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Dedicated to Full Member of the Russian Academy of Sciences I.P. Beletskaya on Her Jubilee

Reaction of Some Dibromomethyl-Substituted Cyclohexadienones with Molecular Bromine

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Abstract—4-Dibromomethyl-4-methyl-2,5-cyclohexadienone and its 2- and 3-methyl-substituted derivatives react with an equimolar amount of molecular bromine in carbon tetrachloride, yielding vinyl bromination products at the α-position with respect to the carbonyl group. The reaction of 4-dibromomethyl-3,4-dimethyl-2,5-cyclohexadienone with a large excess of bromine, apart from the vinyl bromination product, gives the corresponding 3-bromomethyl and 3-dibromomethyl derivatives. 4-Dibromomethyl-2,4-dimethyl-2,5-cyclohexadienone takes up bromine molecule at the $C^2=C^3$ double bond.

During the last three decades, geminal dihalomethyl-substituted cyclohexadienones (Auvers ketones [1, 2]) have been successfully used in the synthesis of pharmaceuticals [3, 4], tropones [5], tropovalene [6], and spirans [7]. These transformations involve the carbonyl group and the dihalomethyl moiety. The reactivity of endocyclic double bonds conjugated with the carbonyl group has been studied to a considerably lesser extent. It is known [8] that concentrated sulfuric acid does not react at the double C=C bonds but reversibly protonates the carbonyl oxygen atom. Hydrogen adds to the unsaturated bonds in the presence of catalysts [3, 9]. 4-Dichloromethyl-4-methyl-2,4-cyclohexadienone reacts with molecular chlorine or bromine to give the corresponding 2-halo ketones [10]. Reactions of halogens with cyclohexadienones having a dibromomethyl group were not studied.

The results of recent studies have shown that brominated cyclohexadienones are natural pharmacophores. For example, *Latrunculia* marine sponge produces previously unknown pentacyclic derivatives, discorhabdins [11, 12], whose high biological activity was believed to originate just from the presence of cyclohexadienone fragment in their molecules. Biologically active 2-(1-hydroxy-4-oxo-2,5-cyclohexadienyl)acetamide was isolated from *Aplisina fistularis* sponge [13, 14].

In the present work we examined reactions of Auvers ketones with molecular bromine. The substrates were 4-dibromomethyl-3,4-dimethyl-2,5-cyclohexadienone (**I**), 4-dibromomethyl-2,4-dimethyl-2,5-cyclohexadienone (**II**), and 4-dibromomethyl-4-methyl-2,4-cyclohexadienone (**III**). A mixture of appropriate ketone and molecular bromine was kept for a certain period at room temperature in the dark. The products were isolated by thin-layer chromatography; their structure was established on the basis of the ^1H and ^{13}C NMR (including selective double-resonance experiments), IR, and UV spectra, and elemental analyses.

Below are considered some general relations observed in the ^1H and ^{13}C NMR spectra of the compounds under study, which should facilitate signal assignment and structure determination. In the ^1H NMR spectra of all these compounds, the $CHBr_2$ proton signal appears in a stronger field (δ 5.6–5.9 ppm) than signals from the olefinic ring protons. In some cases, singlets in the downfield region of the spectrum were assigned to olefinic, dibromomethyl, or bromomethylene fragments by measurement of the direct proton–carbon coupling constants. The $^1J_{CH}$ value for the $CHBr_2$ group is about 180 Hz, which is greater by 10–15 Hz than the corresponding coupling constant for olefinic protons. The $^1J_{CH}$ value for the BrCH= group is 145–146 Hz. Also, couplings through four bonds (*W*-coupling) were observed between protons in positions *2*, *6* and *3*, *5*, respectively: $^4J_{HH}$ = 1.5–3 Hz. The chemical shifts of olefinic

