Synthesis, Crystal Structure, and Circular Dichroism Spectra of (1*S*)-4,8-Diphenylbarbaralane-2,6-dicarbonitrile – Chiroptical Properties of the Transition State of a Degenerate Cope Rearrangement[1]

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Diphenylbicyclo[3.3.1]nonane-2,6-dione *rac*-**3** is resolved in 57 % overall yield by chromatographic separation of the diastereomeric (*R*)-*N*-(1-phenylethyl)carbamates **9** which are obtained from (*R*)-(1-phenylethyl) isocyanate (**8**) and the 6-hydroxydiphenylbicyclo[3.3.1]nonan-2-ones *endo*- and *exo*-**4**. The enantiomers (1*R*)- (e.r. = 98:2) and (1*S*)-**3** (e.r. = 97:3) are regenerated from **9** by reduction with lithium aluminium hydride followed by Swern oxidation of the resulting diols **5**. The title compound (1*S*)-**1** is synthesised in three steps from (1*S*)-**3** in improved yield on the route that had led to *rac*-**1**. The absolute configurations are established by X-ray diffraction analyses of the carbamates *endo*-(1*R*)-**9** and *exo*-(1*S*)-**9**. X-ray diffraction analyses were also performed of the camphanoate (1*R*)-**7**, the intermediates *rac*-*endo*-**4** and (1*S*)-**3**, and the title compound (1*S*)-**1**. Hydroxy ketone *rac*-*endo*-**4** adopts similar conformations in the solid state and in solution as shown by a comparison of vicinal ^{1}H,^{1}H coupling constants from proton spectra with those calculated from torsional angles in the crystal. The molecular structures of (1*S*)-**1** and (1*S*)-**3** closely resemble those of the corresponding racemates investigated previously. These results show (i) that *inter*molecular interactions in the solid state are of minor importance and (ii) that the unusually long C2–C8 distance of (1*S*)-**1** and *rac*-**1** (168 pm) is a molecular but not an averaged property due to a non-degenerate Cope rearrangement in the crystal. CD spectra are reported for (1*R*)- and (1*S*)-**3**, the unsaturated dicarbonitrile (1*S*)-**13**, and (1*S*)-**1**. The CD spectrum of (1*S*)-**1** exhibits a weak positive band at 459 nm where *rac*-**1** shows a temperature-dependent absorption which has been assigned to the higher, vibronic state represented by *rac*-**1***. The intensity of the weak CD band depends on the temperature and the solvents in the same way as the UV/Vis absorption of *rac*-**1**. This supports the conclusion that both bands originate from the same source, viz. the transition state **1*** of the degenerate Cope rearrangement **1** ⇄ **1′**.

Introduction

Barbaralanes and semibullvalenes may be chiral by virtue of their substitution pattern. Such chiral systems that undergo rapid degenerate Cope rearrangements may be isolated in nonracemic form provided that chirality is retained in the Cope transition state, which hence must possess C_2 symmetry. Degenerate Cope rearrangements via transition states of C_S symmetry lead to enantiomerisation, of course.[2] No nonracemic degenerate barbaralane or semibullvalene has yet been prepared. Almost two decades ago, Paquette and coworkers have synthesised a single nonracemic semibullvalene, viz. (+)-2(4)-methylsemibullvalene, which is not however, degenerate.[3] Here we report synthesis, X-ray diffraction analysis and circular dichroism spectra of the title compound (1*S*)-**1**, which is the first nonracemic *degenerate* Cope system. Two intriguing problems induced us to embark on the present project.

(i) The racemic barbaralanedicarbonitrile *rac*-**1** is thermochromic owing to a temperature-dependent UV/Vis absorption around 450 nm.[4] The increase of this band with temperature has been ascribed to an equilibrium between the two degenerate localised ground states **1**, **1′** and a long wavelengths absorbing, delocalised state, which is located just above the flat potential energy maximum between the ground states; that is, in an area of the energy hypersurface where vibronic interaction is strong. The latter state is to be considered as the transition state of the degenerate Cope rearrangement **1** ⇄ **1′** and may be represented by the bishomoaromatic C_2 structure **1***.[5] This simple model applies only to the gas-phase and solutions in nonpolar or weakly polar solvents, however, because, in strongly dipolar, aprotic solvents, solvations terms predominate over the gas-phase enthalpy difference between **1**, **1′** and **1*** thus rendering the *solvated* delocalised structure **1*** *more stable* than the *solvated* localised structures **1**, **1′**.[6] A nonracemic barbaralanedicarbonitrile (1*R*)- or (1*S*)-**1** would offer the unique opportunity to investigate the chiroptical properties of the transition structure (1*R*)- or (1*S*)-**1***. The circular dichroism spectra are expected to be characterised by the same effects of temperature and solvents that have been documented for the near-UV/Vis spectra of the equilibrating racemic species **1** ⇄ **1*** ⇄ **1′**.[6] This is indeed the case.

(ii) The racemic barbaralanedicarbonitrile *rac*-**1** forms a racemate in the solid state.[4] Because the nonracemic compound must crystallise in a different space group, a com-

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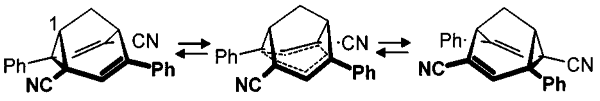
parison of the molecules embedded in two different crystal lattices promised to demonstrate their importance for the apparent molecular geometry. In the case of *rac*-**1** and other degenerate barbaralanes and semibullvalenes, unusual atomic distances have been interpreted in terms of average values associated with the Cope rearrangement of two valence tautomers whose degeneracy is lifted in the solid state owing to the particular crystal lattice of each system.[7]

We report our results in several sections. First, we detail the enantiomer resolution of 4,8-diphenylbicyclo[3.3.1]nonane-2,6-dione (*rac*-**3**) which is the crucial intermediate on the route to the the racemic barbaralanedicarbonitrile *rac*-**1**.[4] Subsequently, we give a brief description of the synthesis of (1*S*)-**1** from (1*S*)-**3** on that route. Experimental procedures were simplified and improved yields obtained in each step. In the next section, solid state structures of racemates are compared to those of the corresponding enantiomers. Finally, we investigate chiroptical properties of the barbaralanedicarbonitrile (1*S*)-**1** and intermediates of its synthesis.

