Synthesis and stereochemistry of new spiranes containing 2,5-cyclohexadiene and 2,3,3a,6,7,7a-hexahydrobenzofuranone fragments

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The reaction of 4-dihalomethyl-4-methyl-2,5-cyclohexadien-1-ones with $(Me_3Si)_2NNa$ yielded spiro[(2,3,3a,6,7,7a-hexahydro-3,3-dihalo-3a-methylbenzofuran-6-one)-2,1'-(4'-dihalomethyl-4'-methyl-2',5'-cyclohexadienes)]. The structures of the spiro compounds were established based on the data of ^1H and ^{13}C NMR, UV, and IR spectroscopy and mass spectrometry. The mechanism and stereochemistry of the reaction are discussed.

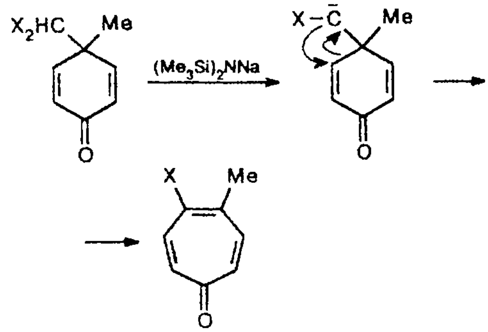
Key words: spiro-2,5-cyclohexadienes, synthesis, stereoisomerism, mechanism of formation.

It is known that sodium hexamethyldisilylamide reacts with dihalomethanes to form halocarbene.[1—4]

$$CH_2X_2 + (Me_3Si)_2NNa \rightarrow \bar{C}HX + (Me_3Si)_2NH + NaX$$

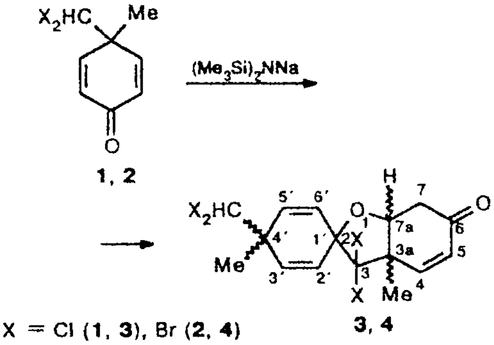
$$X_2 = Cl_2,\ Br_2,\ ClBr$$

We suggested that if the reaction is carried out with the use of 4-dihalomethyl-4-methyl-2,5-cyclohexadien-1-ones **1** or **2** instead of dihalomethane, the reagent would be expected to react with the dihalomethyl group of cyclohexadienone to form a halogen-containing carbenoid particle followed by ring enlargement through insertion of the carbene carbon atom into the adjacent C—C bond:



X = Cl, Br

However, contrary to the expectations, spiro compounds, namely, spiro[(2,3,3a,6,7,7a-hexahydro-3,3-dihalo-3a-methylbenzofuran-6-one)-2,1'-(4'-dihalomethyl-4'-methyl-2',5'-cyclohexadienes)] **3** and **4**, were isolated from the reaction mixture.



X = Cl (**1**, **3**), Br (**2**, **4**)

The data on spiro compounds containing the cyclohexadiene fragment reported in the literature within the last three decades are scarce. A number of spirocyclohexadienedioxetanes were synthesized by the reaction of substituted *exo*-methylenecyclohexadienes with singlet oxygen. These spirocyclohexadienedioxetanes were used as models for studying chemical conversions under the conditions of "photochemistry without light".[5] Decomposition of 2-diazonium-*N*-alkylbenzanilide tetrafluoroborates in the presence of copper[6] or sodium iodides[7] as well as photolysis of 2-iodo-*N*-alkylbenzanilides[8] afforded dimers of spirocyclohexadienyl radicals. Several spirocyclohexadienes (spirocyclohexadienylisoxazoline and spirocyclohexadienyloxazoline) are the structural fragments of biologically active compounds isolated from some species of marine sponges.[9—13] Spirocyclohexadiene, whose geminal unit contains the trichloromethyl group, was prepared by the reaction of stabilized arsenic ylide with the product of condensation of *gem*-trichloromethyl-substituted cyclohexadienone with dimedone.[14]

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Results and Discussion

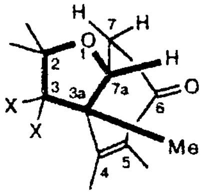
The structures of compounds **3** and **4** were established based on the ^1H and ^{13}C NMR spectra, homonuclear double resonance, proton-decoupled ^{13}C NMR spectra, IR and UV spectra, mass spectrometry, and the data of elemental analysis. In the mass spectra of products **3** and **4**, the molecular ion peaks at *m/z* 380 and 556 were observed, which corresponds to twice the molecular weights of the initial cyclohexadienones. The multiplicities of the peaks were typical of compounds containing four halogen atoms.

Compounds **3** and **4** are characterized by a variety of possible conformations. Let us consider their stereochemical features.

