Reaction of stereoisomeric bis(cyclohexyl)-2,2′-diones with hydrogen peroxide: structure of the formed adducts

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The reaction of *meso*- and D,L-forms of bis(cyclohexyl)-2,2′-dione with a methanol solution of hydrogen peroxide in a neutral medium has been studied. It has been established that in the case of the D,L-form *rac*-(1*R*,4*R*,9S,10*S*)-1,4-dihydroxy-2,3-dioxatricyclo-[8.4.0.0^{4,9}]tetradecane is formed, while the *meso*-form affords *rac*-(1*R*,4*R*,9*S*,10*R*)-1-methoxy-4-hydroxy-2,3-dioxatricyclo[8.4.0.0^{4,9}]tetradecane. The structures of the compounds have been established by X-ray structural analysis and by ^{1}H and ^{13}C NMR spectroscopy.

Key words: bis(cyclohexyl)-2,2′-dione, peroxides; stereoisomers; X-ray structural analysis.

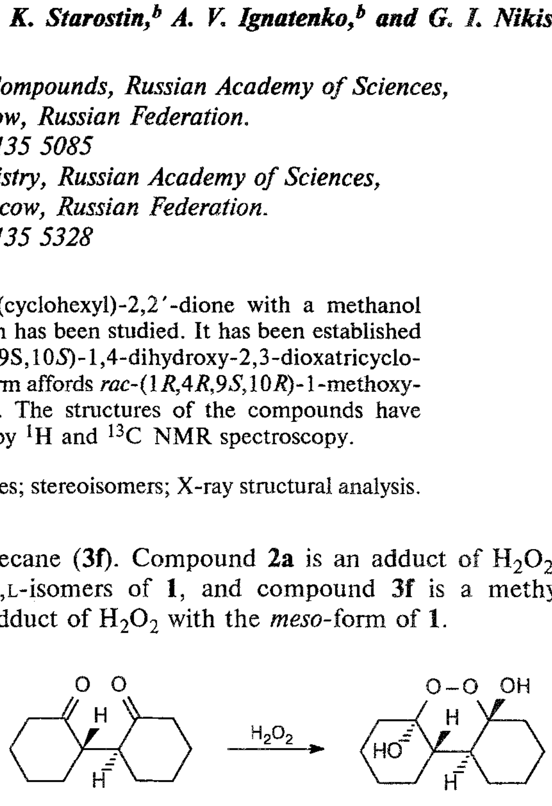
Reactions of monocyclic aliphatic ketones with hydrogen peroxide were the subject of many studies[1–3] including our own works.[4,5] It has been established that the composition and yields of the products are mainly determined by temperature and the pH of solutions.[3,6] Reactions of bis(cycloalkyl)diones have been considerably less studied though these compounds are available reagents that can be readily obtained, *e.g.*, by dehydrodimerization of cycloalkanes with oxides or metal peroxides.[7,8]

Previously, a method for the synthesis of bis(cycloalkyl)diones from cycloalkanones with a high yield (up to 80 %) was developed.[9] Manganese triacetate was used as the oxidant, and the product was obtained as a mixture of diastereoisomers: *meso*- and D,L-forms.

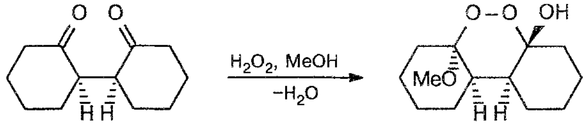
It was of interest to compare the reactivity of the stereoisomers of bis(cycloalkyl)diones in the reaction with hydrogen peroxide. For this purpose in this work, we obtained the products of the reaction of *meso*- and D,L-diastereoisomers of bis(cyclohexyl)-2,2′-dione (**1**) with H_2O_2 in a neutral medium and studied their structures.

Results and Discussion

Based on the results of ^{13}C and ^{1}H NMR spectroscopy and X-ray structural analysis, we succeeded in determining the chemical structure of the products of the reaction of diastereoisomers **1** with H_2O_2 in methanol: *rac*-(1*R*,4*R*,9*S*,10*S*)-1,4-dihydroxy-2,3-dioxatricyclo[8.4.0.0^{4,9}]tetradecane (**2a**) and *rac*-(1*R*,4*R*,9*S*,10*R*)-1-methoxy-4-hydroxy-2,3-dioxatricyclo[8.4.0.0^{4,9}]tetradecane (**3f**). Compound **2a** is an adduct of H_2O_2 with D,L-isomers of **1**, and compound **3f** is a methylated adduct of H_2O_2 with the *meso*-form of **1**.