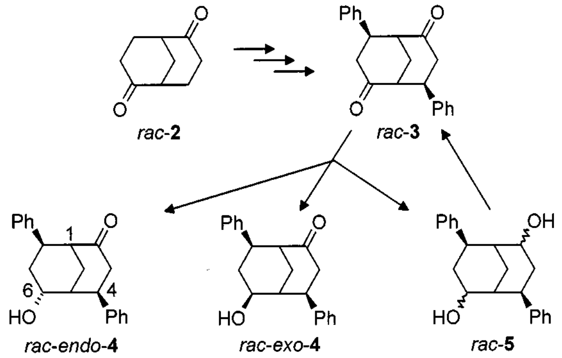


(1*S*)-**1** (1*S*)-**1*** (1*S*)-**1'**

Results and Discussion

Enantiomer Resolution of *exo*,*exo*-4,8-Diphenylbicyclo[3.3.1]nonane-2,6-dione

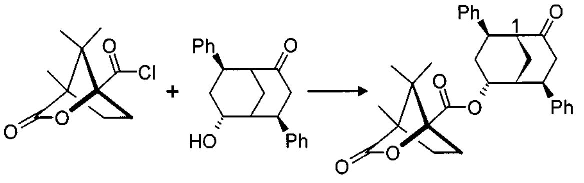
Attempts to separate the racemic barbaralanedicarbonitrile *rac*-**1** by analytical HPLC on chiral columns met with failure.[8] Because other separation techniques appeared even less attractive, we resorted to an enantioselective synthesis. The racemic compound *rac*-**1** has been obtained in seven steps from Meerwein's ester.[4] Of all intermediates on this route, only the 2,6-diketones *rac*-**2** and *rac*-**3** offered the opportunity of an efficient enantiomer resolution on a preparative scale. In fact, Gerlach has obtained (1*S*)-**2** on a gramme scale from the corresponding racemic *endo*,*endo*-diol by fractionating crystallisation of the diastereomeric bis[(1*S*)-camphanoates] followed by hydrolysis and oxidation.[9][10] Various preparations of single enantiomers of **2** or corresponding alcohols involving kinetic enantiomer resolutions with baker's yeast[11] or enzymes[12] are rendered unattractive, however, by low reactivity and modest yields,[11] and the necessity of several steps including cumbersome experimental and isolation procedures.[12] On the other hand, the diphenyl diketone *rac*-**3** is readily available from *rac*-**2** in three steps with an overall yield of 50−60% on a 0.1 mole scale[13][14] and lies already halfway on the route to *rac*-**1**. Exploratory experiments with the view of resolving *rac*-**3** by enantioselective HPLC gave only unsatisfactory results on microcrystalline triacetylcellulose (eluent methanol) but a fair, albeit not with base-line separation, on tris(phenylcarbamoyl)cellulose−silica[15] (eluent ethanol).[16] Unfortunately, a preparative column packed with the latter adsorbent was unavailable. Therefore, we set out to resolve *rac*-**3** via diastereomeric derivatives. This strategy appeared particularly promising since efficient preparative high-resolution chromatography (MPLC) was at hand.[17] A host of procedures have been documented for the resolution of enantiomeric ketones in this way.[18] One of the most versatile and reliable involves reduction to the racemic secondary alcohols and reoxidation after separation and hydrolysis of their diastereomeric derivatives.[9]



While the reduction of the diketone *rac*-**2** with complex hydrides is highly diastereoselective, affording the *endo*,*endo*-diol,[19] sodium borohydride reduced the diphenyl diketone *rac*-**3** to a mixture which was separated into three components, viz. two hydroxy ketones, *rac*-*endo*-**4** (56%) and *rac*-*exo*-**4** (25%) and a mixture of diastereomeric diols *rac*-**5** (19%). The latter could be recycled almost quantitatively by Swern oxidation[20] to the starting diketone *rac*-**3**. Attempts to improve the poor diastereoselectivity by employing other reducing agents[21] met with failure but attested to the lower reactivity of *rac*-**3** compared to that of *rac*-**2**.

The assignment of the structures to the two hydroxy ketones *rac*-**4** was based on carbon-13- (Table 8) and proton-NMR spectra which were completely analysed for the protons of the bicyclic skeletons (Tables 5 and 6). The relative configurations may be deduced from the γ-*gauche* effect of the 6-hydroxy groups on the chemical shifts of the carbon-13 atoms C4 which absorb at $\delta = 35.0$ and 42.1. Clearly, the former value is indicative of the *endo* configuration.

(1*S*)-Camphanoyl chloride (**6**) has a longstanding record in the resolution of racemic alcohols,[18] including the *endo*,*endo*-diol derived from *rac*-**2**.[9] Treatment of the hydroxy ketone *rac*-*endo*-**4** with **6** in the presence of 4-(dimethylamino)pyridine afforded an almost quantitative yield of the diastereomeric camphanoates **7** which showed base-line separation on a high-resolution reversed-phase HPLC column. Unfortunately, a preparative column of this sort was unavailable, and attempts at separation on normal silica-gel columns met with failure. Slow crystallisation of the crude product from ethyl acetate afforded fine needles in 52% yield of a single diastereomer whose absolute configuration (1*S*)-**7**[22] was proved by an X-ray diffraction analysis (Figure 1). The moderate yield and the lack of an efficient chromatographic separation of the diastereomers deterred us from further pursuing this method.