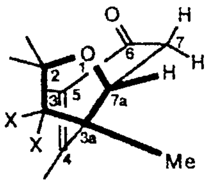
1. The exocyclic CHX_2 group and the CX_2 fragment of the tetrahydrofuran ring can have a mutual *cis* or *trans* arrangement.

2. The five-membered tetrahydrofuran ring and the six-membered cyclohexenone rings can be *cis* or *trans* fused. In the first case, the hydrogen atom and the Me group at positions 7a and 3a, respectively, adopt conformations intermediate between synperiplanar (*sp*) and synclinal (*sc*). In the second case, the conformation is intermediate between antiperiplanar (*ap*) and anticlinal (*ac*). Hereinafter, we shall denote the cyclohexadiene, tetrahydrofuran, and cyclohexenone rings by *A*, *B*, and *C*, respectively. To denote stereoisomers with different mutual arrangements of the CHX_2 and CX_2 groups, we shall add lower-case letters **a** (for *cis*) or **b** (for *trans*) to the order numbers of compounds. For stereoisomers in which the rings *B* and *C* are *cis* or *trans* fused, we shall add prefixes *s* (synperiplanar or synclinal) or *a* (antiperiplanar or anticlinal).

3. When the rings *B* and *C* are *cis* fused, the O atoms of the ether and carbonyl groups can be in a transoid or cisoid orientation with respect to each other depending on the mode of puckering of the benzofuranone fragment O(1)C(2)C(3)C(3a)C(4)C(5)C(6)C(7)C(7a). The conformers with transoid and cisoid orientations of O atoms will be denoted by the terminal indices *t* and *c*, respectively:



3-*t*, 4-*t*

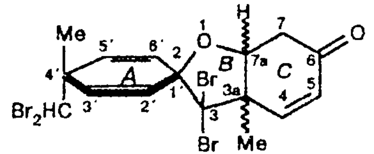


3-*c*, 4-*c*

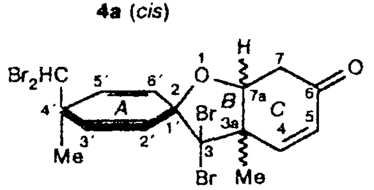
When the rings are *trans* fused, cisoid and transoid conformers do not occur.

4. The compounds have two chiral centers at the C(3a) and C(7a) atoms as well as the chiral axis.

The ^1H and ^{13}C NMR spectra (the parameters of the spectra are given in Experimental) of compound **4** show twice the number of all signals. For each pair of signals, the ratio of integrated intensities was 1.0 : 1.7, which apparently was associated with the presence of two isomers in the mixture (in the ratio of 1.0 : 1.7). We believe that the difference between these isomers is determined by a *cis* or *trans* arrangement of the exocyclic $CHBr_2$ group and the CBr_2 fragment of the tetrahydrofuran ring (isomers **4a** and **4b**).



4a (*cis*)



4b (*trans*)

In the ^1H and ^{13}C NMR spectra of both isomers, the multiplicities of the signals and the spin-spin coupling constants of protons are identical, and the differences in their chemical shifts are insignificant. Therefore, hereinafter we shall discuss the spectral parameters of major isomer **4b** only. The ^1H NMR spectrum of **4b** shows the presence of six coupled olefin protons ($^3J_{(HC=CH)_{cis}}$ = 10.4 Hz). The downfield shift of one of these protons, namely H(4), (δ ~7) coupled with the doublet of H(5) indicates that the molecule contains the conjugated HC=CH—C=O fragment, whereas the chemical shifts of other protons, namely, H(2′), H(3′), H(5′), and H(6′) (δ ~6), are consistent with the absence of conjugation between the corresponding double bonds and the carbonyl group. This is also confirmed by the ^{13}C NMR spectrum in which one low-field signal of C(4) (δ 149.4) and five signals of C(2′), C(3′), C(5′), C(6′), and C(5) (δ ~128—133) were observed. The chemical shift of the only C atom of the carbonyl group, namely C(6), (δ 194.8) is consistent with the presence of one double bond conjugated with this atom, whereas for the initial 4-dibromomethyl-4-methyl-2,5-cyclohexadien-1-one δ(C=O) is 184.8. In addition to the signals of olefin protons, one dibromomethyl, and two methyl groups, the ^1H NMR spectrum has a quadruplet of the H(7a) proton (δ 4.73) with the splitting of 2.8 Hz (in the ^{13}C NMR spectrum, the signal of the C(7a) atom (δ 78.0, $^1J_{C-H}$ = 158 Hz) corresponds to the last-mentioned quadruplet) and the AB system of two protons 2 H(7) (δ 2.89 and 2.57, J_{AB} = 18 Hz). The homonuclear double resonance demonstrated that each line of this AB system is additionally split into a doublet (^3J = 2.8 Hz) on the H(7a) proton. The selective H(7a) proton decoupling is indicative of the presence of the long-range spin-spin interaction with the H(4) proton

($^4J_{\mathrm{H(4)-H(7a)}}$ = 2.8 Hz). In the ^{13}C NMR spectrum, the signal of the CH_2 group (δ 37.9) with two different direct spin-spin ^{13}C—^{1}H coupling constants (^1J = 122 and 135 Hz) corresponds to two nonequivalent 2 H(7) protons.