(D,L)-**1** **2a**



meso-**1** **3f**

Previously, based on the results of investigations performed under similar conditions, it was assumed that a second product, the hydroxyhydroperoxyperhydrodibenzofuran, was formed along with peroxide **2a**.[10]

According to the X-ray structural data, molecule **2a** (Fig. 1) has the unstrained *trans,trans*-fused structure of a tricyclic framework. All three six-membered cycles including the peroxide ring adopt the optimum chair conformation. In this molecular structure, the adjacent cycles occupy diequatorial positions with respect to each other, while both hydroxyl groups located in the region of fusion occupy axial positions. When D,L-**1** is peroxidized, two more enantiomer pairs could be formed:

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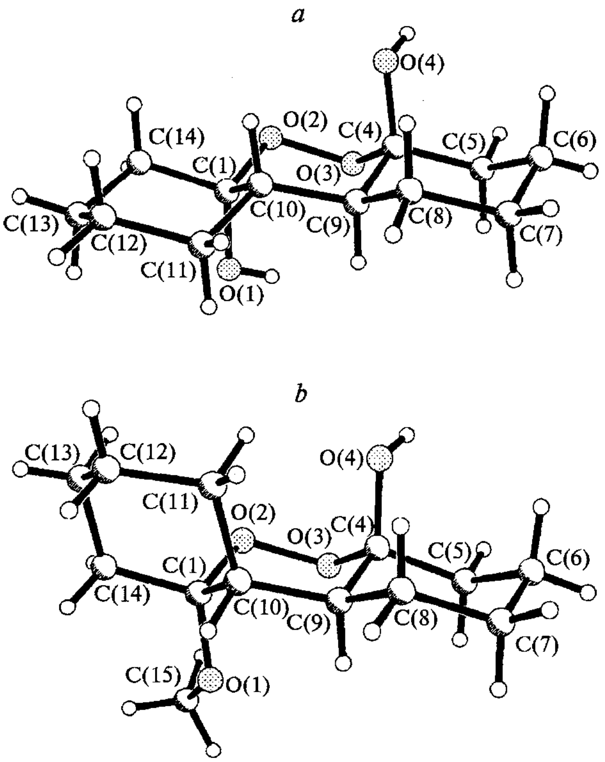
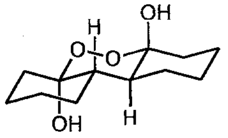
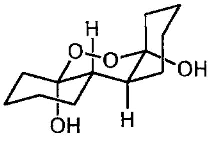


Fig. 1. Structure of molecule **2a** (*a*) and molecule **3f** (*b*; one of two crystallographically independent molecules, **3fA**, is shown; the other molecule, **3fB**, has a similar structure).

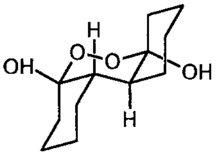
rac-(1*R*,4*S*,9*S*,10*S*)-**2** * (**2b**) and *rac*-(1*S*,4*S*,9*S*,10*S*)-**2** (**2c**), in which one or both aliphatic cycles are *cis*-fused to the central peroxide ring. However, these diastereoisomers are absent in the mixture of reaction products, which is indicative of a high stereoselectivity of this reaction.



2a



2b



2c

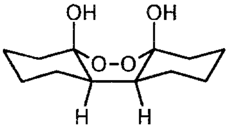
The stereochemical control can have a thermodynamic character. Indeed, both enantiomer pairs not found among the reaction products (**2b** and **2c**) are energetically less favorable because the retention of the optimum chair conformation of the central peroxide ring requires sterically hindered axial-equatorial fusion of the six-membered rings.

However, stereochemical control can be realized at the kinetic stage, *i.e.*, at the moment of nucleophilic addition of the H_2O_2 molecule to the initial dione.

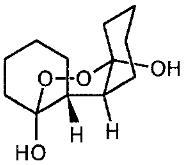
If molecule **1** has the optimum conformation with six-membered rings adopting a chair conformation and occupying equatorial positions with respect to each other, the steric conditions for the nucleophilic attack are actually nonequivalent.

Apparently, the attack on the equatorial position affording the *trans*-isomer is more favorable than the axial interaction producing the *cis*-isomer. However, without specific information on the structure of the transition state, it is presently difficult to estimate quantitatively the factors determining a particular direction of attack. Nevertheless, the experimental data on the structure of compound **3f** favor the *trans*-fusion of the peroxide and aliphatic cycles occurring at the stage of nucleophilic addition of H_2O_2 to a dione.