6 *rac-endo*-**4** (1*R*)-**7** + (1*S*)-**7**

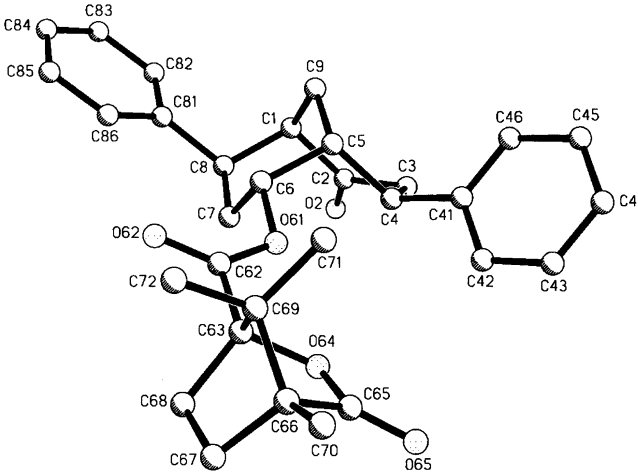


Figure 1. Stereographic projection of the camphanoate (1*R*)-**7** with the numbering of the atoms[22]

Much better results were obtained when (*R*)-(1-phenylethyl) isocyanate (**8**) was employed as resolving agent.[18] In the presence of 4-(dimethylamino)pyridine, it converted quantitatively both racemic hydroxy ketones *endo*- and *exo*-**4** into the corresponding mixtures of diastereomeric *N*-(1-phenylethyl)carbamates **9**. Both mixtures could be separated by preparative chromatography on silica gel. While cyclic MPLC was required for the complete separation of *endo*-(1*R*)- and *endo*-(1*S*)-**9** (Figure 2),[17c−17f] flash chromatography sufficed for separation of the diastereomers *exo*-(1*R*)- and *exo*-(1*S*)-**9** to be separated into fractions with diastereomeric ratios (d.r.) > 97:< 3. MPLC improved these ratios further.

It was very convenient that one diastereomer of the *endo* pair and one of the *exo* pair, viz. *endo*-(1*R*)- and *exo*-(1*S*)-**9**,[22] formed crystals suitable for X-ray diffraction analyses which obviated the necessity of establishing the absolute configurations by other methods (Figure 3).

Cleavage of carbamates is usually carried out with alkali alkoxides, lithium aluminium hydride,[23] or, under particularly mild conditions, with trichlorosilane in the presence of triethylamine.[24] Treatment of the *N*-(1-phenylethyl)carbamate *endo*-(1*R*)-**9** with the latter reagent gave, surprisingly, only 46% of the hydroxy ketone *endo*-(1*R*)-**4** besides 22% of a by-product. On the basis of NMR evidence, we assigned the enamine structure **11** to the minor product. Enamine **11** apparently arises from the major product and the secondary amine **10** formed by reduction of the *N*-(1-phen-

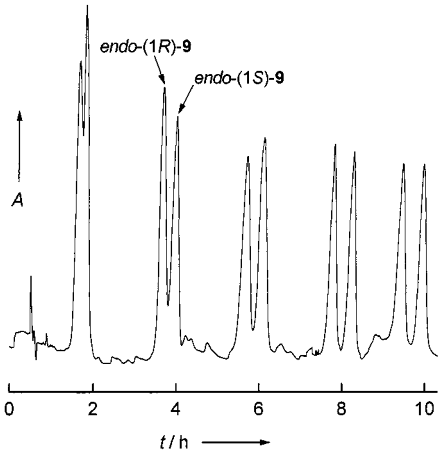


Figure 2. UV trace (λ = 254 nm) recorded during medium-pressure liquid chromatography (MPLC, five cycles) of the diastereomeric *N*-(1-phenylethyl)carbamates *endo*-**9** (2 g) on a (70 × 7)-cm silica column with petroleum ether/ethyl acetate

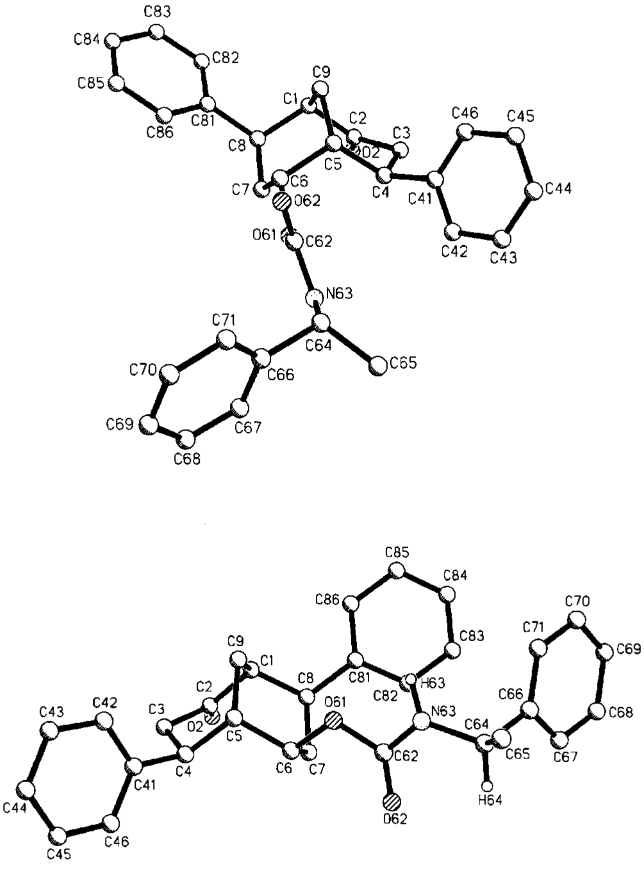
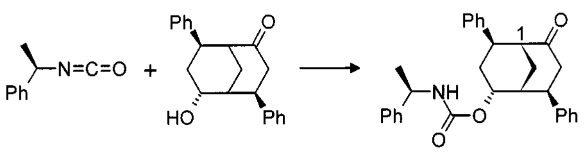


Figure 3. Stereographic projections of the diastereomeric *N*-(1-phenylethyl)carbamates *endo*-(1*R*)-**9** (above) and *exo*-(1*S*)-**9** (below) with the numbering of the atoms[22]



8 *rac-endo*-**4** *endo*-(1*R*)-**9** + *endo*-(1*S*)-**9**

ylethyl)carbamoyl moiety. Attempts to hydrolyse **11** with hydrochloric acid in ethanol were frustrated by the formation of three unknown products besides only small amounts of *endo*-(1*R*)-**4**. Therefore, *endo*-(1*R*)-**9** as well as the other three diastereomers were reduced with an excess of lithium aluminium hydride to afford the corresponding 2,6-diols **5**, which were not characterised. Instead, the crude products were converted by Swern oxidation[20] into the enantiomeric diphenyl diketones (1*R*)- and (1*S*)-**3** which could be isolated in yields of 72−80% based on the single hydroxy ketones **4** (Table 1).

