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New chiral spiro[2.5]octanones as products of methylenation of (3*R*,6*R*)-2-arylidene-6-isopropyl-3-methylcyclohexanones with dimethylsulfoxonium methylide. Synthesis, stereochemistry, and behavior in liquid-crystalline systems

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Methylenation of (3*R*,6*R*)-2-(4-X-benzylidene)-6-isopropyl-3-methylcyclohexanones (X = F, Cl, Ph) with dimethylsulfoxonium methylide occurs stereoselectively to give 1(*S*)-(4-X-phenyl)-5(*R*)-isopropyl-8(*R*)-methyl-3(*R*)-spiro[2.5]octanones, whose stereochemistry was established by ^{1}H NMR spectroscopy. The configuration of the chiral centers in the cyclohexanone fragment and its preferred conformation (methyl is axial and isopropyl is equatorial) in the products do not change with respect to the starting enones. The mutual *trans*-arrangement of the carbonyl and aryl groups at the newly formed three-membered ring was established; the aryl group also occupies the *trans*-position with respect to the axial methyl group of the cyclohexanone fragment. Using methylenation of the compound with X = Ph as an example, a mixture of by-products resulting from oxidative hydroxylation at the α-position relative to the carbonyl group was isolated. The resulting chiral spiro[2.5]octanones induce a helical supramolecular ordering in the nematic mesophase of 4-pentyl-4′-cyanobiphenyl and exhibit a twisting power only somewhat (by 20—30%) lower than the starting enones.

Key words: (3*R*,6*R*)-2-arylidene-6-isopropyl-3-methylcyclohexanones, methylenation, dimethylsulfoxonium methylide, cyclopropanation, (1*S*,3*R*,5*R*,8*R*)-1-aryl-5-isopropyl-8-methyl-3-spiro[2.5]octan-4-ones, ^{1}H NMR spectroscopy, induced cholesteric liquid-crystalline systems, twisting power.

Chiral 2-arylidene-6-isopropyl-3-methylcyclohexanones **1** are known as effective chirality-inducing dopants to nematic and C-smectic liquid crystals.[1,2] The reversible photochemical *E*—*Z* isomerization[3—5] they tend to undergo attracts attention of specialists engaged in the design of materials for optical information recording, in particular, photosensitive liquid-crystalline polymers.[6—8] However, the pronounced decrease in the twisting power of the photoisomerization products, *Z*-isomers of these compounds, with respect to the initial *E*-isomers[1,3,9] restricts the scope of applicability of induced cholesteric systems with selective reflection of visible light that contain the chiral dopants. This stimulated us to search for modified structures that would contain no double bond but still retain the alkyl substitution pattern in the cyclohexanone fragment and general features of the molecular form important for the existence of the optimal twisting properties in liquid-crystalline systems.

One route for such modification of compounds **1a—c** is apparently the synthesis of spiro[2.5]octanones **2a—c** (Scheme 1)* containing a rigid photostable cyclopropane fragment.

The most convenient method for the synthesis of functionally substituted cyclopropanes includes methylenation of Michael acceptors (olefins activated by electron-withdrawing substituents) with sulfoxonium methylides gen-

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* For convenience of the subsequent comparative analysis of the spectra of compounds of series **1** and **2**, similar atom numbering as cyclohexanone derivatives is used for the compounds under study in Scheme 1 and subsequently in the text and Tables.

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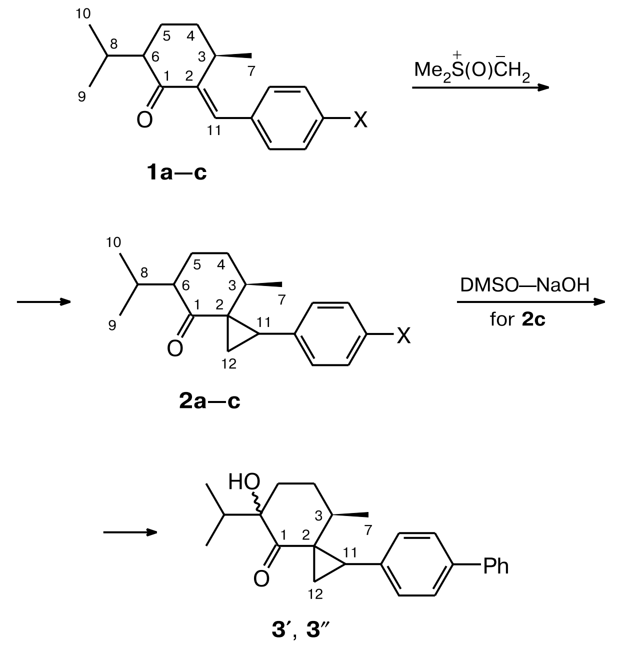
Scheme 1



X = F (**a**), Cl (**b**), Ph (**c**)

erated by treatment of sulfoxonium salts with bases.[10,11] Previously,[12,13] a similar strategy has been successfully used to methylenate racemic 2-R-substituted 3-arylidene derivatives of chroman-4-ones; the reactions gave mixtures of stereoisomers with one of them markedly predominating.

The spiro compound with the *trans*-orientation of the carbonyl and aryl groups with respect to the cyclopropane fragment has been prepared earlier[14] by cyclopropanation of a 4-methylenebicyclo[4.3.0]nonan-3-one using a sophisticated reagent. The closest achiral structural analog of compounds **2**, 1-phenylspiro[2.5]octan-4-one, was prepared by a different route, namely, by the reaction of the phosphonate derivative of cyclohexanone with styrene oxide,[15] the reaction giving only one diastereomer pair. According to X-ray diffraction data, the carbonyl and phenyl groups in the product are also *trans*-oriented relative to the cyclopropane fragment.

Thus, the data available on methylenation of α,β-unsaturated ketones possessing fixed s-*cis*-configuration with sulfonium ylides[12—14] and, especially on the stereochemistry of the resulting products are limited and those for chiral substrates are missing. Therefore, study on the stereoselectivity of methylenation of compounds **1** with sulfonium ylides is of obvious interest.

This study pursued the following goals: elucidation of the diastereoselectivity of methylenation of chiral compounds **1** with dimethylsulfoxonium methylide, determination of the absolute configuration and the spatial structure of the major reaction product, and study of the properties of the obtained compounds **2a—c** as chiral components of liquid-crystalline systems. ^{1}H NMR spectroscopy and semiempirical quantum-chemical calculations were used to determine configurations of the chiral centers and to study the conformational equilibrium of the cyclohexanone fragment in these compounds in solutions and its possible change with respect to the corresponding enones.