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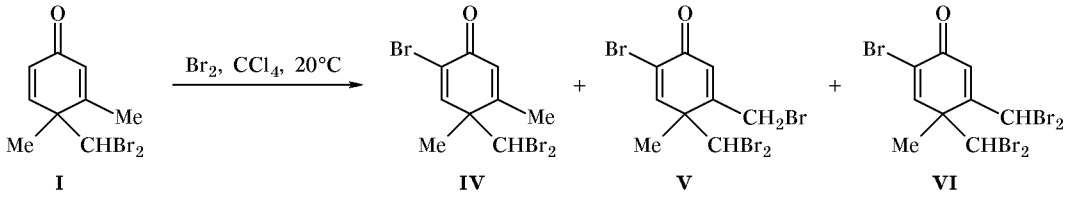
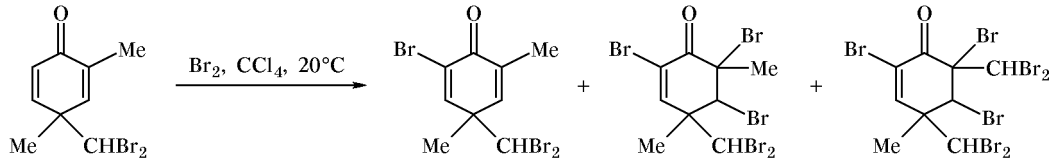
Scheme 1.



I **IV** **V** **VI**

Ratio **I**:Br_2	Reaction time, h	Yield, %			
		I	**IV**	**V**	**VI**
1:1	24	16	65	18	–
1:25	24	–	8	25	55
1:25	48	–	–	–	98

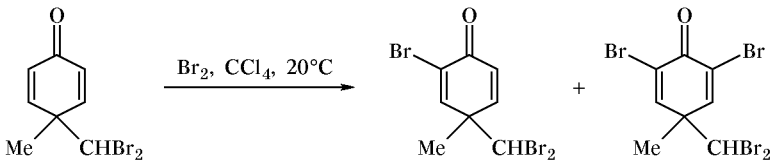
Scheme 2.



II **VII** **VIII** **IX**

Ratio **II**:Br_2	Reaction time, h	Yield, %		
		II	**VII**	**VIII + IX**
1:1	24	2	87	Traces
1:25	48	–	Traces	79

Scheme 3.



III **X** **XI**

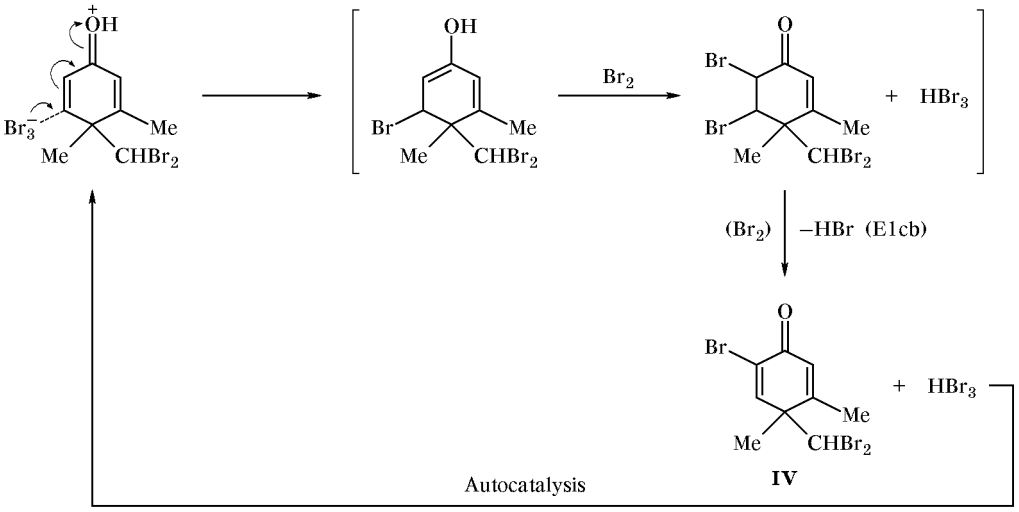
Ratio **III**:Br_2	Reaction time, h	Yield, %		
		III	**X**	**XI**
1:1	24	1.4	74	14
1:25	24	–	12	64
1:25	48	–	–	96

protons located in the α-position with respect to the carbonyl group were always smaller by 0.5–1 ppm than those of the β-protons. Replacement of the α-hydrogen atom by bromine leads to further downfield shift of the β-proton signal (by about 0.5 ppm).