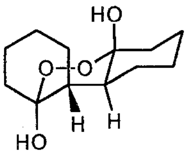
The addition of H_2O_2 to *meso*-**1** could afford two *meso*-diastereoisomers and one pair of enantiomers **2**: *meso*-(1*S*,4*R*,9*S*,10*R*)-**2** (**2d**), *meso*-(1*R*,4*S*,9*S*,10*R*)-**2** (**2e**), and *rac*-(1*R*,4*R*,9*S*,10*R*)-**2** (**2f**),* which have *trans,trans*-, *cis,cis*-, and *cis,trans*-fusion of the cycles, respectively.



2d



2e



2f

Detailed consideration reveals that the retention of the optimum chair conformation of the peroxide cycle is possible only for diastereoisomers **2e** and **2f**, while *trans,trans*-fusion of the cycles is possible only if the peroxide ring adopts a boat conformation (or a twisted boat conformation). In the latter case, the peroxide group should be substantially *cis*-flattened, which is

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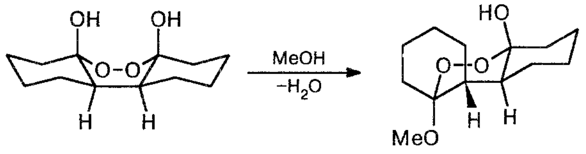
* Equivalent to the (1*S*,4*R*,9*S*,10*S*) configuration within the atomic numbering scheme due to the symmetry of the structural formula of **2**.

* Equivalent within the atomic numbering scheme to the (1*R*,4*S*,9*R*,10*S*), (1*S*,4*R*,9*R*,10*S*), and (1*R*,4*R*,9*R*,10*S*) configurations, respectively.

quite untypical and unfavorable; hence, this form (**2d**) cannot be stable.

Therefore, if the direction of the reaction of isomers **1** with H_2O_2 was controlled only thermodynamically, *i.e.*, it depended only on the comparative steric strain of the final products, the least hindered *cis,trans*-fused diastereoisomer **2f** should be obtained from *meso*-**1**.

The *cis,trans*-configuration of the actually isolated substituted product **3f** observed for both its symmetrically independent molecules (**3fA** and **3fB**) in the crystal (see Fig. 1) coincides with the above-mentioned conformation, which is the most favorable among the (9*S*,10*R*)-isomers of **2**; however, a methoxy group was unexpectedly determined instead of one of the hydroxyl groups, namely, the group in the region of the *cis*-fusion of the rings. The formation of only the monomethoxy derivative **3f** starting from *meso*-**1** is possible only if kinetic control, *i.e.*, the preference of the equatorial direction of the nucleophilic attack on the carbonyl group with *trans*-fusion of the peroxide and aliphatic rings, is assumed to be the determining stage of the process of asymmetric induction. In this case, sterically strained unstable *meso*-(1*S*,4*R*,9*S*,10*R*)-intermediate **2d** should be formed at the first stage of the peroxidation of *meso*-**1** and then rapidly converted to the stable *rac*-(1*R*,4*R*,9*S*,10*R*)-form, compound **3f**, with inversion of one (anyone) of the hydroxy-substituted chiral centers (C(1) or C(4)) as a result of interaction with the solvent molecule (methanol) *via* the S_N2 mechanism.



2d **3f**

Therefore, both symmetrically independent molecules **3f** have nearly identical structures characterized by *cis,trans*-fusion of the tricyclic framework and by the location of the methoxy group in the region of the *cis*-fusion of the rings. All three six-membered rings including the peroxide ring adopt a chair conformation (see Fig. 1 and Table 1). The *trans*-fused rings occupy mutually diequatorial positions, and the *cis*-fused rings occupy the axial-equatorial positions. The methoxy group is in the axial position with respect to the peroxide cycle and in the equatorial position with respect to the aliphatic cycle. The hydroxyl group is in the axial position with respect to both *trans*-fused cycles. The mutual orientation of the methoxy and hydroxyl groups at the peroxide cycle of molecule **3f** is identical to that of two hydroxyl groups in molecule **2a**, *i.e.*, the *trans* orientation.

It is known[11] that in the absence of steric hindrances the peroxide group adopts a conformation characterized by an R—O—O—R torsion angle (τ) within the range from 90° to 120°. Substantial deviations from this range may be caused either by the presence of bulky substituents R (*e.g.*, in the molecule of 1,1′-dihydroxycyclohexyl peroxide,[12] τ = 156.1(4)°) or by the involvement of the peroxide group in rather small cyclic or framework systems (in the six-membered peroxide cycles,[13] τ varies in the range of 65—75°). In the structures studied, the angle τ is −69.8(3)° in molecule **2a** and −66.2(2)° and −66.9(2)° in molecules **3fA** and **3fB**, respectively (see Table 1), *i.e.*, the conformation of the peroxide group is hindered, but it is quite typical for these systems. It is of interest to note a decrease in the angle τ in sterically more strained (because of the *cis*-fusion of the rings) molecules **3f**, compared to molecule **2a**.