During the reaction in an alkaline medium, the (*R*)-configuration of the C(3) atom of the starting (−)-menthone was retained during transformation into compounds **1**. In the general case, the formation of two new chiral centers at the C(2) and C(11) or C(12) atoms may give rise to four diastereoisomers **A—D** (Fig. 1), provided that the configuration of C(6) does not change either.

Results and Discussion

According to HPLC, the reaction mixture resulting from methylenation of compound **1a** contained, in addition to the major product (55%), three minor products (1.4, 4.9, and 4.2%), two of which do not differ much in the retention time from the major product, and two more polar components (11.6 and 20.3%). According to GC/MS analysis, the major product (mass 274) is the expected spiro[2.5]octanone **2a**; the minor compounds are presumably its diastereomers. Both polar products differ from the major product in the molecular weight, which is greater by 16 a.u. Most likely, these are diastereomeric products of oxidative hydroxylation of compounds **2** into position 6. In the case of methylenation of enone **1c**, these by-products (**3**′ and **3″**) were isolated.* Their ^{1}H NMR spectra exhibit no signal for the C(6)H proton of the cyclohexanone fragment but contain two singlets for the hydroxyl protons, six doublets for the methyl groups, two multiplets for the isopropyl CH protons, two sets of multiplets for the cyclopropane protons, and doubled, markedly overlapping multiplets for the cyclohexanone protons. The intensity ratio of these multiplets is 0.45 : 0.55. Evidently, the oxidative hydoxylation, which takes place after the formation of spiro products **2**, is not diastereoselective, giving rise to a mixture of the 6(*S*)- and 6(*R*)-diastereoisomers **3**′ + **3″** (see Scheme 1). According to X-ray diffraction data, the product isolated from the mixture represented the 6(*S*)-diastereomer **3**′.

The content of the polar minor products increases with an increase in the reaction time (HPLC data); simultaneously, the yield of the target product diminishes, even when the reaction is carried out under inert atmosphere (argon) and in DMSO as the solvent. When this reaction mixture has been kept for 5 days, the ratio of the

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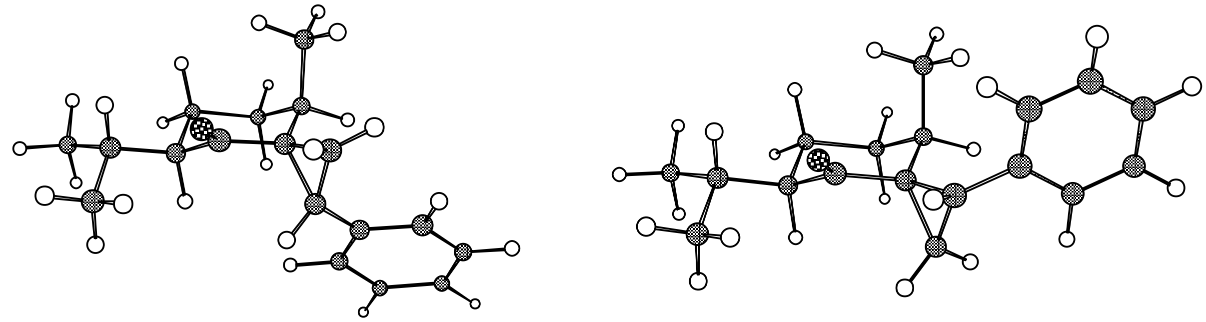
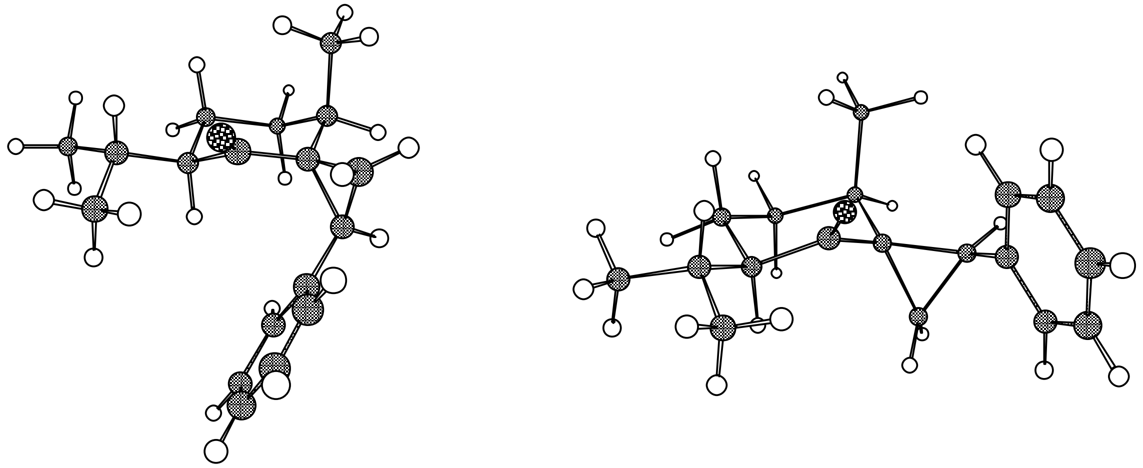
* The X-ray data for one of side hydroxy substituted spiro[2.5]octanones will be published separately. The second diastereomer could not be isolated in a pure state.



A (*trans—trans*) **B** (*trans—cis*)



C (*cis—trans*) **D** (*cis—cis*)

Fig. 1. Alternative diastereomeric structures of model compound **2d** (X = H). First, the position of the benzene ring relative to the carbonyl group is indicated and then the position of the substituted methylene group of cyclopropane relative to the axial methyl substituent in the cyclohexanone fragment is given.

target spiro[2.5]octanone **2c** to oxidative hydroxylation products (**3´** + **3″**) equals 26 : 74. The methylenation of compound **1c** in DMF under inert atmosphere does not give hydroxy ketones of type **3**. According to HPLC, the conversion of enone **1c** both in DMSO and in DMF is higher than 90% over a period of 1 h.