The ^{1}H NMR spectrum of the chlorine-containing product **3** is virtually identical to that described above except for the difference in the chemical shifts determined by the replacement of halogen. The **3a** : **3b** ratio was 1.0 : 4.6.

In the ^{13}C NMR spectrum of compound **3**, the substantial downfield shift of the signal of the carbon atom of the dihalomethyl group (δ($CHBr_2$) 53.6 and δ($CHCl_2$) 78.3) and the downfield shift of the signal of the C(3) atom, which is directly bonded to the halogen atom, (δ(C(3)Br_2) 85.3 and δ(C(3)Cl_2) 102.0) were observed. The chemical shifts of other signals changed insignificantly.

Based on the analysis of the NMR spectra, it was concluded that molecules **3** and **4** contain the conjugated HC=CH—C=O fragment. This conclusion was also confirmed by the data of IR and UV spectroscopy. The IR spectra of compounds **3** and **4** show an intense band at 1700 cm^{-1}, which corresponds to the stretching vibrations of the carbonyl group. The parameters of the UV spectra indicate that the carbonyl group is conjugated with the double C=C bond: λ_{max} = 218 and 216 nm (ε 14 000 and 13 000 L mol^{-1} cm^{-1}) for X = Cl and Br, respectively. For comparison, note that in the spectrum of cyclohexen-2-one containing the analogous fragment, λ_{max} = 226 nm (ε 10 400 L mol^{-1} cm^{-1}).[15]

We suggest the following mechanism of formation of spiro compounds **3** and **4**. First, the dihalomethyl group of cyclohexadienones **1** and **2** reacts with $(Me_3Si)_2NNa$ to form carbanion **5** (the methylene component), which then adds at the carbonyl group of nonconsumed initial dienone (Scheme 1).

The O atom of anion **6** attacks the C atom (adjacent to the geminal unit) of the CH=CH—C=O fragment to form enolate anion **7**, which is converted to spiro compounds **3** or **4**.

The data of NMR spectroscopy and LC-MS spectrometry demonstrated that the yields of both tetrachloro and tetrabromo derivatives of spirocyclohexadienyl compounds **3b** and **4b** with a transoid orientation of the CHX_2 substituent (ring *A*) and the CX_2 group of the five-membered tetrahydrofuran ring (ring *B*) were substantially higher (by factors of 1.7 and 4.6 for X = Br and Cl, respectively) than the yields of isomers **3a** and **4a** with a cisoid arrangement of these groups.

With the aim of elucidating the causes of this selectivity, we carried out quantum-chemical calculations of the geometry, heats of formation, and energies of the frontier orbitals of various stereoisomers of compounds **3** and **4** by the semiempirical PM3 method. The results of calculations are given in Table 1.

It can be seen from the data in Table 1 that the calculated values of the bond lengths agree as a whole with the so-called typical bond lengths given in various handbooks. Taking into account that in individual cases, the bond lengths can deviate from the normal values, it is believed that the results of calculations of the geometries of the molecules under study by the PM3 method are in reasonably good agreement with their real structures. (However, note that the calculated values of the C—Br bond lengths are 0.03—0.06 Å smaller than the typical values.)

The calculated heats of formation (see Table 1) allow conclusions that the compounds with the *cis* fusion of the rings *B* and *C* (*s* structures) are more stable (by 7—9 kcal mol^{-1}) than the corresponding compounds with the *trans* fusion of these rings (*a* structures). The value of $\Delta_f H$ is virtually unaffected by the mutual arrangement of the O atoms of the ether and carbonyl groups (*-c* or *-t*).