Some specific features of the ^{13}C NMR spectra can also be noted. The presence of bromine in the α-position relative to the carbonyl group induces an upfield shift (by ~7 ppm) of the carbonyl carbon signal and a downfield shift (by ~3 ppm) of the C^4 signal. The ^{13}C chemical shifts of the methyl and dibromomethyl groups almost do not change. The assignment of the ^{13}C NMR signals of product mixtures was performed with account taken of their relative intensities.

In the initial period, the reaction was slow; later on, evolution of hydrogen bromide was observed, and the

Scheme 4.



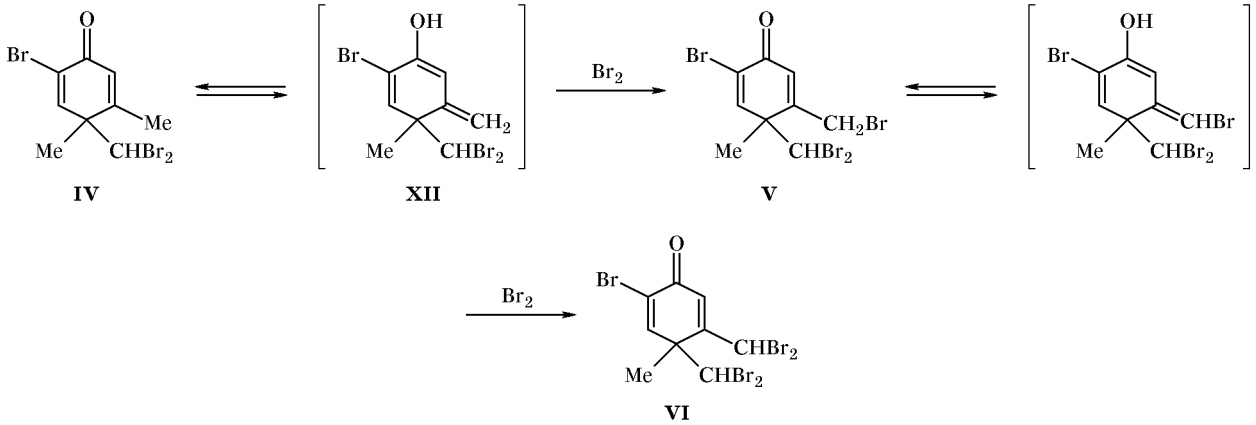
reaction became much faster. The structure of the products obtained from compounds **I**–**III** and their yields (depending on the reactant ratio and reaction time) are given in Schemes 1–3. It is seen that the reaction with methyl-substituted cyclohexadienones initially occurs at the unsubstituted $C^5=C^6$ bond and that bromine replaces hydrogen in the α-position with respect to the carbonyl group. In the presence of excess bromine and on increasing the reaction time, the substituted $C^2=C^3$ bond is involved. Here, compound **I** (which can be enolized with participation of the 3-methyl group) gives rise to hydrogen replacement product at the methyl group, while nonenolizable ketone **II** takes up bromine molecule at the substituted double bond to give compound **VIII** which then undergoes bromination at the methyl group with formation of bromomethyl derivative **IX**.

Let us consider in more detail initial bromination of the unsubstituted double bond. Dienones are Michael substrates to which bromine addition may be either electrophilic or nucleophilic, depending on fine details of the alkene structure and reaction conditions. The fact that the addition of bromine occurs first at the unsubstituted double bond cannot be interpreted in terms of electrophilic mechanism. Also, it is hardly consistent with radical mechanism which cannot be ruled out (although the reactions were carried in the dark), for some amount of oxygen is always present in the system. Hence we presume that the mechanism of bromine addition at the $C^5=C^6$ bond is nucleophilic. Nucleophilic addition of bromine at the $C^5=C^6$ bond of **I** could occur by the action of hydrogen tribromide as shown in Scheme 4. Although in the initial period the reaction solution contains no hydrogen tribromide (only Br_2 is present), it is generally assumed that molecular bromine always contains an admixture of HBr (HBr_3) due to the presence of traces of water and other impurities. Micro amounts of HBr_3 initiate nucleophilic addition of bromine to the unsubstituted $C^5=C^6$ bond, and subsequent elimination of hydrogen bromide (most probably, according to the E1cb mechanism) gives product **IV** together with an appreciable amount of HBr. In such a way, the process becomes autocatalytic, as in the addition of bromine to acrylic acid derivatives in acetic acid [15].