Table 1. Principal torsion angles (θ) in molecules **2a** and **3f**

Angle	θ/deg		
	2a	**3fA**	**3fB**
C(15)—O(1)—C(1)—O(2)		−57.5(2)	−45.2(3)
H(O-1)—O(1)—C(1)—O(2)	54(4)		
C(15)—O(1)—C(1)—C(10)		−176.7(2)	−165.2(2)
H(O-1)—O(1)—C(1)—C(10)	−69(4)		
C(15)—O(1)—C(1)—C(14)		58.4(2)	70.2(2)
H(O-1)—O(1)—C(1)—C(14)	168(4)		
O(3)—O(2)—C(1)—C(10)	63.4(3)	63.5(2)	63.1(2)
O(3)—O(2)—C(1)—C(14)	−178.2(2)	−173.7(1)	−173.6(1)
C(1)—O(2)—O(3)—C(4)	−69.8(3)	−66.2(2)	−66.9(2)
O(2)—O(3)—C(4)—C(5)	174.7(2)	177.8(1)	178.1(1)
O(2)—O(3)—C(4)—C(9)	65.4(3)	59.9(2)	59.8(2)
H(O-4)—O(4)—C(4)—O(3)	−62(3)	−68(2)	−62(2)
H(O-4)—O(4)—C(4)—C(5)	54(3)	47(2)	54(2)
H(O-4)—O(4)—C(4)—C(9)	179(3)	170(2)	176(2)
O(2)—C(1)—C(10)—C(9)	−56.6(3)	−56.2(2)	−54.1(2)
O(2)—C(1)—C(10)—C(11)	175.8(2)	71.4(2)	73.2(2)
C(14)—C(1)—C(10)—C(9)	−171.0(2)	−172.9(2)	−171.4(2)
C(14)—C(1)—C(10)—C(11)	61.4(3)	−45.3(2)	−44.1(2)
C(10)—C(1)—C(14)—C(13)	−60.0(3)	44.9(3)	45.9(3)
C(9)—C(4)—C(5)—C(6)	−58.4(3)	−59.6(2)	−60.2(2)
O(3)—C(4)—C(9)—C(8)	175.6(2)	174.7(2)	177.1(2)
O(3)—C(4)—C(9)—C(10)	−56.3(3)	−55.5(2)	−52.7(2)
C(5)—C(4)—C(9)—C(8)	60.2(3)	61.3(2)	62.4(2)
C(5)—C(4)—C(9)—C(10)	−171.7(2)	−168.9(1)	−167.5(1)
C(4)—C(5)—C(6)—C(7)	55.5(4)	56.0(3)	54.8(3)
C(5)—C(6)—C(7)—C(8)	−55.8(4)	−54.3(3)	−52.8(3)
C(6)—C(7)—C(8)—C(9)	56.4(4)	54.4(2)	54.2(3)
C(7)—C(8)—C(9)—C(4)	−57.6(3)	−57.5(2)	−58.3(3)
C(4)—C(9)—C(10)—C(1)	51.6(3)	52.1(2)	48.4(2)
C(8)—C(9)—C(10)—C(11)	−60.6(4)	53.6(2)	48.9(3)
C(1)—C(10)—C(11)—C(12)	−58.0(3)	53.4(2)	51.4(2)
C(10)—C(11)—C(12)—C(13)	54.9(4)	−60.6(3)	−59.3(3)
C(11)—C(12)—C(13)—C(14)	−53.5(4)	58.9(3)	59.4(3)
C(12)—C(13)—C(14)—C(1)	55.2(4)	−51.4(3)	−53.1(3)

The O(2)—O(3) bond length (Table 2) is 1.474(3) Å in molecule **2a** and 1.479(2) and 1.475(2) Å in molecules **3fA** and **3fB**, respectively. These values are somewhat larger than the values typical of the known[13] six-membered peroxide cycles (1.45—1.47 Å). Apparently, a slight elongation of the O—O bond in molecules **2a** and **3f** is due to their relative steric overcrowding (the presence of two cycles fused to the peroxide ring). Note that we found no data in the literature on the structures