The structures of the main diastereomers of **2a—c** were determined using ^{1}H NMR data and molecular modeling. In the ^{1}H NMR spectra recorded in $CDCl_3$ or DMSO-d_6 at 500 MHz, the multiplets for almost each proton are observed separately. In both solvents, the doublet for the $C(7)H_3$ methyl group overlaps with the signal of one Me group of the isopropyl fragment. The $H(3)/C(7)H_3$ proton decoupling showed that the signal of this Me group overlaps with the low-field doublet of the isopropyl Me group (Table 1, Fig. 2). The multiplets for all cyclohexanone protons of compounds **2a—c** are similar to those for the arylidene analogs,[16,17] which suggests minor changes in the spatial structure of this part of the molecule. The signals of three protons of the cyclopropane fragment form an ABX system and were assigned relying on their characteristic multiplicity.[18] Using decoupling NMR experiment and computational modeling of second-order spin systems for the protons of the cyclohexanone and cyclopropane fragments, full assignment and analysis of all proton multiplets of the compounds under study was carried out. The obtained ^{1}H NMR parameters of compounds **1** and **2** (chemical shifts and coupling constants) are summarized in Tables 1 and 2. It can be seen from Table 1 that the replacement of the *para*-halogen in the benzene ring (F or Cl) by the phenyl group results in regular downfield shifts of all proton signals by 0.55—0.02 ppm in both series of compounds.[19]

^{1}H NMR spectra and configuration of the substitution in the cyclohexanone and cyclopropane fragments. The two relatively small spin-spin coupling constants in the H(3) multiplet of compounds **2a—c** (see Table 2) attest to a substantial fraction of conformers with axial-equatorial and equatorial-equatorial interactions of this proton with the $C(4)H_2$ protons of the cyclohexanone fragment. Hence, the axial position is preferred for the C(3)Me group. The values of the $^3J_{H(6),H(5)}$ constant

Table 1. Proton chemical shifts (δ) and their change (Δδ) upon the replacement of the double bond by a cyclopropane fragment in the ^{1}H NMR spectra of compounds **1a—c** and **2a—c** (in $CDCl_3$)

Compound	H(3)	H(6)	H(5′)	H(5)	H(4′)	H(4)	H(8)	$C(7)H_3$	$C(9)H_3$, $C(10)H_3$	*o*-H	*m*-H	H(11)	H(12)	H(12′)
								δ						
1a	3.363	2.231	1.888	1.867	1.898	1.786	2.557	1.183	0.963, 0.895	7.335	7.060	7.066	—	—
1b	3.354	2.233	1.887	1.871	1.897	1.789	2.549	1.172	0.965, 0.899	7.280	7.340	7.040	—	—
1c	3.482	2.256	1.910	1.879	1.927	1.806	2.580	1.236	0.977, 0.914	7.449	7.613	7.160	—	—
2a	1.289	2.230	1.829	1.813	1.576	1.460	2.519	0.954	0.954, 0.851	7.148	7.000	2.132	2.048	0.932
2b	1.301	2.220	1.824	1.801	1.563	1.452	2.499	0.949	0.949, 0.847	7.109	7.271	2.115	2.048	0.936
2c	1.406	2.279	1.850	1.820	1.640	1.473	2.538	0.984	0.969, 0.868	7.259	7.547	2.206	2.087	1.037
								−Δδ*						
1a, **2a**	2.074	0.001	0.059	0.054	0.322	0.326	0.038	0.229	0.009, 0.044	0.187	0.060	—**	—	—
1b, **2b**	2.053	0.013	0.063	0.070	0.334	0.337	0.050	0.223	0.016, 0.052	0.171	0.069	—**	—	—
1c, **2c**	2.076	0.023	0.060	0.059	0.287	0.333	0.042	0.252	0.008, 0.046	0.190	0.066	—**	—	—

* $\Delta\delta = \delta_2 - \delta_1$, where δ_2 and δ_1 are the chemical shifts for compounds **2** and **1**, respectively; the sign "minus" implies an upfield shift of the signal.

** The Δδ values are not given, because these protons refer to different fragments.

(12.4—12.9 Hz) in the H(6) proton multiplet attest to the preferred equatorial position of the isopropyl group. Since the (*R*)-configuration of the C(3) chiral center in the starting ketones is retained during the cyclopropanation, the equatorial orientation of the isopropyl substituent is indicative of its *cis*-position with respect to the axial Me group and, hence, the (*R*)-configuration of the C(6) chiral center. Thus, the C(3) and C(6) configurations have not changed upon the replacement of the exocyclic double bond by the cyclopropane fragment; therefore, the compounds obtained have the (3*R*,6*R*)-structure of substitution in the cyclohexanone fragment and belong to the isomenthone series.

The stereoisomers **A—D** proposed for model structure **2d** (X = H), which may be formed upon methylenation of the double bond in compounds **1**, are shown in Fig. 1. In structures **A** and **B**, the aryl group is *trans*-oriented with respect to the carbonyl group, while in structures **C** and **D**, these groups are *cis*-configured. In addition, in stereoisomers **A** and **C**, the axial substituted methylene group, C(11)HAr, occurs in the *trans*-position relative to the axial methyl group of the cyclohexanone fragment, whereas in structures **B** and **D**, this C(11)HAr group is equatorial and *cis*-oriented relative to the axial Me group.

Conformational analysis of the reaction products is important to decide between the alternative stereoiso-

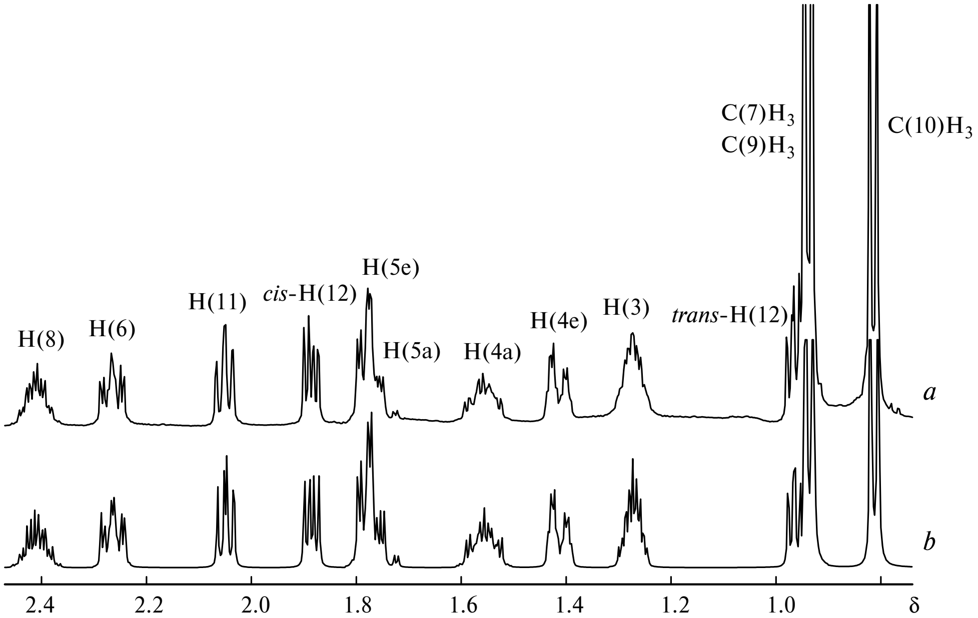


Fig. 2. Experimental (*a*) and simulated (*b*) fragments of the spectrum of compound **2a** in DMSO-d_6 (500 MHz).