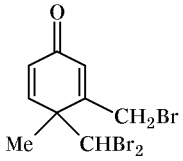
Compound **IV** is a much less reactive Michael substrate, as compared to **I**, since donor effect of lone electron pair on the bromine atom considerably reduces the positive charge on the α-carbon atom, induced by the carbonyl group. Therefore, nucleophilic addition stops after introduction of only one bromine atom.

Unlike the $C^5=C^6$ bond, the reaction at the $C^2=C^3$ bond gives no hydrogen replacement product at C^2, and the bromination occurs exclusively at the allylic position, i.e., at the 3-methyl group. It is commonly believed that allylic bromination is a radical process [16, 17]. In fact, in many cases, this reaction is very sensitive to radical initiators and inhibitors, and it does not occur in the absence of at least traces of radical initiator. As applied to the reaction under study, the mechanism of allylic bromination may be trivial: it may be a secondary process initiated by hydrogen bromide which is released during primary autocatalytic nucleophilic bromination at the unsubstituted $C^5=C^6$ bond. Therefore, the formation of an appreciable amount of dienol form **XII** of the

Scheme 5.



β-methyl-α,β-unsaturated ketone is highly probable. The latter reacts with bromine at the exocyclic double bond as shown in Scheme 5. These scheme explains the formation of products **V** and **VI** (see Scheme 1). However, compound **XIII** having no bromine atoms in the ring is not formed. This means that allylic bromination of initial substrate **I** occurs at a much lower rate than nucleophilic addition at the unsubstituted double bond.



XIII

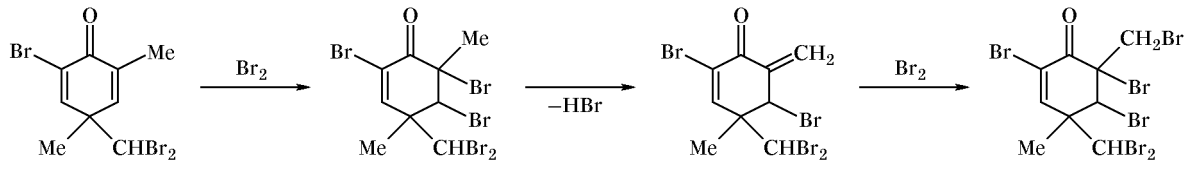
The bromination of **II** also begins with nucleophilic addition at the unsubstituted double bond to give product **VII**. Excess bromine reacts further at the substituted double bond, affording polybrominated derivatives **VIII** and **IX** (Scheme 1). Their structure was established on the basis of the ^{1}H and ^{13}C NMR spectra. The signals were assigned with account taken of their relative intensities and proton-coupled ^{13}C NMR spectra; the coupling constants $^1J_{CH}$ for the $CHBr_2$ and =CHBr groups were deduced from the ^{13}C satellites, 178 and 145–146 Hz, respectively. Unfortunately, we failed to separate product mixture **VIII**/**IX** by thin-layer chromatography. According to the ^{1}H NMR data, the ratio **VIII** : **IX** is 2.62.

A plausible mechanism of this reaction includes initial electrophilic addition at the substituted double bond, elimination of hydrogen bromide, and secondary nucleophilic or electrophilic bromine addition to the newly formed exocyclic double bond (Scheme 6).