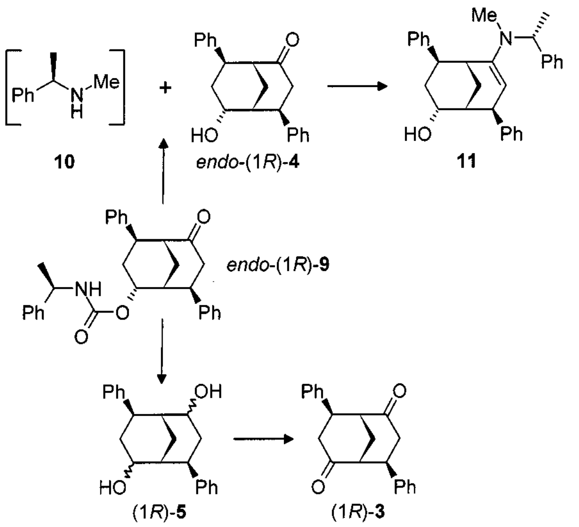


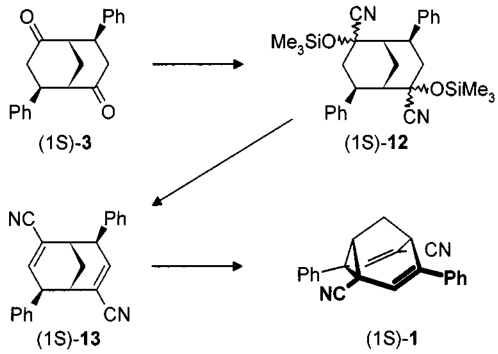
Table 1. Starting materials, reagents, yields, melting points and IR data; yields and melting points of racemic mixtures are given in brackets for comparison;[4] *endo* and *exo* are abbreviated as *n* and *x*, respectively

Cpd.	Starting material	Reagent (separation)	Yield [%]	d.r.	m.p. [°C]	IR (KBr) [cm^{-1}] C=O	IR (KBr) [cm^{-1}] OH
rac-n-**4**	*rac*-**3**	$NaBH_4$ (MPLC)	56		139–141	1691	3610[a]
rac-x-**4**			25		107–108	1690	3600[a]
rac-**5**			19[b]				
(1*R*)-**7**	*rac-n*-**4**	**6**, 4-(Me_2N)py (cryst)	52[c]	100 : 0	204–206	1780 1711	
							NH
n-(1*R*)-**9**	*rac-n*-**4**	**8**, 4-(Me_2N)py (MPLC)	96[c]	100 : 0	163–164	1676	3415[a]
n-(1*S*)-**9**			96[c]	99 : 1	62–69[d]	1708	3328
x-(1*R*)-**9**	*rac-x*-**4**		88[c]	100 : 0	48–52[d]	1702	3332
x-(1*S*)-**9**			86[c]	99 : 1	118–119	1696	3425
(1*R*)-**3**	*n*-(1*R*)-**9**	1. $LiAlH_4$	77		139–141		
	x-(1*R*)-**9**	2. $(F_3CCO)_2O$, DMSO, NEt_3	72		(135–137)		
(1*S*)-**3**	*n*-(1*S*)-**9**		73				
	x-(1*S*)-**9**		80				
(1*S*)-**12**[e]	(1*S*)-**3**	Me_3SiCN, KCN/18-crown-6	91 (69)				
(1*S*)-**13**	(1*S*)-**12**[e]	$POCl_3$, HF, py	55 (43)		229–231 (225–227)		
(1*S*)-**1**	(1*S*)-**13**	NaOH, $Bu_4N^+OH^-$, C_2Cl_6	65 (57)		224–225 (216–218)		

[a] Recorded for a solution in [D]trichloromethane (1-cm Infrasil quartz cuvette). − [b] The crude product obtained by flash chromatography was recycled by Swern[20] oxidation to *rac*-**3**. − [c] Based on the enantiomer in the racemic starting material. − [d] Temperature range of softening of the semi-solid material. − [e] Mixture of *endo,endo*-, *endo,exo*- and *exo,exo*-(1*S*)-**12** [41:45:14, RP-HPLC; *endo* and *exo* refer to the (*O*-trimethylsilyl)oxy groups].

Synthesis of (1*S*)-4,8-Diphenylbarbaralane-2,6-dicarbonitrile

The racemic barbaralanedicarbonitrile *rac*-**1** has been prepared from the diphenyl diketone *rac*-**3** in three or four steps involving the conversion of *rac*-**3** to the unsaturated dicarbonitrile *rac*-**13** in the usual way via a mixture of diasteromeric bis[(*O*-trimethylsilyl)cyanohydrins] *rac*-**12**. The crucial cyclisation of *rac*-**13** to *rac*-**1** was performed either by the *N*-bromosuccinimide bromination−zinc-copper couple debromination sequence or, in a single step, by phase transfer-catalysed chlorination−dehydrochlorination with hexachloroethane in the presence of concentrated aqueous sodium hydroxide.[4] For the synthesis of (1*S*)-**1** from (1*S*)-**3**, the second, shorter route was followed and simplified further by omitting the purification of the intermediate cyanohydrins (1*S*)-**12**. It was gratifying to obtain improved yields for each step. Yields and melting points of the nonracemic compounds with the absolute configuration (1*S*) are listed in Table 1 together with the data of the racemic compounds for comparison.