Table 2. Bond lengths (*d*) and bond angles (ω) in molecules **2a** and **3f**

Bond	*d*/Å		
	2a	**3fA**	**3fB**
O(1)—C(1)	1.405(4)	1.425(3)	1.426(3)
O(1)—C(15)		1.435(3)	1.438(3)
O(1)—H(O-1)	0.74(5)		
O(2)—O(3)	1.474(3)	1.479(2)	1.475(2)
O(2)—C(1)	1.437(4)	1.436(3)	1.430(2)
O(3)—C(4)	1.447(4)	1.439(2)	1.434(2)
O(4)—C(4)	1.413(4)	1.400(3)	1.405(2)
O(4)—H(O-4)	0.86(5)	0.83(2)	0.83(2)
C(1)—C(10)	1.538(4)	1.543(3)	1.536(3)
C(1)—C(14)	1.520(4)	1.526(3)	1.528(4)
C(4)—C(5)	1.526(4)	1.532(3)	1.523(4)
C(4)—C(9)	1.535(4)	1.530(3)	1.532(3)
C(5)—C(6)	1.533(5)	1.533(3)	1.529(4)
C(6)—C(7)	1.532(5)	1.527(3)	1.527(4)
C(7)—C(8)	1.539(5)	1.531(3)	1.523(4)
C(8)—C(9)	1.527(4)	1.527(2)	1.532(3)
C(9)—C(10)	1.530(4)	1.533(3)	1.536(3)
C(10)—C(11)	1.537(4)	1.534(3)	1.535(3)
C(11)—C(12)	1.531(4)	1.519(3)	1.522(5)
C(12)—C(13)	1.532(5)	1.521(3)	1.524(4)
C(13)—C(14)	1.528(5)	1.515(5)	1.512(4)

Angle	ω/deg		
	2a	**3fA**	**3fB**
C(1)—O(1)—C(15)		117.0(2)	116.9(2)
C(1)—O(1)—H(O-1)	104.0(4)		
O(3)—O(2)—C(1)	107.7(2)	110.2(2)	110.0(2)
O(2)—O(3)—C(4)	109.4(2)	109.9(1)	109.9(1)
C(4)—O(4)—H(O-4)	109.0(3)	110.0(2)	110.0(1)
O(1)—C(1)—O(2)	110.3(2)	111.1(2)	110.9(1)
O(1)—C(1)—C(10)	114.4(2)	105.7(2)	106.0(2)
O(2)—C(1)—C(10)	109.3(2)	109.9(1)	110.6(1)
O(1)—C(1)—C(14)	107.4(2)	111.8(2)	111.0(2)
O(2)—C(1)—C(14)	104.4(2)	104.2(2)	104.3(2)
C(10)—C(1)—C(14)	110.6(2)	114.2(2)	114.3(2)
O(3)—C(4)—O(4)	110.1(2)	111.4(2)	111.1(2)
O(3)—C(4)—C(5)	104.9(2)	103.6(1)	104.5(2)
O(4)—C(4)—C(5)	112.0(2)	111.3(1)	111.6(2)
O(3)—C(4)—C(9)	108.7(2)	109.3(1)	110.1(1)
O(4)—C(4)—C(9)	109.1(2)	110.5(1)	109.3(1)
C(5)—C(4)—C(9)	112.0(2)	110.6(2)	110.2(2)
C(4)—C(5)—C(6)	108.8(3)	108.7(2)	109.4(2)
C(5)—C(6)—C(7)	111.6(3)	111.9(2)	111.6(2)
C(6)—C(7)—C(8)	111.6(3)	112.0(2)	112.8(3)
C(7)—C(8)—C(9)	109.8(3)	110.3(2)	110.0(2)
C(4)—C(9)—C(8)	109.3(2)	109.8(1)	109.0(2)
C(4)—C(9)—C(10)	108.8(2)	112.2(2)	112.3(2)
C(8)—C(9)—C(10)	116.3(2)	115.5(2)	116.1(2)
C(1)—C(10)—C(9)	110.5(2)	107.5(1)	108.8(2)
C(1)—C(10)—C(11)	108.7(2)	111.6(2)	111.9(2)
C(9)—C(10)—C(11)	115.4(2)	115.5(1)	114.3(2)
C(10)—C(11)—C(12)	110.3(3)	111.5(2)	112.3(2)
C(11)—C(12)—C(13)	112.3(3)	109.8(2)	109.8(2)
C(12)—C(13)—C(14)	111.4(3)	111.3(3)	110.7(3)
C(1)—C(14)—C(13)	109.9(2)	113.9(2)	113.9(2)

of tricyclic systems similar to **2a** and **3f**.[13] The influence of the *trans*-effect[14] (a decrease in the C—C—O bond angle in the transoid CCOO fragment) in molecules **2a** and **3f** is substantially depressed, apparently owing to the involvement of the corresponding transoid C(14)C(1)O(2)O(3) and C(5)C(4)O(3)O(2) fragments (see Table 1) in the cyclic systems, though the O(2)—C(1)—C(14) and O(3)—C(4)—C(5) bond angles have the minimum values (103.6—104.9(2)°, see Table 2) among the bond angles of these atoms (the C—C—O angle in organic peroxides is normally reduced down to 100°, *e.g.*, to 100.8(2)° in the molecule of 1,1-diphenylethylhydroperoxide[15]).