Thus, molecules of the examined substrates possess both electrophilic and nucleophilic reaction centers. The transformation of electrophilic double bond into nucleophilic is achieved by introduction of a methyl group. In the molecule of compound **III**, which has no methyl group at the double bonds, both these bonds are electrophilic. Therefore, the reaction of **III** with excess bromine yields 2,6-dibromo-4-dibromomethyl-4-methyl-2,5-cyclohexadienone (**XI**, see Scheme 3) as a result of double addition of nucleophilic brominating agent.

To conclude, it should be emphasized that the mechanism of bromine reactions with unsaturated compounds remains an interesting matter of further studies and discussions. Michael substrates could take up bromine according to either electrophilic or nucleophilic mechanism. Here, even such a factor as the presence of a methyl group at the C=C bond may be crucial. The substrates examined in the present work contain two double bonds conjugated to carbonyl group, i.e., two idependent Michael systems. The unsubstituted C=C bond reacts with bromine follow-

Scheme 6.



ing the nucleophilic substitution pattern, with hydrogen replacement at the α-position relative to the carbonyl group. The reaction of bromine with the other, methyl-substituted double bond, follows the electrophilic mechanism, finally leding to allylic substitution product (with substrate **I**) or electrophilic addition product (compound **II**). Compound **III** has a symmetric structure with two equivalent Michael systems; both double bonds therein have no methyl substituents, so that they react according to the nucleophilic mechanism.

EXPERIMENTAL

The ^{1}H and ^{13}C NMR spectra were recorded on a Varian VXR-400 spectrometer at 25°C using $CDCl_3$ as solvent and tetramethylsilane as internal reference. The IR spectra were obtained on a UR-20 instrument from samples dispersed in mineral oil. The UV spectra were measured on a Specord M-40 spectrophotometer from solutions in ethanol. The progress of reactions was monitored by TLC on Silufol UV-254 plates. Preparative separation of product mixtures was performed by TLC on silica gel (Silpearl UV-254) applied to 250 × 250-mm glass plates.

4-Dibromomethyl-4-methyl-2,5-cyclohexadienone (**III**) was synthesized by the procedure reported in [1]. Its spectral parameters were in agreement with the data of [18].

4-Dibromomethyl-3,4-dimethyl-2,5-cyclohexadienone (I). Bromoform, 17.4 ml (0.2 mol), was added over a period of 30 min to a mixture of 10 g (0.081 mol) of 3,4-dimethylphenol and 20 g (0.5 mol) of NaOH in 180 ml of H_2O under vigorous stirring at 57°C. The mixture was heated for 4 h, and the precipitate was filtered off, washed with two portions of petroleum ether, and dried. The product was subjected to column chromatography on SiO_2 using $CHCl_3$ as eluent. Yield 7.1 g (30%). mp 130°C (from benzene); published data [19]: mp 132°C. UV spectrum: λ_{max} 231 nm (log ε 4.18). IR spectrum: ν(C=O) 1670 cm^{-1}. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.47 s (3H, 4-Me); 2.03 d (3H, 3-Me, ^4J = 1.2); 5.87 s (1H, $CHBr_2$); 6.19 m (1H, 2-H); 6.46 d.d (1H, 6-H, ^3J = 10.0, ^4J = 1.6); 7.18 d (1H, 5-H, ^3J = 10.0). ^{13}C NMR spectrum, δ_C, ppm (*J*, Hz): 18.70 q (3-Me, $^1J_{CH}$ = 129); 24.83 q (4-Me, ^1J = 132); 49.77 d (4-$CHBr_2$, ^1J = 180); 49.90 s (C^4); 129.58 d (C^2 or C^6, ^1J = 165); 130.77 d (C^6 or C^2, ^1J = 167); 149.47 d (C^5, ^1J = 163); 157.80 s (C^3); 185.19 s (C=O).