Table 2. Experimental coupling constants (J/Hz) in the ^{1}H NMR spectra of compounds **1** and **2**

Protons	$J_{H,H}$/Hz					
	1a	**1b**	**1c**	**2a**	**2b**	**2c**
H(3), H(4)	2.4	2.5	2.2	2.4	2.3	2.4
H(3), H(4´)	3.9	4.2	4.0	4.3	4.1	4.3
H(6), H(5)	5.6	5.7	5.5	6.1	6.0	6.1
H(6), H(5´)	12.9	12.8	12.9	12.6	12.4	12.4
H(5), H(4)	3.3	3.3	3.0	3.2	3.0	3.2
H(5), H(4´)	3.2	3.2	3.1	3.3	3.2	3.3
H(5´), H(4)	3.5	3.3	3.2	3.4	3.6	3.4
H(5´), H(4´)	13.9	13.8	14.1	13.1	13.1	13.2
H(6), H(8)	3.5	3.4	3.3	3.4	3.4	3.4
H(5), H(5´)	−13.1	−13.2	−13.1	−13.3	−13.2	−13.4
H(4), H(4´)	−13.4	−13.3	−13.1	−13.2	−13.2	−13.2
H(3), C(7)H_3	7.0	7.0	7.0	7.0	7.1	7.0
H(8), C(9)H_3 (C(10)H_3)	7.0	7.0	7.0	7.0	7.0	7.0
H(11), H(12)	—	—	—	9.0	8.9	8.8
H(11), H(12´)	—	—	—	6.5	6.7	6.7
H(12), H(12´)	—	—	—	−4.9	−4.7	−4.8

mers. Judging by the results of modeling of structure **2d**, the following conformations are theoretically possible: a chair with axial methyl and equatorial isopropyl substituents (chair *ae*), inverted chair (chair *ea*), three twist forms, and three rotamers due to hindered rotation of the isopropyl group (for all the indicated structures). Full optimization of all structures was performed by the AM1 and PM3 calculations. Both methods describe almost identically the relative stability, and, hence, the occupancies of the alternative conformers of the cyclohexanone fragment. Therefore, in the subsequent discussion, we will use only AM1 results.

The results of modeling for the most probable conformers of the diastereomeric (3*R*,6*R*)-structures **2d** (substructures **A—D**), differing in the configuration of the exocyclic chiral centers, C(2) and C(11) or C(12) (Table 3), show that in the case of diastereomers **A**, **B**, and **C**, the conformational state of the cyclohexanone fragment barely depends on the configuration of the exocyclic chiral centers. As in the case of the starting compounds **1**, conformers of the chair *ae* type substantially predominate (94.9, 98.1, and 97.5% for diastereomers **A**, **B**, and **C**, respectively). For the sterically crowded diastereomer **D** (close proximity of the carbonyl and phenyl groups), the modeling predicts a shift of the equilibrium toward the inverted chair *ea* (44.8%) and the twist form (31.3%); this is at variance with the ^{1}H NMR spectrum obtained for the major methylenation product.

The replacement of the double bond in compound **1** by the three-membered carbon ring also does not entail a change in the rotamer state of the isopropyl fragment: rotamers with the *gauche*-orientation of the H(6) and H(8) protons predominate in the equilibrium. This is indicated by both the results of modeling (see Table 3) and the experimental $^3J_{H(6),H(8)}$ values (see Table 2), which nearly coincide with those for the initial compounds **1**.[17] It is noteworthy that according to the modeling results, the presence of the spiro center does not substantially distort the geometry of the cyclohexanone fragment (the calculated intracyclic torsion angles (in absolute magnitude) vary in the range of 47—58°; see Table 3).

To elucidate experimentally the real configuration and the conformational state of the cyclohexanone fragment using compound **2a** as an example, we analyzed the vicinal coupling constants between the cyclohexanone protons ($^3J_{H,H}$). Their values for the alternative conformers were calculated from the proton—proton torsion angles (according to the results of AM1 modeling) using the modified Karplus—Conroy equation[20] (Table 4).

According to the calculations, the vicinal coupling constants, $^3J_{H(3),H(4)}$, $^3J_{H(6),(5')}$, $^3J_{H(5),H(4)}$, and $^3J_{H(5'),H(4')}$, are conformationally sensitive, *i.e.*, for the alternative chair *ae*, chair *ea*, and twist conformations, they are considerably different. Note that the experimental $^3J_{H(6),(5')}$ value for the H(5) proton located in the *trans*-position to the carbonyl group is greater than the $^3J_{calc}$ value calculated for model diastereomers **A—C**, as

Table 3. Calculated energy characteristics (ΔE) and some torsion angles (ϕ_i) for the most probable conformers of diastereomer **A** of compound **2a** (AM1 method)

Conformer	ΔE /kcal mol^{-1}	Fraction (%)	ϕ_1	ϕ_2	ϕ_3	ϕ_4	ϕ_5	ϕ_6	$\phi_{6,8}$	ϕ_{CO}	ϕ_{CH_3}
			deg								
Chair *ae*-1	0	47.24	−46.6	51.8	−57.7	56.1	−51.9	48.3	73.5	79.7	77.9
Chair *ae*-2	0.16	36.02	−48.4	51.3	−56.2	55.3	−53.9	51.8	163.1	84.8	76.0
Chair *ae*-3	0.71	14.18	−47.4	51.7	−57.1	55.8	−52.1	49.2	−66.7	80.3	77.1
Chair *ea*	2.57	0.61	41.4	−50.2	58.9	−56.1	49.6	−43.3	171.0	−9.1	164.0
Twist	1.88	1.95	29.4	−61.1	27.7	31.7	−64.4	31.4	170.0	67.0	152.0

Note. Angles: ϕ_1, C(1)—C(2)—C(3)—C(4); ϕ_2, C(2)—C(3)—C(4)—C(5); ϕ_3, C(3)—C(4)—C(5)—C(6); ϕ_4, C(4)—C(5)—C(6)—C(1); ϕ_5, C(5)—C(6)—C(1)—C(2); ϕ_6, C(6)—C(1)—C(2)—C(3); $\phi_{6,8}$, H(6)—C(6)—C(8)—H(8); ϕ_{CO}, O—C(1)—C(2)—C(11); ϕ_{CH_3}, C(7)—C(3)—C(2)—C(1).