In the crystal, molecules **2a** form helical chains along the 2_1 axes through the O(4)—H(O-4)...O(3)′ hydrogen bonds (the O...O and H...O distances are 2.807(3) and 1.99(5) Å, respectively; the O—H—O angle is 159(6)°); these chains are additionally strengthened by the O(1)—H(O-1)...O(4)″ hydrogen bonds between translationally equivalent molecules in the same chain (the O...O and H...O distances are 2.922(3) and 2.23(5) Å, respectively; the O—H—O angle is 157(6)°). The system of H-bonds in the structure of **3f** consist of chains extended along the [110] direction. Alternating molecules of **3fA** and **3fB** form O(4′)—H(O-4′)...O(1) and O(4)—H(O-4)...O(1′)′ contacts with each other (the O...O distances are 2.779(2) and 2.789(2) Å, the H...O distance is 1.97(2) and 1.96(2) Å, and the O—H—O angles are 165(4)° and 176(4)°, respectively).

The ^{1}H NMR spectrum of compound **2a** carries little information. This spectrum shows the broadened singlet δOH 4.6 and the complex multiplet of the CH_2 and CH groups in the region 0.9—1.8 ppm with an intensity ratio of 1 : 9. In the $^{13}C\{^{1}H\}$ NMR spectrum, six signals are observed (see Experimental) owing to high molecular symmetry of isomer **2a**, which is confirmed by the X-ray structural data.

In the ^{1}H NMR spectrum of compound **3f**, the multiplet (δ 2.10) corresponding to the methine protons at the C(9) and C(10) atoms and the complex multiplet of the CH_2 groups in the region 0.9—1.8 ppm are observed in addition to two singlets, δOH 4.8 and δOMe 3.26. Integrated intensities of the above-mentioned signals are in agreement with the structure of **3f** established by X-ray structural analysis. Because of the *cis,trans*-fusion of the rings and different effects of the OH and OMe groups, all C atoms in molecule **3f** are nonequivalent, and the $^{13}C\{^{1}H\}$ NMR spectrum of this compound exhibits 13 signals (see Experimental).

Experimental

The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC-200P spectrometer in standard modes. The INEPT mode was used for the assignment of the signals of CH and CH_2 groups in the ^{13}C NMR spectrum.

Reaction of dione 1 with H_2O_2. MeOH (4.0 mL) and a 30 % H_2O_2 solution (5.6 mL, 0.043 mol) were added to compound **1** (a 1 : 2 mixture of the *meso*- and D,L-forms; 4.2 g, 0.0216 mol). The homogeneous solution was kept for 48 h at ~20 °C. The crystalline precipitate formed (2.45 g)

Table 3. Atomic coordinates (×10^4; ×10^3 for H atoms) in the structure of **2a**

Atom	*x*	*y*	*z*
O(1)	−183(2)	−1196(4)	8104(1)
O(2)	542(2)	2733(4)	7680(1)
O(3)	1835(2)	1884(4)	7824(1)
O(4)	2169(2)	5981(4)	8327(1)
C(1)	−206(3)	1595(6)	8139(1)
C(4)	2317(3)	3195(6)	8385(1)
C(5)	3681(3)	2389(7)	8455(1)
C(6)	4256(3)	3530(8)	9066(2)
C(7)	3535(3)	2655(8)	9620(2)
C(8)	2154(3)	3410(7)	9532(1)
C(9)	1591(2)	2209(6)	8929(1)
C(10)	207(2)	2728(6)	8780(1)
C(11)	−664(3)	1654(8)	9258(1)
C(12)	−2009(3)	2418(8)	9073(2)
C(13)	−2415(3)	1504(8)	8416(2)
C(14)	−1520(3)	2485(6)	7945(1)
H(O-1)	48(5)	−152(9)	813(2)
H(O-4)	259(4)	655(9)	803(2)
H(5a)	411(4)	309(9)	811(2)
H(5b)	374(4)	43(10)	848(2)
H(6a)	503(5)	304(9)	908(2)
H(6b)	432(4)	556(10)	904(2)
H(7a)	364(4)	66(10)	968(2)
H(7b)	392(4)	335(9)	999(2)
H(8a)	181(4)	276(8)	993(2)
H(8b)	209(4)	543(9)	952(2)
H(9)	164(4)	21(9)	893(2)
H(10)	8(4)	470(9)	875(2)
H(11a)	−44(4)	232(9)	963(2)
H(11b)	−59(4)	−26(10)	931(2)
H(12a)	−212(4)	423(9)	907(2)
H(12b)	−260(4)	179(9)	940(2)
H(13a)	−325(4)	205(9)	831(2)
H(13b)	−252(4)	−46(10)	840(2)
H(14a)	−171(4)	175(9)	753(2)
H(14b)	−157(4)	438(9)	791(2)