4-Dibromomethyl-2,4-dimethyl-2,5-cyclohexadienone (II) was synthesized in a similar way. The product was isolated by steam distillation. mp 60–61°C (from petroleum ether). Yield 4.6 g (20%). UV spectrum, λ_{max}: 236 nm (log ε 4.00). IR spectrum, ν, cm^{-1}: 1620, 1645, 1670. ^{1}H NMR spectrum, d, ppm (*J*, Hz): 1.48 s (3H, 4-Me); 1.95 d (3H, 2-Me, $^4J_{HH}$ = 1.2); 5.67 s (1H, $CHBr_2$); 6.38 d (1H, 6-H, $^3J_{HH}$ = 10.0); 6.71 m (1H, 3-H); 6.92 d.d (1H, 5-H, $^3J_{HH}$ = 10.0, $^4J_{HH}$ = 3.2). ^{13}C–{^{1}H} NMR spectrum, δ_C, ppm: 16.04 (2-Me); 24.46 (4-Me); 47.35 (C^4); 51.06 ($CHBr_2$); 130.27 (C^6); 137.15 (C^2); 144.63 (C^3); 149.09 (C^5); 185.43 (C=O). Found, %: C 37.02; H 3.30. $C_9H_{10}Br_2O$. Calculated, %: C 37.16; H 3.17.

Reaction of 4-dibromomethyl-3,4-dimethyl-2,5-cyclohexadienone (I) with molecular bromine (Scheme 1). *a. Reactant ratio 1 : 1.* A mixture of 0.1 g (0.34 mmol) of dienone **I** and 0.054 g (0.34 mmol) of bromine in 5 ml of carbon tetrachloride was kept for 24 h at room temperature in the dark. The mixture was evaporated, and the residue was subjected to chromatographic separation using benzene–ether (1 : 1) as eluent. Fractions with R_f 0.25, 0.45, and 0.65 were collected. The first fraction (R_f 0.25) contained initial dienone **I**. Yield 0.016 g. mp 121°C (reprecipitation from benzene with hexane).

2-Bromo-4-dibromomethyl-4,5-dimethyl-2,5-cyclohexadienone (IV). R_f 0.45. Yield 0.082 g. mp 125°C (reprecipitation from chloroform with hexane). UV spectrum: λ_{max} 249 nm (log ε 4.00). IR spectrum, ν, cm^{-1}: 1610, 1660, 1675. 1H NMR spectrum, δ, ppm (*J*, Hz): 1.50 s (3H, 4-Me); 2.03 d (3H, 5-Me, ^4J = 1.2); 5.78 s (1H, $CHBr_2$); 6.29 q (1H, 6-H, ^4J = 1.2); 7.61 s (1H, 3-H). ^{13}C–{^{1}H} NMR spectrum, δ_C, ppm: 18.59 (5-Me); 24.92 (4-Me); 48.61 ($CHBr_2$); 53.36 (C^4); 126.90 (C^2); 128.12 (C^6); 149.66 (C^3); 158.22 (C^5); 178.18 (C=O). Found, %: C 28.69; H 2.28. $C_9H_9Br_3O$. Calculated, %: C 28.95; H 2.41.

2-Bromo-5-bromomethyl-4-dibromomethyl-4-methyl-2,5-cyclohexadienone (V). R_f 0.65. Yield 0.028 g. mp 101°C (reprecipitation from chloroform with hexane on cooling). UV spectrum: λ_{max} 253 nm (log ε 4.01). IR spectrum, ν, cm^{-1}: 1600, 1630, 1670. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.66 s (3H, 4-Me); 4.13 (2H, CH_2Br, *AB* system, ^1J = 12.4); 5.89 s (1H, $CHBr_2$); 6.73 s (1H, 6-H); 7.55 s (1H, 3-H). ^{13}C–{^{1}H} NMR spectrum, δ_C, ppm: 25.12 (4-Me); 26.61 (CH_2Br); 48.06 ($CHBr_2$); 53.45 (C^4); 126.55 (C^2); 131.90 (C^6); 149.70 (C^3); 154.94 (C^5); 178.13 (C=O). Found, %: C 23.80; H 1.85. $C_9H_8Br_4O$. Calculated, %: C 23.89; H 1.76.

b. Reactant ratio 1 : 25. The reaction of 0.1 g (0.34 mmol) of ketone **I** with 1.44 g (9 mmol) of

bromine was carried out as described above in *a*. Three products with R_f 0.45, 0.65, and 0.82 were isolated. The product with R_f 0.45 (0.01 g) was 2-bromo-4-dibromomethyl-4,5-dimethyl-2,5-cyclohexadienone (**IV**), and that with R_f 0.65 (0.04 g) was 2-bromo-5-bromomethyl-4-dibromomethyl-4-methyl-2,5-cyclohexadienone (**V**).

