3 ml of CH_2Cl_2 for 1 h. The precipitate was filtered off, the solvent was evaporated, the residue was chromatographed collecting the fractions with R_f 0.27 and R_f 0.47.

3-Bromo-1,7-dimethyl-1,7-bis(dichloromethyl)-5,8-ethenodecalin-3-ene-2,6-dione (III). The com-

Table 2. Crystallographic data, experimental details,and structure refinement of compounds **II, III,** and **IV**

Parameter	II	III	IV
Empirical formula	$C_{16}H_{16}Cl_4O_2$	$C_{16}H_{15}Br_1Cl_4O_2$	$C_{16}H_{16}Br_2Cl_4O_2$
Molecular weight	382.09	460.99	541.91
Crystal size, mm	0.35×0.20×0.15	0.40×0.04×0.03	0.35×0.25×0.20
Temperature, K	150	293	293
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/n$
a, Å	13.8483(4)	13.2269(8)	18.8295(8)
b, Å	9.8593(3)	6.9398(4)	11.3300(5)
c, Å	12.0659(4)	19.5404(11)	19.8017(8)
β, deg	98.162(1)	99.859(1)	113.397(1)
V, Å^3	1630.72(4)	1767.16(18)	3877.1(3)
Z	4	4	8
d_{calc}, g cm^{-3}	1.556	1.733	1.857
F(000)	784	920	2128
μ(MoK_α), mm^{-1}	0.729	2.936	4.740
Scanning area, θ, deg	2.54–26.99	2.41–26.99	2.12–26.00
Measured reflections	13304	14356	33672
Independent reflections	3546 (R_{int} 0.0164)	3827 (R_{int} 0.0319)	7610 (R_{int} 0.0257)
Reflections with $I > 2\sigma(I)$	3233	2932	5975
Number of refined variables	201	210	437
R-factors for $I > 2\sigma(I)$	R_1 0.0259, wR_2 0.0694	R_1 0.0347, wR_2 0.0764	R_1 0.0357, wR_2 0.0854
R-factors for all reflections	R_1 0.0288, wR_2 0.0708	R_1 0.0532, wR_2 0.0806	R_1 0.0520, wR_2 0.0908
$GOOF$	1.058	1.033	1.039
Residual electron density, min/max, e Å^{-3}	–0.241/0.368	–0.604/0.502	–0.929/1.016

pound **III** was isolated from the fraction with R_f 0.27 in the above experiment and purified by reprecipitation with hexane from a solution in chloroform. Yield 0.075 g (32%), mp 171°C. UV spectrum: λ_{max} 263 nm (log ε 3.96), λ_{max} 312 nm (log ε 2.64). IR spectrum, ν, cm^{-1}: 1620, 1710, 1720. ^{1}H NMR spectrum, δ, ppm, *J,* Hz: 1.43 s (3H, Me), 1.46 s (3H, Me), 3.07 d.d [^{1}H, H^{8a}, $^3J(H^{8a}–H^{4a})$ = 8.4, $^3J(H^{8a}–H^8)$ = 2.0] 3.18 d.d.d [^{1}H, H^8, $^3J(H^8–H^9)$ = 6.4, $^3J(H^8–H^{8a})$ = 2.0, $^4J(H^8–H^{10})$ = 1.7], 3.32 d.d.d [^{1}H, H^{4a}, $^3J(H^{4a}–H^{8a})$ = 8.4, $^3J(H^{4a}–H^4)$ = 4.6, $^3J(H^{4a}–H^5)$ = 2.4], 3.41 d.d.d [^{1}H, H^5, $^3J(H^5–H^{10})$ = 6.1, $^3J(H^5–H^{4a})$ = 2.4, $^4J(H^5–H^9)$ = 1.3], 5.76 s (^{1}H, $CHCl_2$), 5.84 s (^{1}H, $CHCl_2$), 6.11 d.d.d [^{1}H, H^{10}, $^3J(H^{10}–H^9)$ = 8.1, $^3J(H^{10}–H^5)$ = 6.1, $^4J(H^{10}–H^8)$ = 1.7], 6.48 d.d.d [^{1}H, H^9, $^3J(H^9–H^{10})$ = 8.1, $^3J(H^9–H^8)$ = 6.4, $^4J(H^9–H^5)$ = 1.3], 6.82 d [^{1}H, H^4, $^3J(H^4–H^{4a})$ = 4.6]. ^{13}C–{^{1}H} NMR spectrum, δ, ppm: 14.78, 15.62 (1,7-Me), 39.77, 40.94, 44.81, 53.51 (CH^{4a}, CH^5, CH^8, CH^{8a}), 55.24, 57.87 (C^1, C^7), 76.49, 78.66 (1,7-$CHCl_2$), 121.86 (C^3), 128.98 (CH^9), 134.47 (CH^{10}), 143.82 (CH^4), 190.15 (C^2), 205.59 (C^6). Found, %: C 41.67, H 3.27. $C^1{}_6H15BrCl_4O_2$. Calculated, %: C 41.64, H 3.25.