X-ray Diffraction Analyses of the Bicyclic Ketones *rac-endo*-4 and (1*S*)-3, and Barbaralanedicarbonitrile (1*S*)-1

X-ray diffraction analyses of the hydroxy ketone derivatives that were prepared with resolving reagents, viz. *endo*-(1*R*)-**7**, *endo*-(1*R*)-, and *exo*-(1*S*)-**9**, established the absolute configurations for all nonracemic compounds of this study. An X-ray diffraction analysis of the racemic hydroxy ketone *rac-endo*-**4** itself not only confirmed the *endo* configuration of the hydroxy group, which was derived on the basis of NMR evidence, but also allowed a comparison of the conformations in the solid state and in solution by means of torsional angles and vicinal ^1H,^1H coupling constants. The molecule adopts the boat-chair conformation in the solid state (Figure 4). That this conformation is also preferred in solution is shown by the similarity between the vicinal coupling constants that were calculated from torsional angles φ in the crystal according to the Karplus equation [Equation (1)][25] and those obtained by analysis of the 600-MHz proton spectrum taken from a solution in [D]trichloromethane (Tables 2 and 5). The same arguments have led to similar results in previous comparative studies of the conformations adopted by other bicyclo[3.3.1]nonanes, including *rac*-**3**,[4] in the solid state and in solution.[26][27] Surprisingly, large vicinal coupling constants are missing in the high-field proton spectrum of the *exo*-hydroxy ketone *rac-exo*-**4** (Table 6). This shows that there are no antiperiplanar ^{1}H,^{1}H relationships that exist long enough for detection on the NMR time scale. Therefore, the molecule *rac-exo*-**4** adopts either a single, very flattened configuration or two boat-chair conformations that rapidly equilibrate.

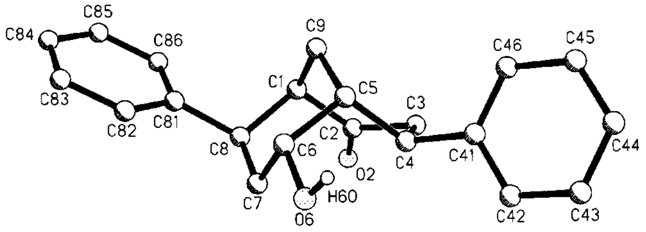


Figure 4. Stereographic projections with the numbering of the atoms of the (1*R*) enantiomer in the crystal of the racemic hydroxy ketone *rac-endo*-**4**

Table 2. Torsional angles φ [°] obtained by X-ray diffraction analysis, and calculated (Equation 1) and experimental vicinal ^{1}H,^{1}H coupling constants (^3J [Hz]) for the hydroxy ketone *rac-endo*-**4**; *endo* and *exo* are abbreviated as *n* and *x*, respectively

Torsional angles	φ [degree]	Vicinal ^{1}H,^{1}H coupling constants [Hz]	
		calc.	found
1H–C1–C8–8H$_n$	70.2	2.8	2.2
3H$_n$–C3–C4–4H$_n$	–53.5	4.9	6.6
3H$_x$–C3–C4–4H$_n$	–173.4	12.9	11.3
4H$_n$–C4–C5–5H	119.9	5.0	2.0
5H–C5–C6–6H$_x$	60.1	4.0	5.0
6H$_x$–C6–C7–7H$_n$	–176.1	13.0	12.3
6H$_x$–C6–C7–7H$_x$	–57.2	4.4	5.1
7H$_n$–C7–C8–8H$_n$	47.9	5.8	6.4
7H$_x$–C7–C8–8H$_n$	–71.0	2.7	1.4

$$^3J = 7 - \cos\varphi + 5 \cdot \cos(2 \cdot \varphi)\ [\mathrm{Hz}] \tag{1}$$

Cooperative interactions between molecules in the solid state determine space group and crystal system, and may modify conformations of flexible molecules. The synthesis of nonracemic molecules, i.e. diphenyl diketones (1*R*)- and (1*S*)-**3**, and barbaralanedicarbonitrile (1*S*)-**1**, whose racemates had been studied by X-ray diffraction analyses,[4] offered the opportunity to probe the effect of those cooperative interactions in *different* crystal structures on (i) the conformations and (ii) the equilibrium associated with a rapid Cope rearrangement of *nondegenerate* valence tautomers of **1**. The racemic diphenyl diketone *rac*-**3** takes the boat-chair conformation with both wings being considerably flattened.[4] Exactly the same conformation is adopted by the nonracemic compound (1*S*)-**3** (Figure 5). The molecules of *rac*-**3** and (1*S*)-**3** are distinct only by virtue of somewhat different torsional angles involving their phenyl groups. The *intra*molecular interactions that determine the boat-chair conformation obviously predominate over any *inter*molecular interactions. The boat conformation of the β-phenylcyclohexanone moiety appears particularly resistant to changes at the other cyclohexane ring of the bicyclo[3.3.1]nonane system. This becomes evident by a comparison of no less than six structures, viz. *rac*-[4] and (1*S*)-**3**, *rac-endo*-**4**, (1*R*)-**7**, *endo*-(1*R*)- and *exo*-(1*S*)-**9** (Figures 5, 4, 1, and 3, respectively). In the case of *exo*-(1*S*)-**9**, even two large *exo* groups occupy the 1,3 diaxial conformation at the chair cyclohexane ring rather than invert the conformations at both sides.

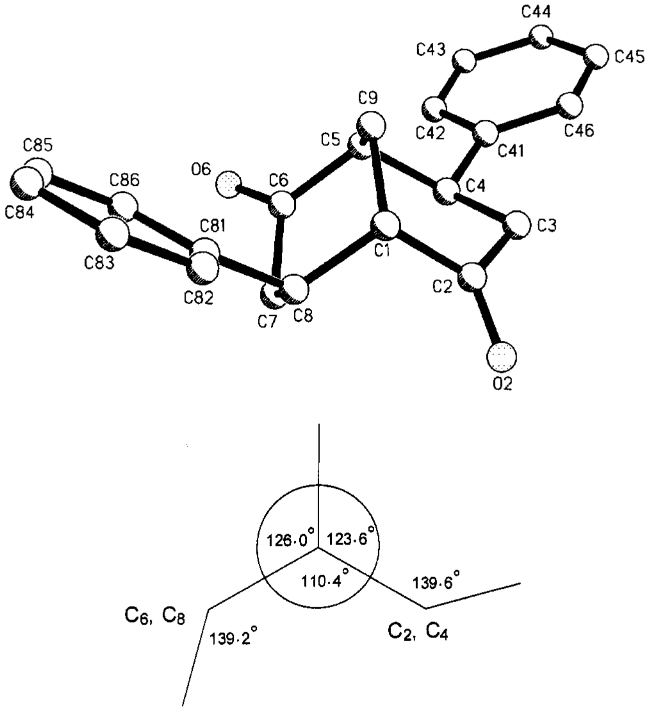


Figure 5. Stereographic projections of the diphenyl diketone (1*S*)-**3** with the numbering of the atoms (above) and angles between the planes of the bicyclo[3.3.1]nonane skeleton (below)