Scheme 1

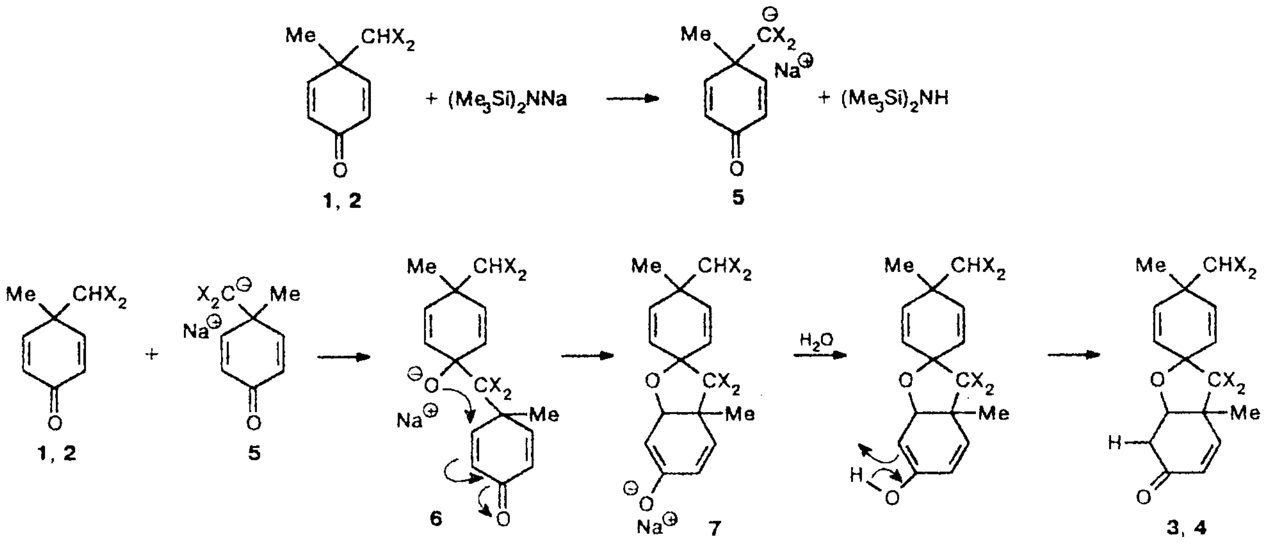


Table 1. Geometric and energy parameters of spiro compounds **3** and **4** calculated by the PM3 method

Compound	Bond lengths/Å									Torsion angle/deg		$-\Delta_f H$ /kcal mol^{-1}	$-\varepsilon_{HOMO}$ /eV[e]	$-\varepsilon_{LUMO}$ /eV[f]
	C—Cl (1.77)[a]		C—Br (1.94)[a]		C—O (1.43)[a]		C=C (1.34)[a]		C=O					
	$CHCl_2$	CCl_2	$CHBr_2$	CBr_2	C(7a)—O	C(2)—O	C(4)=C(5)	C(2')=C(3')[b]	(1.22)	α[c]	β[d]			
s-**3a**-*c*	1.77	1.77			1.43	1.44	1.33	1.33	1.216	73	43	54.22	10.39	0.39
s-**3a**-*t*	1.77	1.76			1.425	1.45	1.33	1.33	1.215	50	166	55.32	10.39	0.41
s-**3b**-*c*	1.77	1.77			1.43	1.44	1.33	1.33	1.216	73	43	54.21	10.39	0.37
s-**3b**-*t*	1.77	1.76			1.43	1.45	1.33	1.33	1.215	49	166	56.77	10.44	0.45
a-**3a**	1.77	1.77			1.425	1.46	1.34	1.33	1.216	62	179	49.70	10.46	0.50
a-**3b**	1.77	1.755			1.425	1.46	1.34	1.33	1.216	62	179	49.72	10.46	0.49
s-**4a**-*c*			1.91	1.89	1.43	1.44	1.33	1.33	1.215	70	46	14.40	10.38	1.11
s-**4a**-*t*			1.91	1.89	1.43	1.45	1.33	1.33	1.215	44	160	15.37	10.44	1.15
s-**4b**-*c*			1.91	1.89	1.43	1.45	1.33	1.33	1.215	70	46	13.97	10.43	1.03
s-**4b**-*t*			1.91	1.89	1.43	1.45	1.33	1.33	1.215	44	160	15.17	10.52	1.07
a-**4a**			1.91	1.88	1.43	1.46	1.34	1.33	1.216	62	179	6.14	10.48	1.12
a-**4b**			1.91	1.88	1.43	1.46	1.34	1.33	1.216	62	179	5.84	10.54	1.05

[a] The typical values of the bond lengths (Å) are given in parentheses.

[b] Or C(5')—C(6').

[c] The H(7a)—C(7a)—C(7)—H(7) torsion angle.

[d] The H(7a)—C(7a)—C(7)—H(7') torsion angle, where H(7) is the hydrogen atom bonded to the C(7) atom (in the Newman projection along the C(7a)—C(7) bond, this atom is located between the oxygen atom of the ether group and H(7a)) and H(7') is the hydrogen atom bonded to the C(7) atom.

[e] The bonding combination of the bonding π orbitals of the C(2')=C(3') and C(5')=C(6') bonds. Near to HOMO the orbital is located (for example, for compound *s*-**3a**-*c*, its energy $\varepsilon = -10.53$ eV), which corresponds to the antibonding combination of these orbitals.

[f] The antibonding π* orbital of the carbonyl group.