Table 4. Atomic coordinates (×10^4; ×10^3 for H atoms) in the structure of **3f**

Atom	*x*	*y*	*z*
O(1)	−2948(1)	−4818(1)	−1442(1)
O(2)	−3581(1)	−2788(1)	−1000(1)
O(3)	−5039(1)	−2614(1)	−1328(1)
O(4)	−4964(1)	−578(1)	−2574(1)
C(1)	−2563(2)	−3598(2)	−1555(1)
C(4)	−5168(2)	−1856(2)	−2418(1)
C(5)	−6694(2)	−1813(2)	−2648(2)
C(6)	−6938(2)	−1095(2)	−3818(2)
C(7)	−5834(2)	−1742(2)	−4538(2)
C(8)	−4305(2)	−1863(2)	−4267(1)
C(9)	−4085(2)	−2590(2)	−3101(1)
C(10)	−2556(2)	−2894(2)	−2749(1)
C(11)	−1872(2)	−1698(2)	−3016(2)
C(12)	−397(2)	−2084(3)	−2579(2)
C(13)	−501(3)	−2621(3)	−1383(2)
C(14)	−1154(2)	−3820(3)	−1049(2)
C(15)	−3108(3)	−5640(3)	−386(2)
O(1′)*	2813(1)	−9215(1)	−1501(1)
O(2′)	1285(1)	−7243(1)	−1275(1)
O(3′)	66(2)	−7808(1)	−1314(1)
O(4′)	−878(2)	−5997(1)	−2718(1)
C(1′)	2493(2)	−7801(2)	−1859(2)
C(4′)	−410(2)	−7386(2)	−2371(1)
C(5′)	−1622(2)	−8070(3)	−2308(2)
C(6′)	−2198(3)	−7722(3)	−3406(2)
C(7′)	−1014(3)	−8056(3)	−4215(2)
C(8′)	245(2)	−7448(3)	−4232(2)
C(9′)	802(2)	−7849(2)	−3121(1)
C(10′)	2174(2)	−7434(2)	−3031(1)
C(11′)	2154(3)	−5972(2)	−3593(2)
C(12′)	3487(3)	−5583(3)	−3411(2)
C(13′)	3619(4)	−5816(3)	−2234(2)
C(14′)	3705(3)	−7259(3)	−1645(2)
C(15′)	2810(3)	−9807(3)	−378(2)
H(O-4)	−564(3)	−14(2)	−228(2)
H(5a)	−682(2)	−271(2)	−249(2)
H(5b)	−738(2)	−135(2)	−220(2)
H(6a)	−791(2)	−105(2)	−395(2)
H(6b)	−693(2)	−16(2)	−391(2)
H(7a)	−595(2)	−263(2)	−447(2)
H(7b)	−600(2)	−120(2)	−528(2)
H(8a)	−408(2)	−103(2)	−443(2)
H(8b)	−359(2)	−239(2)	−466(2)
H(9)	−434(2)	−346(2)	−296(2)
H(10)	−196(2)	−358(2)	−306(2)
H(11a)	−249(2)	−95(2)	−275(2)
H(11b)	−181(2)	−129(2)	−378(2)
H(12a)	−1(2)	−135(2)	−278(2)
H(12b)	24(2)	−269(2)	−287(2)
H(13a)	−104(2)	−193(2)	−114(2)
H(13b)	38(3)	−285(2)	−111(2)
H(14a)	−131(2)	−406(2)	−28(2)
H(14b)	−52(2)	−449(2)	−121(2)
H(15a)	−219(3)	−611(2)	−15(2)
H(15b)	−356(2)	−505(2)	4(2)
H(15c)	−369(2)	−630(2)	−38(2)
H(O-4′)	−156(2)	−576(2)	−233(2)
H(5a′)	−120(2)	−903(2)	−200(2)
H(5b′)	−233(2)	−777(2)	−188(2)
H(6a′)	−291(3)	−820(2)	−333(2)
H(6b′)	−266(2)	−680(3)	−359(2)
H(7a′)	−65(2)	−905(2)	−403(2)
H(7b′)	−138(2)	−775(2)	−492(2)
H(8a′)	−5(2)	−651(2)	−450(2)
H(8b′)	102(2)	−780(2)	−469(2)
H(9′)	104(2)	−886(2)	−287(2)
H(10′)	297(2)	−796(2)	−333(2)
H(11a′)	130(3)	−542(2)	−338(2)
H(11b′)	209(2)	−581(2)	−435(2)
H(12a′)	346(2)	−464(2)	−381(2)
H(12b′)	433(3)	−608(2)	−370(2)
H(13a′)	276(3)	−523(2)	−199(2)
H(13b′)	451(3)	−556(2)	−214(2)
H(14a′)	377(2)	−745(2)	−87(2)
H(14b′)	460(3)	−779(2)	−188(2)
H(15a′)	321(3)	−1070(3)	−29(2)
H(15b′)	178(3)	−972(2)	−10(2)
H(15c′)	339(2)	−939(2)	4(2)