The (1*S*) enantiomer in the racemate *rac*-**1**[4] and a molecule of (1*S*)-**1** are almost superimposable. Only small differences are found for the torsional angles involving the phenyl groups (Figure 6) and for the atomic distances of the tricyclic skeleton. In most cases (Table 3), the differences only slightly exceed the standard deviations. Very small energy barriers for the degenerate Cope rearrangement in solutions of certain barbaralanes and semibullvalenes,[28] and solid-state NMR evidence[7] support the suggestion that, in principle, this rearrangement may also occur very rapidly in the solid state where it may be *nondegenerate*, however, because intermolecular interactions render the two valence tautomers nonequivalent. In these cases, the observed average lengths of the atomic distances C2−C8 and C4···C6 have been considered as a measure for the positions of such equilibria, which could be calculated on the basis of nonrearranging models.[7] Thus, *rac*-**1** was assumed to exist in the crystal as two valence tautomers in the ratio 9:1.[4] The surprisingly small influence of the different crystal lattices on the molecular geometries of *rac*-**1** and (1*S*)-**1**, uncovered in the present work, supports the idea, however, that the molecules are completely locked in one of the valence-tautomeric sites. As a result, the observed atomic distances belong to individual molecules and are *not* average values arising from two nondegenerate valence tautomers. Consequently, the length of the cyclopropane bond C2−C8 (168 pm) adds **1** to the growing group of molecules with exceptionally long carbon−carbon single bonds.[29][30]

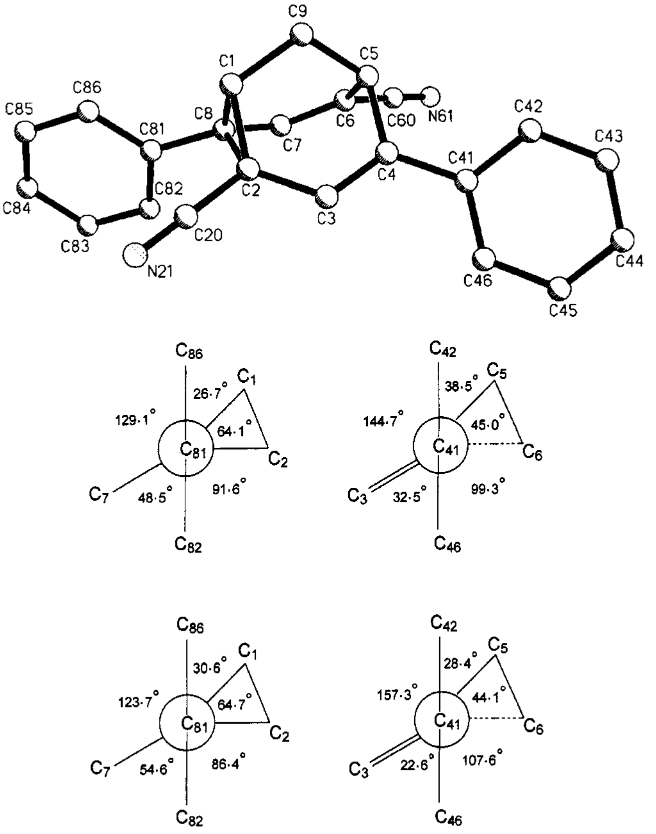


Figure 6. Stereographic projection of the barbaralanedicarbonitrile (1*S*)-**1** with the numbering of the atoms (above). Newman projections along the bonds between the *ipso* carbon atoms of the phenyl groups and the carbon atoms C8 (left) and C4 (right) for (1*S*)-**1** (middle) and the racemate *rac*-**1** (below)[4]

Table 3. Atomic distances *d* [pm] (standard deviations) for the tricyclic skeleton of the racemic (*rac*-**1**)[4] and the nonracemic barbaralanedicarbonitrile (1*S*)-**1** and differences between the distances $\Delta = d(rac\text{-}\mathbf{1}) - d[(1S)\text{-}\mathbf{1}]$

Distance	*d*(*rac*-**1**)	*d*[(1*S*)-**1**]	*Δ*
Cope system			
C2 – C3	145.8(3)	145.3(4)	0.5
C6 – C7	134.7(3)	134.1(4)	0.6
C4 – C3	134.9(3)	134.3(4)	0.6
C8 – C7	145.9(3)	144.9(4)	1.0
C2 – C8	167.7(3)	167.9(4)	−0.2
C6····C4	238.1(5)[a]	239.3(5)	−1.2
other bonds			
C1 – C2	150.7(3)	150.0(5)	0.7
C5 – C6	151.6(3)	152.5(4)	−0.9
C1 – C8	149.5(3)	148.6(4)	0.9
C5 – C4	152.2(3)	153.1(4)	−0.9
C9 – C1	152.2(3)	152.4(4)	−0.2
C9 – C5	153.2(3)	151.5(5)	1.7

[a] The value 237.0(10) pm listed in Table 4 of ref.[4] is in error; the correct figure (238.1 pm) has been given in the text.