Table 4. Torsion angles H—C—C—H (ϕ/deg) and calculated coupling constants ($^3J_{H,H}$/Hz) for the the most probable conformers of compound **2a** based on AM1 calculations

Conformer	Fraction (%)	$\phi_{3,4}$	$^3J_{3,4}$	$\phi_{3,4'}$	$^3J_{3,4'}$	$\phi_{6,5}$	$^3J_{6,5}$	$\phi_{6,5'}$	$^3J_{6,5'}$	$\phi_{5,4}$	$^3J_{5,4}$	$\phi_{5',4'}$	$^3J_{5',4'}$	$\phi_{6,8}$	$^3J_{6,8}$
Chair *ae*-1	47.24	−68.8	1.99	48.3	4.60	56.2	3.88	−179.9	13.57	60.2	3.04	−175.3	13.46	73.5	1.24
Chair *ae*-2	36.02	−69.1	1.96	47.8	4.67	56.1	3.90	177.6	13.55	61.6	2.81	−173.4	13.37	161.3	10.39
Chair *ae*-3	14.18	−68.9	1.98	48.2	4.61	56.0	3.87	−179.9	13.57	60.8	2.94	−174.5	13.43	−66.7	2.00
Chair *ea*	0.61	−171.1	11.6	−54.3	4.16	−52.4	3.98	64.5	2.36	176.5	13.52	−58.3	3.48	171.2	10.97
Twist	1.95	177.6	13.3	−65.9	2.62	38.3	6.60	154.9	11.33	145.4	9.51	−88.9	0.54	169.5	10.89
			(2.17)		(4.40)		(3.91)		(12.91)		(3.05)		(12.70)		(4.71)
			[2.4]		[4.3]		[5.6]		[12.6]		[3.2]		[13.1]		[3.4]

Note. Torsion angles: $\phi_{3,4}$, H(3)—C(3)—C(4)—H(4); $\phi_{3,4}$, H(3)—C(3)—C(4)—H(4′); $\phi_{6,5}$, H(6)—C(6)—C(5)—H(5); $\phi_{6,5'}$, H(6)—C(6)—C(5)—H(5′); $\phi_{5,4}$, H(5)—C(5)—C(4)—H(4); $\phi_{5',4'}$, H(5′)—C(5)—C(4)—H(4′); $\phi_{6,8}$, H(6)—C(6)—C(8)—H(8). The calculated weighed average $^3J_{calc}$ values (taking into account the fraction of each conformer) are given in parentheses and $^3J_{exp}$ are in brackets.

in the case of the starting compounds (see Table 2). The other $^3J_{calc}$ values found by the modeling of structures **A—C** are in satisfactory agreement with the experiment (see Table 4). Thus, the results predicting the energetic preference of the chair *ae* conformation of the cyclohexanone fragment are in line with the NMR data. This implies that AM1 modeling reflects adequately the state of conformational equilibrium in solutions similar to that of the initial arylidene derivatives of isomenthone **1**. Only for the fourth of the possible diastereomers (**D**), were the calculated $^3J_{calc}$ constants of the cyclohexanone protons inconsistent with experimental values. On this basis, isomer **D** (*cis—cis*) can be excluded from further consideration.

Experimental determination of the configuration of the chiral centers of the cyclopropane fragment in compound **2** was done by analyzing the chemical shifts of the cyclohexanone and cyclopropane protons (see Table 1). The chemical shifts of the cyclohexanone (H(6), H(5), and H(5′)) and isopropyl (H(8), C(9)H$_3$, and C(10)H$_3$) protons of compounds **2** differ only slightly from those for compound **1** ($\Delta\delta$ 0.01—0.06, see Table 1). Meanwhile, the H(3), C(7)H$_3$, and C(4)H$_2$ protons of the same compounds show substantial differences ($\Delta\delta$ 0.23—2.07), which is obviously a consequence of the replacement of the double bond in the starting arylidenecyclohexanones **1** by a three-membered carbon ring. Therefore, we calculated the changes in the chemical shifts of the H(3), H(6), and H(8) protons using the model proposed previously[21] with respect to the corresponding enone compounds **1**. This approach is based on the fact that both structural types of compounds have the same (3*R*,6*R*) configuration of the chiral centers in the ring and, according to the above results, analogous predominant conformations of the cyclohexanone fragment (chair *ae*). It can be seen from Fig. 1 that the orientations of the benzene ring, possessing a strong magnetic anisotropy, with respect to the protons of the cyclohexanone fragment and the isopropyl substituent in the predominant conformation chair *ae* of alternative diastereomers **A—C** of compounds **2** are markedly different.

The contributions of the double bond, the carbonyl group, and the benzene and cyclopropane rings to the shielding of H(3), H(6), and H(8) protons in the predominant chair *ae* conformations of the alternative diastereomers were calculated using the modeling-based geometry of the considered structures and published data[21,22] (Table 5). In the case of diastereomers **A** and **B**, the calculated $\Delta\delta_{calc}$ values for these protons are in good agreement with $\Delta\delta_{exp}$ (*cf.* Tables 1 and 5). Thus, the experimental chemical shifts agree with the *trans*-orientation of the aryl group relative to the carbonyl group (structures **A** and **B**); hence, the isomer having structure **C** can be excluded.

The choice between structures **A** and **B** is based on analysis of the proton chemical shifts of the cyclopropane fragments. In isomer **A**, one methylene proton of this ring occurs near the carbonyl group (2.6 Å) and nearly in the same plane with this group (the deviation from the plane was calculated to be ~4°). In isomer **B**, both methylene protons are remote from the carbonyl group, only the benzyl proton being proximate to this group.

Table 5. Calculated (I) and experimental (II) $\Delta\delta$ values for the H(3), H(6), and H(8) cyclohexanone protons for the alternative diastereomers of compounds **2** relative to the protons of compound **1**

Isomer	H(3)		H(6)		H(8)	
	I	II	I	II	I	II
A	−1.96	−2.05— −2.08	0.05	−0.01— −0.02	−0.02	−0.04— −0.05
B	−1.95	—	0.10	—	0.01	—
C	−0.99	—	−0.19	—	−0.14	—

The low-field region of the spectra of compounds **2** exhibit multiplets for two of the three cyclopropane protons. One of these (H(11), δ 2.11—2.21; see Table 1) refers to the benzyl proton. This is indicated unambiguously by the coupling constants that characterize its *trans*- and *cis*-interaction with the corresponding methylene protons (see Table 2) and by the absence of geminal coupling. Another low-field multiplet refers to the methylene-group proton located in the *cis*-position with respect to the benzyl proton (H(12), δ 2.05—2.09, J_{gem} = –4.8 Hz, J_{cis} = 9.0 Hz; see Tables 1 and 2). The deshielding of this proton with respect to geminal H(12´) is indicative of its location near the carbonyl group. The sums of the contributions of the magnetic anisotropy, the electric field, and the steric effect of the carbonyl group calculated using the previously obtained[23—25] results for isomers **A** and **B** are presented in Table 6. These data provide the conclusion that the chemical shifts of the cyclopropane protons correspond to structure **A**. It is noteworthy that the chemical shifts found for compounds **2** are in good agreement with the ^{1}H NMR parameters of 1-phenylspiro[2.5]octan-4-one having a related structure,[15] determined by X-ray diffraction.