Table 2. The geometric and energy parameters of some alkoxide anions, which are precursors of compounds **4a** and **4b**, calculated by the PM3 method

Anion	$-CHBr_2$ and $-CBr_2$	Bond lengths/Å						Distance from O^-/Å		The O^-—C(3)—C(4) angle/deg	$-\Delta_f H$ /kcal mol^{-1}	$-\varepsilon_{HOMO}$ /eV[d]	ε_{LUMO} /eV[e]
		C—Br		C=C		C=O	C(8)—O^-						
		$CHBr_2$	CBr_2	C(3)=C(4)[b]	C(9)=C(10)[c]			O^-...C(3)	O^-...C(7)				
7a	*cis*-	1.92	1.93	1.33	1.33	1.22	1.32	2.68	4.37	152	30.43	5.04	1.97
7b	*trans*-	1.93	1.94	1.34	1.33	1.22	1.32	2.68	4.37	152	27.32	4.90	1.93
7c	*trans*-	1.91	1.92	1.34	1.33	1.22	1.32	2.80	4.34	107	19.51	4.64	1.98

[a] The atomic numbering scheme is given in the text (compound **7a**).

[b] Or C(6)—C(7).

[c] Or C(12)—C(13).

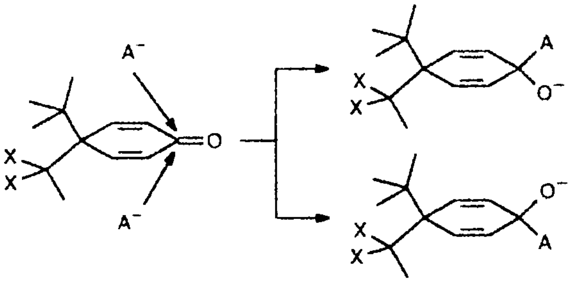
[d] The *p* orbital of the negatively charged oxygen atom.

[e] The complex orbital with the major contribution of the bonding combination of two antibonding orbitals of the C—Br bonds of the exocyclic $CHBr_2$ group.

The energies of HOMO for all 12 molecules listed in Table 1 are nearly identical. The energies of LUMO of the bromine-containing molecules are substantially lower than those of the chlorine-containing molecules. However, both the energies of LUMO and HOMO change only slightly within the series of chlorine- or bromine-containing compounds. (Note that HOMO of the molecules under study is localized mainly on the π orbitals of the double bonds of the ring *A*, whereas LUMO is an antibonding π^* orbital of the carbonyl group of the ring *C*.)

Therefore, the results of calculations leave unexplained the fact that in the reaction under study, products **3b** and **4b** predominated over isomeric compounds **3a** and **4a**. This predominance cannot be determined by the properties of these products. Therefore, the causes should be looked for in the kinetic preference of formation of isomers **3b** and **4b**. According to the mechanism of the reaction discussed above the attack of carbanion **5** at the initial substrates, namely, at *gem*-dihalomethyl-substituted cyclohexadienones **1** or **2**, is a key stage of the process, which determines the stereochemistry of the final product. The characteristic feature of these substrates is their axial prochirality. These compounds belong to compounds of the axial enantiotopic type because when the nucleophile A^- attacks the carbonyl group from above and below with respect to the plane of the molecule, diastereomeric adducts are formed (Scheme 2).

Scheme 2

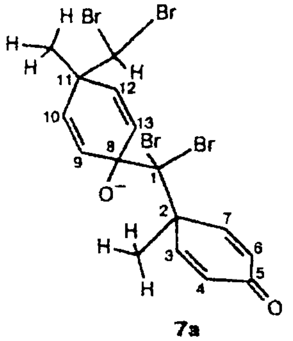


According to the Cram—Prelog's rules[16,17] (deduced for compounds with the central chirality), the attack of methylene component **5** on the C atom of the carbonyl group should occur from the sterically less hindered side (in Scheme 2, from above). This is particularly true in the case of the reaction under consideration because the nucleophile (carbanion **5**) is very bulky. Therefore, the product with a transoid orientation of the CHX_2 and CX_2 groups is favorable. When the attack at the carbanion occurs from the side on which the less bulky (compared to the CHX_2 group) Me group is located, the above-mentioned product is actually formed. As a result, tetrahedral addition product **6** forms. When the reaction proceeds according to this mechanism, the rings *B* and *C* of the products should be *cis* fused. This conclusion was confirmed by a comparison of the calculated torsion angles with the data of ^{1}H NMR spectroscopy. The H(7a)—C(7a)—C(7)—H(7) (α) and H(7a)—C(7a)—C(7)—H(7′) (β) torsion angles calculated by the PM3 method are given in Table 1. Here, the H(7) symbol denotes the proton, which is located between the O atom of the ether group (O_{eth}) and H(7a) in the Newman projection of the ethane fragment [C(7a)—C(7)]. The H(7′) symbol denotes the second proton at the C(7) atom. As can be seen from Table 1, when the rings *B* and *C* are *trans* fused (compounds *a*-**3a,b** and *a*-**4a,b**), the angles α and β are substantially different (62° and 179°), which is inconsistent with the measured values of the spin-spin coupling constants $^3J_{H(7)-H(7a)} \approx {}^3J_{H(7')-H(7a)} \approx 2.8$ Hz. The close values of these spin-spin coupling constants count in favor of *cis* fusion (*cf.* Refs. 18 and 19) with a cisoid mutual arrangement of the O atoms of the ether and carbonyl groups because only in this case are the calculated values of the torsion angles rather close ($\alpha = 73°$ and $\beta = 43°$ when X = Cl; and $\alpha = 70°$ and $\beta = 46°$ when X = Br). In the case of a transoid arrangement of two O atoms, $\alpha = 50°$ and $\beta = 166°$ (when X = Cl) and $\alpha = 44°$ and $\beta = 160°$ (when X = Br) (see Table 1), which is inconsistent with the data of NMR spectroscopy. Therefore, it is believed that the reaction under study gave compounds *s*-**3b**-*c* and *s*-**4b**-*c* as major products (attack at the carbonyl group from the sterically less hindered side) and compounds *s*-**3a**-*c and s*-**4a**-*c* as minor products (attack at the C=O group from the sterically more hindered side).