It is enlightening to compare the conformations of the phenyl groups in the solid state of the diphenylbarbaralanedicarbonitriles *rac*-**1** and (1*S*)-**1** with those of 2,6-diphenylbarbaralane,[31] whose phenyl groups rotate without hindrance by a neighbouring nitrile group. Accordingly, the phenyl group at the cyclopropane ring of the latter adopts an almost perfect bisected conformation. By contrast, the phenyl groups of the former barbaralanes are twisted strongly from this conformation, viz. by 63° (*rac*-**1**) and 59° [(1*S*)-**1**] (Figure 6). There is little doubt that this deviation from the most stable (bisected) conformation is caused by the steric effect of the vicinal nitrile group. The torsional angles involving the phenyl groups and the double bonds at the other ("open") side of the barbaralanes are similar, however, viz. 22.6° (*rac*-**1**), 32.5° ([(1*S*)-**1**] (Figure 6) and 26.5° (2,6-diphenylbarbaralane).[31] This shows that there is no significant steric interaction between the phenyl and the cyano groups at the "open" side of the barbaralane skeleton. While the unfavourable interaction of the phenyl and the cyano group at the cyclopropane ring destabilises the ground state of the molecules **1**, virtually no such interaction is expected in the transition state **1*** of the degenerate Cope rearrangement. Therefore, we conclude that steric interactions of the substituents at the cyclopropane rings of barbaralanes and semibullvalenes contribute to the lowering of the activation barriers by substituents. As a result, these barriers cannot be estimated for 2,4,6,8-substituted systems by merely adding the effects that were measured with 2,6-substituted compounds.[28]

Both *rac*-**1** and (1*S*)-**1** are also orange-coloured and thermochromic in the solid state. These properties attest to the presence of a certain small fraction of the molecules that occupy a higher, vibronic state, which corresponds to the transition state **1*** of the degenerate Cope rearrangement in solution.[5] Because the sum of the atomic distances C2/C4 and C4/C6 of this state is certainly larger than that of a localised valence tautomer, the occupation of such higher, vibronic states is one of the reasons for the large values of this sum measured by X-ray diffraction analyses of thermochromic barbaralanes[4][26] and semibullvalenes.[2,7,32] In the absence of precise knowledge of the proportions and the geometry of the higher states, however, their share in the observed magnitudes of the atomic distances cannot be assessed.

Circular Dichroism Spectra[18a,33]

The enantiomeric ratios for (1*R*)- (98:2) and (1*S*)-**3** (97:3) and the products of the latter, (1*S*)-**1** and (1*S*)-**13**, were calculated from the enantiomeric ratio of the resolving agent employed, viz. the isocyanate **8** (98:2), and the ratios achieved in the separation of the diastereomeric carbamates, i.e. 100:0 for *endo*- and *exo*-(1*R*)-**9**, and 99:1 for *endo*- and *exo*-(1*S*)-**9**.

Optical rotations, circular dichroism (CD) and UV/Vis data are listed in Table 4. The absorption for the barbaralanedicarbonitrile (1*S*)-**1** in the visible range precluded the measurement of the optical rotation. CD spectra recorded for (1*R*)- and (1*S*)-**3**, (1*S*)-**13**, and (1*S*)-**1**, and UV/Vis spectra taken from solutions of the corresponding racemic mixtures are displayed in Figures 7−9. The CD bands of the diphenyl diketones (1*R*)- and (1*S*)-**3**, and the unsaturated dicarbonitrile (1*S*)-**13** are readily correlated with the UV absorptions of the chromophors present. While circular dichroism spectra for a number of bicyclic diketones have been reported,[9,10,34] no data are known for unsaturated nitriles comparable to (1*S*)-**13**.

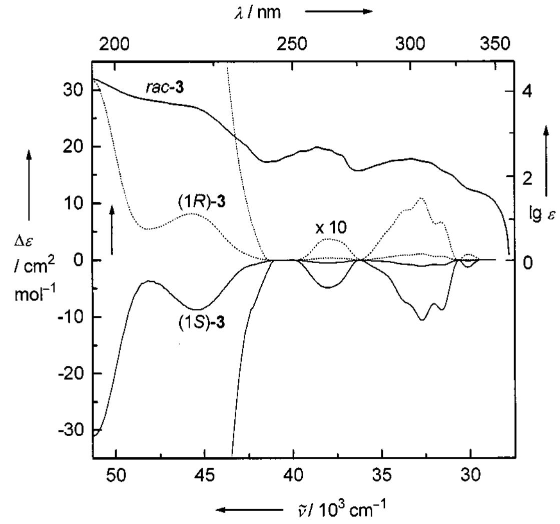


Figure 7. Circular dichroism spectra recorded for solutions of the diphenyl diketones (1*R*)- and (1*S*)-**3** (Δε, left axis) and UV/Vis spectrum taken from a solution of *rac*-**3** (log ε, right axis); solvent acetonitrile; temperature 20−25°C

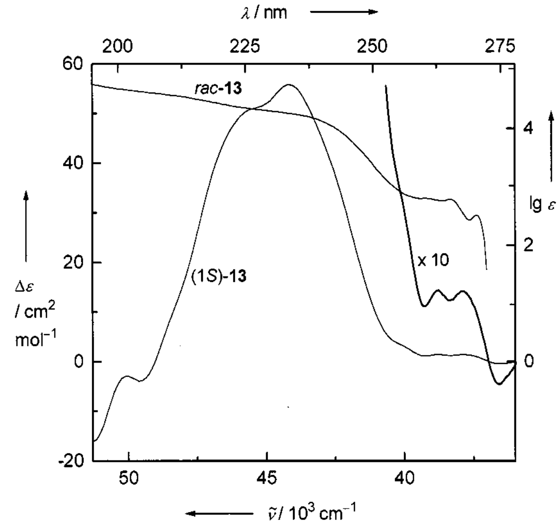


Figure 8. Circular dichroism spectra recorded for a solution of (1*S*)-**13** (Δε, left axis) and UV/Vis spectrum taken from a solution of *rac*-**13** (log ε, right axis); solvent acetonitrile; temperature 20−25°C

The relatively strong positive (λ_{max} = 234 nm) and negative (λ_{max} = 267 nm) bands observed in the CD spectrum of (1*S*)-**1** (Figure 9) may be assigned to the unsaturated nitrile and the styryl chromophor, respectively, as indicated by a comparison with the CD spectrum of the unsaturated dinitrile (1*S*)-**13** (Figure 8).