One more piece of evidence supporting structure **A** for the major methylenation product was provided by the NOESY experiment for compound **2a**. As follows from the geometric parameters for optimized structures **A—D** (Table 7), an intensive cross-peak between the *ortho*-protons of the benzene ring and the H(3) protons could be expected for diastereomers **A** and **B**. However, the NOESY spectrum of structure **B** should also exhibit a cross-peak of comparable intensity between the benzene protons and the protons of the Me group in position 3; however, this is not observed in experiments.

Thus, it follows from the analysis of ^{1}H NMR parameters that the major methylenation product is the *trans—trans* diastereomer **A** (see Fig. 1). Proceeding from the determined product structure and the retention of the configuration of the C(3) chiral center during the reaction, we determined the configurations of the newly formed chiral centers: 2*R*,11*S* (the seniority of substituents varies in the sequence C=O > C(11)Ar > C(3)Me > > C(12)H_2 for the first center and C_6H_4F > C(2)C=O > > C(12)H_2 > H(12) for the second one). Recently, this structure of compound **2a** was confirmed by X-ray diffraction, the results of which will be published separately, together with the structural data for the side product resulting from oxidative hydroxylation.

Table 6. Calculated (I) and experimental (II) Δδ values for the H(11), H(12), and H(12´) cyclopropane protons for compounds **2** relative to the protons of compound **1**

Isomer	H(11)		H(12)		H(12´)	
	I	II	I	II	I	II
A	1.218	1.252	1.158	1.168	0.072	0.052
B	1.657	—	0.403	—	0.086	—

Table 7. Distance between some protons of the cyclohexanone fragment and the *ortho*-protons of the aryl group (*R*) in alternative structures **A—D** and relative intensity (I_{rel}) of the cross-peaks in the NOESY spectrum on irradiation of the *ortho*-protons

Proton	*R*/Å				I_{rel}
	A	**B**	**C**	**D**	
H(3)	3.34 (0.85)*	2.99 (1.04)	4.12	4.47	1.0
C(7)H_3	4.38	2.50 (0.66)	5.58	2.88	0.13
H(4a)	2.42 (1.4)	4.63	2.91	5.88	0.17
H(6a)	2.85	5.65	2.46 (1.1)	5.17	0.21

* Distance between the protons in the predominant conformers of the corresponding isomers; the shortest distances attained by protons during rotation of the benzene ring are given in parentheses.

Chiral spiro[2.5]octanones in induced cholesteric liquid-crystalline systems. After being introduced into the nematic 4-(*n*-pentyl)-4´-cyanobiphenyl mesophase, the synthesized chiral spiro[2.5]octanones **2** induce a helical supramolecular ordering. The efficiency of this process was characterized quantitatively by the twisting power (β) of chiral dopants (CD), defined by the relation[1]

$$P^{-1} = \beta r C, \qquad (1)$$

where *P* is the pitch of the induced helix, *C* is the CD concentration, mole fractions, *r* is the enantiomeric purity of the dopant (equal to 1 for the current compounds).

The β values for compounds **2** are listed in Table 8. For comparison, the same Table gives the β values for **1** measured in the same nematic phase. Chiral compounds of the spiro[2.5]octanone series, like the starting arylidenecyclohexanones **1**, induce a left cholesteric helix (negaive β values) in 4-(*n*-pentyl)-4´-cyanobiphenyl. This implies that the replacement of the π-electronic system of the double bond in the *trans*-cinnamoyl fragment of molecules **2** by the three-membered carbon ring does not affect significantly the interaction of these CD with the

Table 8. Twisting power (β) and temperature dependence of the induced helix pitch (d*P*/d*T*) of spiro[2.5]octanones **2a—c** and their enone analogs **1a—c** in 4-(*n*-pentyl)-4´-cyanobiphenyl

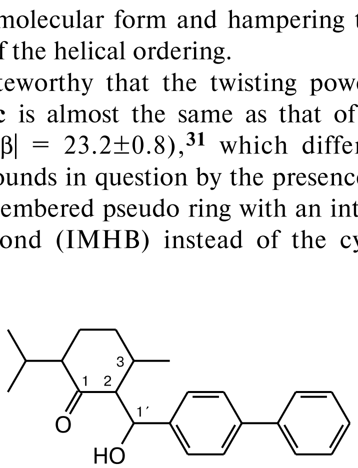
	–β/μm^{-1}		(d*P*/d*T*)/μm deg^{-1}	
	1	**2**	**1**	**2**
a	23.4±0.6	17.0±0.7	0.0024±0.0002	0.023±0.006
b	29.3±2.1	23.2±1.5	0.0034±0.0008	0.028±0.004
c	36.9±0.6	27.4±1.1	0.0000±0.0003	0.018±0.001

nematic environment. This can be considered to be a consequence of similar molecular forms of compounds **2** and **1**, resulting from the *trans*-orientation of the aryl and carbonyl groups in both types of compounds, and similar conformational behaviors of their cyclohexanone fragments (axial orientation of the methyl group). Undoubtedly, an important role is played by the unusual nature of the cyclopropane carbon—carbon bonds, which occupy an intermediate position between σ- and π-bonds.[26] Presumably, like double bonds, they can ensure efficient dispersive interaction of the dopants with the nematic environment, which is significant for efficient twisting in the mesophase.[2]

The above-mentioned structural features of compounds **2** are also responsible for the rather high absolute values of the twisting power, which are only somewhat (by 20—30%) lower than those for the corresponding enones **1** (see Table 8). The observed difference between the β values for compounds **2** and **1** reflects the outcome of the combined action of two major factors. According to the existing views,[2,27,28] the high twisting power of CD of the series **1** is due both to the presence of the axial Me group at the chiral center, giving rise to the stereospecific steric repulsion between the CD molecule and the nematic environment and to the additional chirality element, namely, the helical chirality of the twisted enone fragment of conformationally uniform molecules. This chirality element, rigidly connected to the central chirality, has been evaluated[27] as the crucial factor responsible for the high twisting power of CD **1**. Nevertheless, its elimination upon the replacement of the double bond by the three-membered carbon ring decreases insignificantly the twisting power of compounds **2** (see Table 8), which is attributable to the specific electronic structure of the cyclopropane bonds.[26] One should also bear in mind that the introduction of the cyclopropane group into the initial cyclohexanones **1**, gives rise to one more axial substituent in spirooctanones **2** (substituted methylene group), which potentially enhances the twisting properties of CD. The lower magnitudes of β observed in compounds **2** compared to arylidenecyclohexanones **1** may serve as evidence for the views on a greater contribution of helical chirality to the twisting power of chiral enones. This is even more valid in view of the reasonable assumption that two *trans*-arranged axial substituents in the cyclohexanone fragment may enhance each other's influence on the twisting.[29]

This substitution pattern in the cyclohexanone fragment may serve as one more factor contributing to the decrease in the twisting power of spirooctanones **2**, which has been discussed previously[1,2,9,30] for other types of compounds. This induces a decrease in the molecular anisometry due to the presence of two *trans*-α-substituents in the cyclohexanone fragment and deterioration of the local order in the mesophase related with this change in the CD molecular form and hampering the effective formation of the helical ordering.