* Atoms with primed numbers belong to the second symmetrically independent molecule (**3fB**).

was filtered off, washed with *n*-hexane, and dried. The filtrate was evaporated on a rotary evaporator, and after 24 h, an additional amount of the product (0.4 g) was isolated. The total yield of compound **2a** was 2.65 g (according to the X-ray structural data and the results of ^{1}H and ^{13}C NMR spectroscopy); m.p. 160—161 °C (*cf.* Ref. 10: 159—160 °C). Found (%): C, 63.11; H, 8.74. $C_{12}H_{20}O_4$. Calculated (%): C, 63.25; H, 8.76. ^{13}C NMR, δ: 102.1 (C(1), C(4)); 41.6 (C(9), C(10)); 34.9 (C(5), C(14)); 26.8 (C(8), C(11)); 25.2 (C(7), C(12)); 23.8 (C(6), C(13)).

n-Hexane (5.0 mL) was added to the remaining filtrate, and the solution was kept for 24 h at 0 °C. The crystalline precipitate formed was filtered off and recrystallized from *n*-hexane. Peroxide **3f** was isolated in a yield of 0.7 g (according to the X-ray structural data and the results of ^{1}H and ^{13}C NMR spectroscopy); m.p. 135—136 °C. Found (%): C, 64.19; H, 9.12. $C_{13}H_{22}O_4$. Calculated (%): C, 64.43; H, 9.17. ^{13}C NMR, δ: 103.8 (C(1)); 101.4 (C(4)); 48.3 (C(15)); 41.8 (C(10)); 39.9 (C(9)); 36.5 (C(14)); 33.7 (C(5)); 27.4 (C(11)); 26.6 (C(8)); 26.5 (C(7)); 25.5 (C(12)); 24.4 (C(6)); 24.0 (C(13)).

X-ray structural analysis of 2a and 3f. Crystals of **2a** are monoclinic; the space group is $P2_1/n$; at −120 °C, a = 10.795(8) Å, b = 5.023(4) Å, c = 21.61(1) Å, β = 93.58(1)°, V = 1169(5) Å^3, Z = 4, d_{calc} = 1.297 g cm^{-3}.

Crystals of **3f** are triclinic; the space group is $P\bar{1}$; at −120 °C, a = 9.697(5) Å, b = 10.842(6) Å, c = 13.280(6) Å, α = 72.70(1)°, β = 83.22(1)°, γ = 75.33(1)°, V = 1280.2(9) Å^3, Z = 4, d_{calc} = 1.249 g cm^{-3}.

The unit-cell parameters and intensities of reflections were measured on a Siemens P3/PC automated four-circle diffractometer at −120 °C (λ(Mo-Kα), graphite monochromator, θ/2θ scanning technique, $\theta_{\max}$ = 27°). The structures were solved by the direct method and refined anisotropically by the full-matrix least-squares method for non-hydrogen atoms. Hydrogen atoms were located from a difference Fourier synthesis and included in the refinement with fixed thermal parameters (U_{iso} = 0.04 Å^2). Atomic coordinates for the structures of **2a** and **3f** are given in Tables 3 and 4, respectively. The final R factors were as follows: R = 0.061, R_w = 0.064 using 1579 independent reflections with $I > 3.5\sigma(I)$ for the structure of **2a** and R = 0.044, R_w = 0.046 using 3267 independent reflections with $I > 3.5\sigma(I)$ for the structure of **3f**. All calculations were performed on an IBM PC/AT-286 computer using the SHELXTL PLUS program package.[16]

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