2-Bromo-4,5-bis(dibromomethyl)-4-methyl-2,5-cyclohexadienone (VI). R_f 0.82. Yield 0.12 g. mp 184°C (reprecipitation from THF with hexane at low temperature). UV spectrum: λ_{max} 260 nm ($\log\varepsilon$ 4.01). IR spectrum, ν, cm^{-1}: 1610, 1630, 1650. ^1H NMR spectrum, δ, ppm (*J*, Hz): 1.68 s (3H, 4-Me); 5.81 s (1H, 4-$CHBr_2$); 6.22 s (1H, 5-$CHBr_2$); 7.28 s (1H, 6-H); 7.40 s (1H, 3-H). ^{13}C–{^1H} NMR spectrum, δ_C: 24.19 (Me); 30.87 (5-$CHBr_2$); 46.65 (4-$CHBr_2$); 53.08 (C^4); 126.50 (C^2); 134.04 (C^6); 148.54 (C^3); 158.80 (C^5); 178.22 (C=O). Found, %: C 20.36; H 1.26. $C_9H_7Br_5O$. Calculated, %: C 20.33; H 1.31.

Reaction of 4-dibromomethyl-2,4-dimethyl-2,5-cyclohexadienone (II) with molecular bromine (Scheme 2). *a. Reactant ratio 1 : 1.* The reaction was carried out as described above for dienone **I**. The products were separated by chromatography using petroleum ether–ether (4 : 1) as eluent. A fraction with R_f 0.23 was collected. It contained 0.11 g of 2-bromo-4-dibromomethyl-4,6-dimethyl-2,5-cyclohexadienone (**VII**). mp 99-100°C (reprecipitation from chloroform with hexane in the cold). UV spectrum: λ_{max} 236 nm ($\log\varepsilon$ 4.14). IR spectrum, ν, cm^{-1}: 1620, 1650, 1665. ^1H NMR spectrum, δ, ppm (*J*, Hz): 1.52 s (3H, 4-Me); 2.01 d (3H, 6-Me, $^4J_{HH}$ = 1.6); 5.66 s (1H, $CHBr_2$); 6.74 m (1H, 5-H); 7.38 d (1H, 3-H, $^4J_{HH}$ = 2.8). ^{13}C–{^1H} NMR spectrum, δ_C, ppm: 16.78 (6-Me); 24.30 (4-Me); 49.72 ($CHBr_2$); 50.11 (C^4); 126.44 (C^2); 136.17 (C^6); 144.78 (C^5); 149.29 (C^3); 178.61 (C=O). Found, %: C 28.87; H 2.26. $C_9H_9Br_3O$. Calculated, %: C 28.95; H 2.41.

b. Reactant ratio 1 : 25. From the reaction mixture we isolated a mixture of two brominated compounds, 2,5,6-tribromo-4-dibromomethyl-4,6-dimethyl-2-cyclohexenone (VIII) and 2,5,6-tribromo-6-bromomethyl-4-dibromomethyl-4-methyl-2-cyclohexenone (**IX**) at a ratio of 2.62 : 1 (R_f 0.8, eluent petroleum ether–ether, 2 : 1). Yield 0.181 g.

Ketone **VIII**. ^1H NMR spectrum, δ, ppm (*J*, Hz): 1.83 s (3H, 4-Me); 2.15 s (3H, 6-Me); 4.85 s (1H, $CHBr_2$); 7.55 s (1H, =CH). ^{13}C NMR spectrum, δ_C, ppm (*J*, Hz): 20.44 q (4-Me, $^1J_{CH}$ = 133); 29.81 q (6-Me, $^1J_{CH}$ = 133); 51.85 s (C^4); 54.82 d ($CHBr_2$, $^1J_{CH}$ = 178); 59.25 d (CHBr, $^1J_{CH}$ = 146); 61.47 s (C^6); 122.23 s (C^3); 148.39 d (=CH, $^1J_{CH}$ = 170); 181.54 s (C=O).