3,4-Dibromo-1,7-dimethyl-1,7-bis(dichloromethyl)-5,8-ethenodecalin-2,6-dione (IV). Compound **IV** was isolated from fractions with R_f 0.47 and purified by reprecipitation from chloroform with hexane. Yield 0.127 g (57%), mp 182°C. UV spectrum: λ_{max} 211 nm (log ε 2.98). IR spectrum, ν, cm^{-1}: 1720. ^{1}H NMR spectrum, δ, ppm, *J,* Hz: 1.34 s (3H, 7-Me), 1.56 s (3H, 1-Me), 3.19 d.d.d.d [^{1}H, H^{4a}, $^3J(H^{4a}–H^4)$ = 12.0, $^3J(H^{4a}–H^{8a})$ = 10.8, $^3J(H^{4a}–H^5)$ = 2.6, $^4J(H^{4a}–H^{10})$ = 0.9], 3.62 d.d.d [^{1}H, H^{8a}, $^3J(H^{8a}–H^{4a})$ = 10.8, $^3J(H^{8a}–H^8)$ = 1.6, $^4J(H^{8a}–H^9)$ = 0.5], 3.78 d.d.d [^{1}H, H^5, $^3J(H^5–H^{10})$ = 6.2, $^3J(H^5–H^{4a})$ = 2.6, $^4J(H^5–H^9)$ = 1.5] 3.91 d.d.d [^{1}H, H^8, $^3J(H^8–H^9)$ =6.3, $^3J(H^8–H^{8a})$ = 1.6, $^4J(H^8–H^{10})$ = 1.6], 4.8 d.d [^{1}H, H^4, $^3J(H^4–H^{4a})$ = 12.0, $^3J(H^4–H^3)$ = 3.1], 4.69 d [^{1}H, H^3, $^3J(H^3–H^4)$ = 3.1], 5.83 s (^{1}H, 7-$CHCl_2$), 6.31 s (^{1}H, 1-$CHCl_2$), 6.47 d.d.d.d [^{1}H, H^{10}, $^3J(H^{10}–H^9)$ = 8.1, $^3J(H^{10}–H^5)$ = 6.2,

$^4J(H^{10}–H^8)$ = 1.6, $^4J(H^{10}–H^{4a})$ = 0.9], 6.72 d.d.d.d [^{1}H, H^9, $^3J(H^9–H^{10})$ = 8.1, $^3J(H^9–H^8)$ = 6.3, $^4J(H^9–H^5)$ = 1.5, $^4J(H^9–H^{8a})$ = 0.5]. $^{13}C–\{^1H\}$ NMR spectrum, δ, ppm: 15.95 (7-Me); 25.62 (1-Me); 35.22, 45.54, 45.74, 46.94, 52.96, 54.31 (CH^3, CH^4, CH^{4a}, CH^5, CH^8, CH^{8a}); 54.95, 56.45 (C^1, C^7), 76.83, 78.56 (1,7-$CHCl_2$), 127.53 (CH^9), 136.79 (CH^{10}), 199.79 (C^2), 207.07 (C^6).

Reaction of **II** with molecular bromine (ratio of **II**:Br_2 = 1:10) was carried out similarly using a mixture of 0.191 g (0.5 mmol) of compound **II** and 0.80 g (5 mmol) of Br_2. By chromatography the fraction with R_f 0.47 was isolated. The yield of compound **IV** 0.27 g (97%) Found, %: C 35.53; H^3.09. $C^1{}_6H_{16}Br_2Cl_4O_2$. Calculated, %: C 35.42, H2.95. .

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