It is noteworthy that the twisting power of spirooctanone **2c** is almost the same as that of β-hydroxyketone **4** (|β| = 23.2±0.8),[31] which differs from the spiro compounds in question by the presence of a rather stable six-membered pseudo ring with an intramolecular hydrogen bond (IMHB) instead of the cyclopropane fragment.



4 (2*R*,3*R*,6*S*,1´*S*)

In this conformationally uniform compound, the C(2)—C(1´) bond is equatorial, which makes the exocyclic fragment anisometric and differing little in shape from compound **1c**. The observed tendency for a higher twisting power of spirooctanone **2c** (see Table 8) compared to compound **4** can be due to different spatial orientations of the substituted methylene group in the cyclopropane fragment in the former case (axial) or in the pseudo ring with the IMHB in the latter case (equatorial).

Worth noting are also the parallel patterns of variation of the twisting power in the series of compounds **1** and **2** upon variation of the *para*-substituent in the benzene ring. For both types of chiral dopants, the highest twisting power is found for compounds containing a *para*-phenyl substituent. This is in line with the views on the enhancement of the dispersive interaction of the CD with the nematic medium upon this structural change.[2,27]

A specific feature of the behavior of CD **2** in liquid-crystalline systems is the weak temperature dependence of the pitch of the induced helical structure, although the tendency of the cholesteric helix to unwind with temperature rise ($dP/dT > 0$, see Table 8) is more pronounced for CD **2** than for **1**. In view of the less anisometric molecular shape of CD **2** compared to **1** (a consequence of the presence of the axial substituted methylene group of the cyclopropane fragment in the *trans*-position to the methyl group in position 3), these data correspond to the conclusions[30,32] concerning the dependence of the dP/dT parameter on the molecular anisometry of the CD.

As expected, compounds **2** were found to be photostable. UV irradiation of their solutions in octane or irradiation of crystals with subsequent dissolution did not induce any changes in their electronic spectra. No changes have been observed in the induced helical pitch of the liquid-crystalline 4-(*n*-pentyl)-4´-cyanobiphenyl—CD **2c** composition (CD concentration, 1.32 mol.%) after UV irradiation for 1.5 h ($P = 2.97$ μm before irradiation and 2.91 μm after irradiation).

In the conclusion, the replacement of the double bond by the three-membered carbon ring in the molecules of compounds **1**, which are efficient chiral components of liquid-crystalline systems with induced helicity, imparts photochemical stability to the methylenation products and does not deteriorate markedly the twisting properties. An important feature peculiar in liquid-crystalline composites with these CD is weak temperature dependence of the induced helix pitch, which is needed for stable operation of liquid-crystalline electrooptical devices.

Experimental

IR spectra were recorded on a Specord IR-75 spectrophotometer in KBr pellets. UV spectra were measured in octane on a Hitachi U3210 spectrophotometer. HPLC analysis was carried out on a Hewlett—Packard 1050 liquid chromatograph (spectrophotometric detector, detection wavelength 254 nm, a 150×4.6 mm column packed with Nucleosil 100-5 C18, particle size 5 μm, column temperature 30 °C). The mobile phases were: 0.01 *M* acetate-ammonium buffer (pH 4.7)—acetonitrile (95 : 5, v/v) (*A*); acetonitrile (*B*). The gradient elution was carried out according to the following schedule: 0 min, 50% *A* and 50% *B*; 25 min, 100% *B*. The velocity of the mobile phase was 1 mL $\min^{-1}$.

GC/MS analysis was carried out using an Agilent 1100 Series high-perfomance liquid chromatograph equipped with an Agilent LC/MSD SL diode matrix and mass selective detector; and a ZorbaxSB-C18 column (1.8 μm, 4.6 mm × 15 mm). The solvents were acetonitrile—water (95 : 5) and 0.05%) of formic acid (*A*); water (0.05% of formic acid) (*B*). The eluent flow rate was 3 mL $\min^{-1}$ with 1 : 1 flow splitting. The gradient elution was carried out according to the following schedule: 0 min, 0% *A*; 0.01 min, 0% *A*; 0.5 min, 100% *A*; 0.95 min, 100% *A*; 0.96 min, 0% *A*. The sample volume was 1 μL. The atmospheric pressure chemical ionization (APCI), ionization mode, and simultaneous scanning of positive and negative ions in the mass range of 80—1000 *m*/*z* were used.

^{1}H NMR spectra were recorded on a Bruker Avance DRX 500 spectrometer (500.133 MHz) using Me_4Si as the internal standard. The proton multiplets observed in the second-order spectra were interpreted using decoupling experiments; this was confirmed by computational spin system simulation using the NUTS 4.35 quantum-chemical software. The spectra of compounds were simulated using four spin subsystems: the H(5), H(5´), H(4), H(4´), H(3), and C(7)H_3 eight-spin subsystem (for computer simulation of the H(3) proton multiplet), the C(10)H_3, C(9)H_3, H(8), H(6), H(5), and H(5´) ten-spin subsystem (for computer simulation of the H(6) and H(8) proton multiplets), H(8), H(6), H(5), H(5´), H(4), H(4´), and H(3) seven-spin subsystem (for computer simulation of the protons at C(5) and C(4)), and the H(11), H(12), and H(12´) three-spin subsystem (for computer simulation of the multiplets from the cyclopropane protons). The chemical shifts were determined to an accuracy of 0.001, and coupling constants, to an accuracy of 0.1 Hz (calculation results).

The initial structures of the compounds for optimization were constructed using HyperChem modeling programs. The structures of the alternative stereoisomers and their conformers were found by full AM1 optimization of all geometric parameters implemented in the MOPAC 6.0 package.