Ketone **IX**. ^1H NMR spectrum, δ, ppm (*J*, Hz): 1.82 s (3H, 4-Me); 4.07 d and 4.53 d (1H, CH_2Br, $^2J_{HH}$ = 10.2); 5.79 s (1H, CHBr); 5.88 s (1H, $CHBr_2$); 7.65 s (1H, =CH). ^{13}C NMR spectrum, δ_C, ppm (*J*, Hz): 20.82 q (4-Me, $^1J_{CH}$ = 133); 35.56 t (CH_2Br, $^1J_{CH}$ = 162); 51.46 s (C^4); 54.41 d ($CHBr_2$, $^1J_{CH}$ = 176); 54.70 d (CHBr, $^1J_{CH}$ = 145); 63.37 s (C^6); 122.23 s (C^3); 149.83 d (=CH, $^1J_{CH}$ = 170); 178.93 s (C=O).

Reaction of 4-dibromomethyl-4-methyl-2,5-cyclohexadienone (III) with molecular bromine (Scheme 3). *a. Reactant ratio 1 : 1.* A mixture of 0.1 g (0.36 mmol) of dienone **III** and 0.056 g (0.36 mmol) of bromine in 5 ml of carbon tetrachloride was kept for 24 h at room temperature in the dark. The solution was evaporated, and the oily residue was dissolved in ether. The solution was washed with a 10% solution of sodium acetate, dried over Na_2SO_4, and evaporated, and the residue was subjected to chromatographic separation using benzene–petroleum ether (4 : 1) as eluent. Fractions with R_f 0.17, 0.37, and 0.64 were collected. The fraction with R_f 0.17 contained unreacted ketone **III**.

2-Bromo-4-dibromomethyl-4-methyl-2,5-cyclohexadien-1-one (X). R_f 0.37. Yield 0.095 g. mp 63–64°C (reprecipitation from chloroform with hexane). UV spectrum: λ_{max} 250 nm ($\log\varepsilon$ 4.01). IR spectrum, ν, cm^{-1}: 1600, 1640, 1665. ^1H NMR spectrum, δ, ppm (*J*, Hz): 1.55 s (3H, 4-Me); 5.60 s (1H, $CHBr_2$); 6.50 d (1H, 6-H, ^3J = 10.0); 6.99 d.d (1H, 5-H, ^3J = 10.0, ^4J = 3.2); 7.41 d (1H, 3-H, ^4J = 3.2). ^{13}C NMR spectrum, δ_C, ppm (*J*, Hz): 24.32 q (4-Me, ^1J = 132); 48.67 d ($CHBr_2$, ^1J = 177); 50.81 s (C^4); 126.48 s (C^2); 128.89 d (C^6, ^1J = 168); 149.41 d and 149.49 d (C^3, C^5, ^1J = 167); 177.68 s (C=O). Found, %: C 26.66; H 1.86. $C_8H_7Br_3O$. Calculated, %: C 26.74; H 1.94.

2,6-Dibromo-4-dibromomethyl-4-methyl-2,5-cyclohexadienone (XI). R_f 0.64. Yield 0.22 g. mp 165°C (from chloroform); published data [19]: mp 165-166°C (from methylene chloride). UV spectrum: λ_{max} 264 nm ($\log\varepsilon$ 4.16). IR spectrum, ν, cm^{-1}: 1600, 1630, 1670. ^1H NMR spectrum, δ, ppm (*J*, Hz): 1.60 s (3H, 4-Me); 5.72 s (1H, $CHBr_2$); 7.45 s (2H, 3-H, 5-H). ^{13}C–{^1H}: 24.13 (4-Me); 47.65 ($CHBr_2$), 53.14 (C^4); 123.77 (C^2, C^6); 149.74 (C^3, C^5); 171.85 (C=O). Found, %: C 21.86; H 1.25. $C_8H_6Br_4O$. Calculated, %: C 21.91; H 1.36.

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