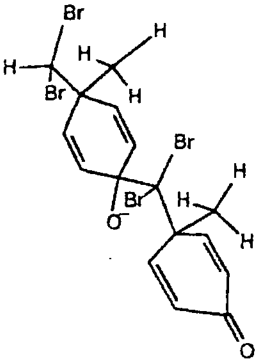
Using the tetrabromo-substituted derivatives as an example, we calculated the geometric and energy parameters of alkoxide ions **6** (X = Br), which are precursors of spiro compounds **4**. Let us denote the calculated structures by **7a**, **7b**, and **7c**. Structure **7a** is formed as a result of attack of the carbanion on the C=O group of the initial molecule from the sterically hindered side of the enantiotopic surface. Structures **7b** and **7c** correspond to more probable attack from the sterically less hindered side (see Scheme 2). The results of calculations are given in Table 2.

Although in anions **7a** and **7b**, the distances between the negatively charged O atom and the C(3) atom (2.68 Å) are shorter than the corresponding distance in anion **7c** (2.80 Å), the O^-—C(3)—C(4) angle in the first two compounds (152°) is substantially larger than in **7c** (107°). Therefore, it is unknown whether conformation **7b** or **7c** is favorable for the most rapid closure of the five-membered ring. Apparently, the angle of the attack plays a more important role because π systems most readily react when the second reagent approaches perpendicular to the plane of the molecule. Then, conformation **7c** is the most favorable for the closure of the five-membered ring.

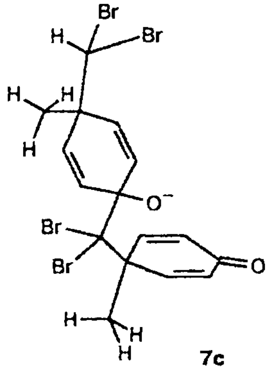
The attack on the C(3) atom is more probable than the attack on the C(7) atom because the C(7) atom is located at a substantially larger distance from the negatively charged O atom (see Table 2). When attack occurs on the C(3) atom, anion **7c** may give spiro com-



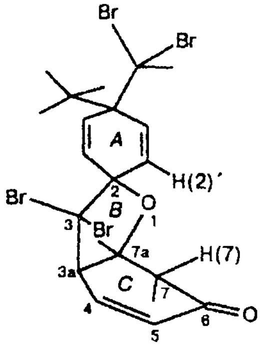
7a



7b

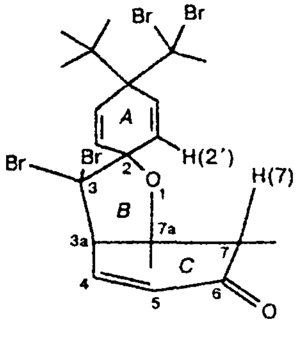


7c



s-**4b**-*c*

H(7)...H(2′) — 4.41 Å
O_{eth}...H(7) — 2.54 Å
O_{eth}...H(2′) — 2.67 Å



s-**4b**-*t*

H(7)...H(2′) — 2.28 Å
O_{eth}...H(7) — 2.61 Å
O_{eth}...H(2′) — 2.71 Å

pounds *s*-**4b**-*c* or *s*-**4b**-*t*. Their molecules contain two chiral centers in which the C(3a) and C(7a) atoms have the *R* and *S* configurations, respectively. However, in these cases, one should not expect the asymmetric synthesis because the C(3) and C(7) atoms change places due to free rotation about the C(1)—C(2) and C(1)—C(8) bonds in the anion, and the C(7) atom instead of the C(3) atom could become the center of attack, which would lead to spirane with the *S* configuration of the C(3a) atom and the *R* configuration of the C(7a) atom, *i.e.*, to the mirror imagination of spirane formed upon attack on the C(3) atom.

The occurrence of conformers with a cisoid orientation of the O atoms of the ether and carbonyl fragments is attributable to the fact that in the transoid conformation, the H(7) and H(2′) atoms are brought very close together compared to the cisoid isomer. The results of calculations of the geometries of molecules *s*-**4b**-*c* and *s*-**4b**-*t* by the PM3 method are discussed below. It follows from these results that the H(7)—H(2′) distance in conformer -*t* is only slightly larger than the sum of the van der Waals radii.