The pitch and the sign of the induced helical structures for the 4-(*n*-pentyl)-4´-cyanobiphenyl—CD composites, in particular, under UV radiation were measured by the Grandjean—Cano wedge method, as described previously.[33,34]

The stability of the obtained CD against UV radiation was studied in relation to compound **2c** for samples dissolved in octane, for the liquid-crystalline composition based on 4-(*n*-pentyl)-4´-cyanobiphenyl, and for a crystalline sample. A small portion of the compound was dissolved in octane, and the resulting solution was diluted until the optical density at the long-wavelength absorption peak (295 nm) decreased to 0.5. The diluted solution was transferred into a sealed cell and the absorption spectrum was recorded in the 240—400 nm range. The sample was irradiated with a monochromatic light at a wavelength of 313 nm from a DRSh 250 high-pressure mercury lamp. The monochromatic light was obtained using a MDR-12 monochromator. Repeated scanning of the absorption spectra was carried out 10, 40, and 320 min after the beginning of the UV exposure. The difference between the solution optical densities before and after the UV exposure were 3.3% at 295 nm and 2.3% at 260 nm, which falls within the experimental error. The greatest duration of irradiation of the solution was 5 h 15 min.

In a study of the photostability of the crystalline sample, a slight amount of crystals of **2c** was placed on a quartz glass of a solid sample holder and exposed to UV light for 12 h. Then the crystals were transferred to octane, and the resulting solution was diluted and subjected to photometry. The spectrum was normalized to the optical density in the absorption peak of the solution prepared from a non-irradiated sample (295 nm). The differences in the optical densities at 260 nm were 0.5%.

(3*R*,6*R*)-2-Arylidene-6-isopropyl-3-methylcyclohexanones 1a—c were prepared as described previously.[29]

Synthesis of (1*S*,3*R*,5*R*,8*R*)-1-(4-X-phenyl)-5-isopropyl-8-methylspiro[2.5]octanones 2a—c (general procedure). Powdered NaOH (1.2 g, 0.03 mmol) was added to a mixture of arylidene derivative **1a—c** (0.01 mol) and DMSO (15 mL), the mixture was stirred for 20 min, and trimethylsulfoxonium iodide (3.3 g, 0.015 mol) was then added. Then the reaction mixture was maintained at 14—18 °C (the maintenance time is indicated in Table 9), poured into 100 g of an ice/water mixture, and allowed to stand for some period. The precipitate was filtered off, dried, and recrystallized from ethanol. The product characteristics are summarized in Table 9.

(1*S*,3*R*,5*S*,8*R*)-5-Hydroxy-5-isopropyl-8-methyl-1-(4-phenylphenyl)spiro[2.5]octan-4-one (3´) and **(1*S*,3*R*,5*R*,8*R*)-5-hydroxy-5-isopropyl-8-methyl-1-(4-phenylphenyl)spiro[2.5]octan-4-one (3″) (mixture).** Powdered NaOH (1.2 g, 0.03 mmol) was added to a mixture of compound **1c** (0.01 mol) and DMSO (15 mL), the mixture was stirred for 20 min, and trimethylsulfoxonium iodide (3.3 g, 0.015 mol) was added. The reaction mixture was stirred for 6 h at ~20 °C, allowed to stand for ~14 h, and treated as described in the general procedure. The product was dissolved in EtOH with heating and left for crystallization to give 150 mg of a white crystalline solid; according to HPLC and ^{1}H NMR, this was a mixture of two products in approximately equal amounts (65 : 35 from HPLC, 55 : 45 from ^{1}H NMR). ^{1}H NMR (C_6D_6), δ: 0.368, 0.631, 0.856, 0.886, 0.886, 0.954 (all d, Me, *J* = 7.1 Hz); 1.010, 1.257, 1.547, 1.833, 2.854, 3.113 (all dd, H of the cyclopropane fragment); 2.143, 2.280 (both s,

Table 9. Characteristics of spiro[2.5]octanones **2a—c** and **3´**

Compound	X	Y	M.p. /°C	Yield (%) (solvent)*	Reaction time/h	Found/Calculated (%)			Molecular formula	IR spectrum, ν(CO)/cm^{-1}
						C	H	X**		
2a	F	H	110	39	24	78.30	8.57	6.79	$C_{18}H_{23}FO$	1682
				(DMSO)		78.80	8.45	6.92		
2b	Cl	H	128	87.5	3	74.10	8.07	11.95	$C_{18}H_{23}ClO$	1672
				(DMSO)		74.34	7.97	12.19		
2c	Ph	H	137	47	3	86.20	8.67	—	$C_{24}H_{28}O$	1682
				(DMSO)		86.70	8.49			
2c	Ph	H	137	60	1.5	86.20	8.67	—	$C_{24}H_{28}O$	—
				(DMF)		86.50	8.53			
3´	Ph	OH	129—131	1.2	24	82.43	8.28	—	$C_{24}H_{28}O_2$	—
				(DMSO)		82.72	8.10			

* The yields of individual products purified by crystallization from ethanol are given.
** X = F or Cl.

2 OH); 2.280, 2.482 (both sept, CH in Pr^i, J = 7.1 Hz); 7.227, 7.502 (both m, H arom.). Fractional crystallization of this mixture gave 15 mg of a crystalline compound (according to HPLC, this was **3´**), m.p. 131 °C. ^{1}H NMR (DMSO-d_6), δ: 0.828, 0.934 (both d, 3 H each, C(9)Me, C(10)Me, ^3J = 7.0 Hz); 0.967 (d, 3 H, C(7)Me, ^3J = 7.1 Hz); 1.156 (m, 1 H, H(4), ^2J = –13.2 Hz, ^3J = 2.9 Hz, ^3J = 2.5 Hz, ^3J = 2.0 Hz); 1.184 (dd, 1 H, *trans*-H(12), ^2J = –4.7 Hz, ^3J = 7.1 Hz); 1.295 (m, 1 H, H(3), ^3J = 7.1 Hz, ^3J = 3.6 Hz, ^3J = 2.0 Hz); 1.606 (m, 1 H, H(5), ^2J = –13.5 Hz, ^3J = 2.9 Hz, ^3J = 2.5 Hz); 1.812 (dd, 1 H, *cis*-H(12), ^2J = –4.7 Hz, ^3J = 8.7 Hz); 1.884 (m, 1 H, H(5´), ^2J = –13.5 Hz, ^3J = 13.6 Hz, ^3J = 2.6 Hz); 1.907 (m, 1 H, H(4´), ^2J = –13.2 Hz, ^2J = 13.6 Hz, ^2J = 3.6 Hz, ^2J = 2.9 Hz); 2.295 (sept, 1 H, H(8), ^3J = 7.0 Hz); 2.312 (dd, 1 H, H(11), ^3J = 8.7 Hz, ^3J = 7.1 Hz); 5.088 (s, 1 H, OH); 7.155 (t, 1 H, *p*-H arom., ^3J = 8.2 Hz); 7.186 (d, 2 H, *o*-H arom., ^3J = 8.2 Hz); 7.256 (t, 2 H, *m*-H arom., ^3J = 8.2 Hz); 7.416, 7.463 (both d, 2 H each, H arom., ^3J = 8.2).

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