We determined the conformations of the rings in the spiro compounds by calculating the puckering parameters and the conformational space formed by the puckering parameters using the known procedure.[20,21] The calculations were carried out using the RICON program,[22] which allows the qualitative and quantitative description of conformations of small and medium-sized rings based on atomic coordinates (obtained in this work by calculations of the geometries of the molecules by the PM3 method). The conformations of the rings were obtained as superimpositions of the particular basis conformations (chair, boat, twist-boat, envelope, *etc.*).

The results demonstrated that the conformations of the rings are virtually independent of whether a molecule contains Cl or Br atoms and whether the $\dot{C}HX_2$ and CX_2 groups are in *cis* or *trans* orientations, but they are substantially affected by the mode of ring fusion.

When rings *B* and *C* are *trans* fused, ring *A* adopts a conformation intermediate between a boat and a half-chair (the contribution of the boat conformation varies from 75 to 86% depending on the compound), ring *B* adopts a distorted twist conformation (the contribution of the basis twist conformation is 84—86%), and ring *C* has a conformation intermediate between an envelope and a twist-boat (the contributions of envelope, boat, and twist-boat conformations are 50—52%, 28—31%, and 16—20%, respectively). When rings *B* and *C* are *cis* fused, ring *A* adopts a conformation intermediate between a half-chair and an envelope (the contribution of the chair conformation is 50—55%), ring *B* adopts a conformation intermediate between an envelope and a twist conformation (the contributions of envelope and twist conformations are 50% and 50%, respectively), and ring *C* has a distorted envelope conformation (the contributions of chair, boat, and twist-boat conformations are 53%, 35—40%, and 10—12%, respectively). In all cases, the conformation of the nine-membered O(1)C(2)C(3)C(3a)C(4)C(5)C(6)C(7)C(7a) bicyclic system is a combination of more than three basis conformations. In the case of *trans* fusion, D_3 and twist-chair conformations make the major contributions (~40% and ~35%, respectively). In the case of *cis* fusion, twist-chair—chair and boat—boat conformations make the major contribution (~30% and ~25%, respectively). The contributions of twist-boat—boat, D_3, and chair—chair conformations are ~15%.

Experimental

Calculations of the geometric and energy parameters of the molecules and ions were carried out by the semiempirical PM3 method using the HYPERCHEM RELEASE4 program package.

The conformations of the rings were classified using the RICON program developed by A. Zotov (Department of Chemistry of the M. V. Lomonosov Moscow State University).

The ^{1}H and ^{13}C NMR spectra were recorded on a Varian VXR-400 spectrometer in $CDCl_3$ at 30 °C with $SiMe_4$ as the internal standard. The IR spectra were recorded on a UR-20 instrument in CCl_4. The UV spectra were measured on a Cary-219 spectrophotometer in ethanol. Chromatography-mass spectra were obtained on a MS-1303 spectrometer.

4-Dichloromethyl-4-methyl-2,5-cyclohexadien-1-one (1) was prepared according to the known procedure.[23]

4-Dibromomethyl-4-methyl-2,5-cyclohexadien-1-one (2) was synthesized under the conditions of phase transfer catalysis according to the procedure reported previously.[24]

Synthesis of spiro compounds (general procedure). Pentane (3 mL) was added with intense stirring to a $1.0 \cdot 10^{-3}$ *M* solution of compound **1** or **2** in benzene (0.5 mL) under an atmosphere of argon at 0 °C. A suspension of $(Me_3Si)_2NNa$ ($2.0 \cdot 10^{-3}$ mol L^{-1}) in a mixture of solvents (0.5 mL of benzene + 1 mL of pentane) was added to the thin suspension formed. After completion of addition of $(Me_3Si)_2NNa$, the yellowish reaction mixture was immediately decomposed with water (2 mL). The solvent was distilled off. The pale-brown wet mass was twice extracted with ether. The organic extracts were washed with water and dried over $MgSO_4$. The solvent was evaporated.

Spiro[(3,3-dichloro-2,3,3a,6,7,7a-hexahydro-3a-methylbenzofuran-6-one)-2,1′-(4′-dichloromethyl-4′-methyl-2′,5′-cyclohexadiene)] (3). The product was obtained in a yield of 0.07 g (37%), m.p. 129—130 °C (from an ether—pentane mixture). Found (%): C, 50.26; H, 4.30; Cl, 37.28. $C_{16}H_{16}Cl_4O_2$. Calculated (%): C, 50.26; H, 4.18; Cl, 37.17. IR, ν/cm^{-1}: 1700 (C=O). UV, λ_{max}/nm: 218 (ε 14000).

^{1}H NMR of isomer **3b**, δ: 1.33, 1.48 (both s, 3 H, Me(3a), Me(4′)); 2.56, 2.89 (the ABX system, 2 H(7), $^2J_{AB}$ = 18.0 Hz, $^3J_{H(7)-H(7a)}$ = 2.8 Hz); 4.65 (q, H(7a), $^3J_{H(7a)-H(7)}$ = $^4J_{H(7a)-H(4)}$ = 2.8 Hz); 5.56 (s, $CHCl_2$); [5.84, 5.96 (2 H, the AB system, $^3J_{AB}$ = 10.4 Hz); 6.16 (br.s, 2 H, the degenerate AB system) (H(2′), H(3′), H(5′), H(6′))]; 6.12 (d, H(5), $^3J_{H(5)-H(4)}$ = 10.4 Hz); 6.97 (dd, H(4), $^3J_{H(4)-H(5)}$ = 10.4 Hz, $^4J_{H(4)-H(7a)}$ = 2.8 Hz). ^{13}C NMR of isomer **3b**, δ: 19.16, 24.30 (both q, Me(3a), Me(4′), $^1J_{^1H-^{13}C}$ = 131 Hz); 37.93 (dd, C(7), $^1J_{^1H-^{13}C}$ = 122 and 136 Hz); 44.45 (s, C(4′)); 53.09 (s, C(3a)); 78.34 (d, $CHCl_2$, $^1J_{^1H-^{13}C}$ = 182 Hz); 78.82 (d, C(7a), $^1J_{^1H-^{13}C}$ = 155 Hz); 83.09 (s, C(2)); 102.01 (s, C(3)); [128.37 (d, $^1J_{^1H-^{13}C}$ = 168 Hz), 128.70 (d, $^1J_{^1H-^{13}C}$ = 166 Hz), 129.15 (d, $^1J_{^1H-^{13}C}$ = 166 Hz), 132.31 (d, $^1J_{^1H-^{13}C}$ = 163 Hz), 133.02 (d, $^1J_{^1H-^{13}C}$ = 164 Hz) (C(2′), C(3′), C(5′), C(6′), C(5))]; 148.48 (d, C(4), $^1J_{^1H-^{13}C}$ = 163 Hz); 194.59 (s, C(6)). MS (50 eV), *m/z*: 380 [M]$^+$.

Spiro[3,3-dibromo-2,3,3a,6,7,7a-hexahydro-3a-methylbenzofuran-6-one)-2,1′-(4′-dibromomethyl-4′-methyl-2′,5′-cyclohexadiene)] (4). The product was obtained in a yield of 0.17 g (60%), m.p. 126—132 °C (from an ether—pentane mixture). Found (%): C, 34.22; H, 2.78; Br, 57.27. $C_{16}H_{16}Br_4O_2$. Calculated (%): C, 34.28; H, 2.85; Br, 57.14. IR, ν/cm^{-1}: 1700 (C=O). UV, λ_{max}/nm: 216 (ε 13000). ^{1}H NMR of isomer **4b**, δ: 1.39, 1.55 (both s, 3 H, Me(3a), Me(4′)); 2.56, 2.89 (the ABX system, 2 H(7), $^2J_{AB}$ = 18.0, $^3J_{H(7)-H(7a)}$ = 2.8 Hz); 4.73 (q, H(7a), $^3J_{H(7a)-H(7)}$ = $^4J_{H(7a)-H(4)}$ = 2.8 Hz); 5.52(s, $CHBr_2$); [5.84, 5.91 (2 H, the AB system, J_{AB} = 10.4 Hz); 6.13, 6.22 (2 H, the AB system, $^3J_{AB}$ = 10.4 Hz) (H(2′), H(3′), H(5′), H(6′))]; 6.08 (d, H(5), $^3J_{H(5)-H(4)}$ = 10.4 Hz); 7.05 (dd, H(4), $^3J_{H(4)-H(5)}$ = 10.4 Hz, $^4J_{H(4)-H(7a)}$ = 2.8 Hz). ^{13}C NMR of isomer **4b**, δ: 21.96, 25.72 (both q, Me(3a), Me(4′), $^1J_{^1H-^{13}C}$ = 129 and 130 Hz); 37.93 (dd, C(7), $^1J_{^1H-^{13}C}$ = 122 and 135 Hz); 43.80 (s, C(4′)); 52.96 (s, C(3a)); 53.59 (d, $CHBr_2$, $^1J_{^1H-^{13}C}$ = 180 Hz); 77.99 (d, C(7a), $^1J_{^1H-^{13}C}$ = 154 Hz); 82.76 (s, C(2)); 85.33 (s, C(3)); [128.31 (d, $^1J_{^1H-^{13}C}$ = 167 Hz), 129.76 (d, $^1J_{^1H-^{13}C}$ = 166 Hz), 130.83 (d, $^1J_{^1H-^{13}C}$ = 167 Hz), 132.45 (d, $^1J_{^1H-^{13}C}$ = 162 Hz), 133.48 (d, $^1J_{^1H-^{13}C}$ = 164 Hz) (C(2′), C(3′), C(5′), C(6′), C(5))]; 149.40 (d, C(4), $^1J_{^1H-^{13}C}$ = 162 Hz); 194.79 (s, C(6)). MS (50 eV), *m/z*: 556 [M]$^+$.

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