Table 4. Optical rotations $[\alpha]_D^{23}$, and circular dichroism and UV/Vis data recorded for solutions in acetonitrile at 20−25°C

Cpd.	$[\alpha]_D^{23}$ [a]	CD λ_{max} ($\Delta\varepsilon$ [cm^2 mol^{-1}])			UV/Vis[b] λ_{max} (log ε)	
(1*R*)-**3**	89.4	219 (8.1)	262 (0.4)	297 (0.9)	219 (3.634)	259 (2.668)
	(2.89)	306 (1.1)	316 (0.7)	332 (0.1)	301 (2.386)	338 (1.618)
(1*S*)-**3**	−89.5	219 (−8.7)	262 (−0.5)	297 (−0.7)		
	(2.37)	306 (−1.1)	316 (−0.9)	332 (−0.1)		
(1*S*)-**13**	329.0	202 (−3.9)	220 (50.9)	227 (55.8)	206 (4.590)	227 (4.262)
	(2.55)	249 (3.7)	258 (0.1)	264 (0.1)	255 (2.805)	261 (2.787)
(1*S*)-**1**	[c]	202 (−22.1)	234 (43.4)	267 (−14.6)	238 (4.345)	283 (4.135)
		459 (0.3)			442 (2.836)	

[a] The concentration [g/100 mL of the solution] is given in brackets. − [b] UV/Vis spectra were taken from solutions of the racemic mixtures. − [c] Measurement of the optical rotation with the light of a sodium or mercury lamp was precluded by the absorption of (1*S*)-**1**.

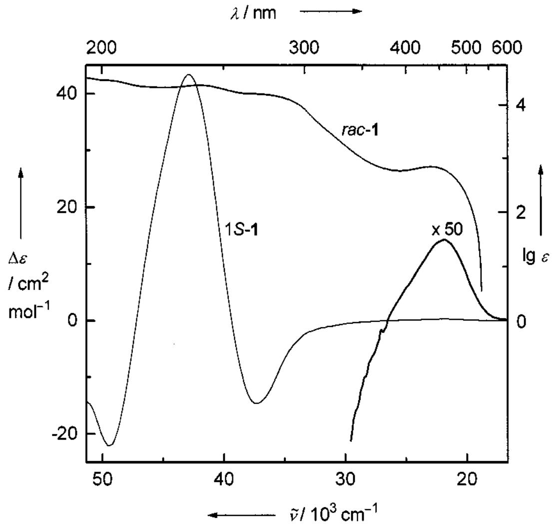


Figure 9. Circular dichroism spectra recorded for a solution of (1*S*)-**1** (Δε, left axis) and UV/Vis spectrum taken from a solution of *rac*-**1** (log ε, right axis); solvent acetonitrile; temperature 20−25°C; the insert shows the expanded CD spectrum (Δε × 50) in the visible range

The most intriguing feature in the CD spectrum of (1*S*)-**1** is the weak, positive band with a maximum at 459 nm which emerges after expansion of the Δε scale. The band is neighbouring upon the UV/Vis absorption around 440 nm, which has been attributed to a higher, vibronic state. In fact, deconvolution of the UV/Vis spectrum of *rac*-**1** with Gauss curves has revealed the precise position of the long-wavelength maximum at 460 nm.[5] Therefore, little room is left for doubts of the identity of the sources for both, the CD band and the UV/Vis band at long wavelengths. Convincing evidence is provided by an investigation of the influence of temperature and solvents on the former band. Rising temperatures do indeed increase it (Figure 10) just as they enhance the UV/Vis absorption of *rac*-**1** at long wavelengths.[4][5] More strongly intensifying effects are exerted by polar, in particular dipolar aprotic solvents (Figure 11), which affect the band of *rac*-**1** in the visible range exactly in the same way.[6] The coincidence of the maximum, and the temperature and solvent dependence of the CD band

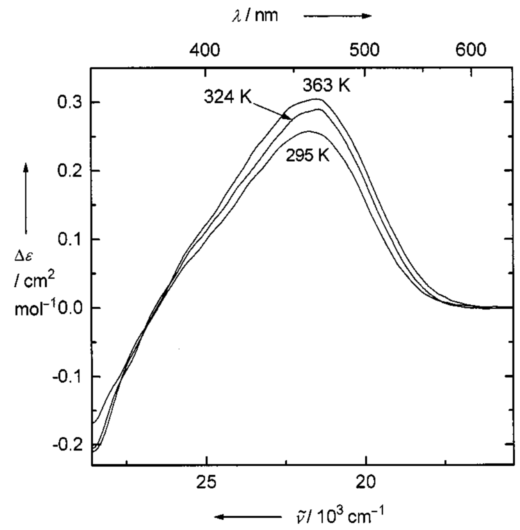


Figure 10. Effect of temperature on circular dichroism spectra taken from a solution of (1*S*)-**1** in butyronitrile; temperature-dependent changes of the volume were taken into account by means of density data;[6] reference temperature 298 K

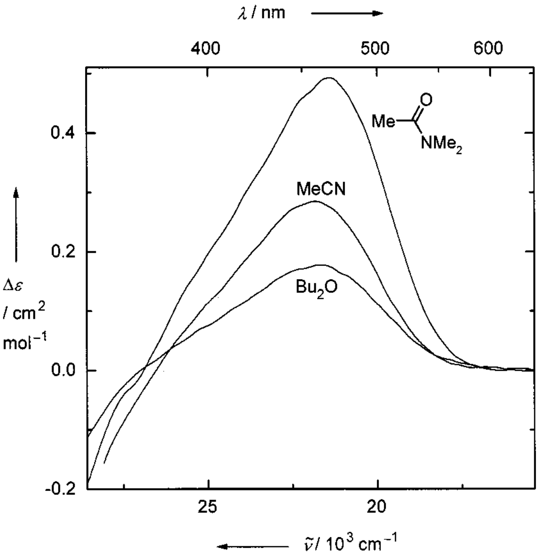


Figure 11. Long-wavelength sections of circular-dichroism spectra recorded for solutions of (1*S*)-**1** in different solvents at 20−25°C

with those of the UV/Vis band cannot be fortuitous. Therefore, the arguments that support the assignment of the UV/Vis band to the vibronic state, which may be represented by the delocalised structure **1***, apply to the CD band as well.[5][6] Consequently, the present study of chiroptical properties of **1*** complements the recent direct observation by UV/Vis spectra of the transition state for the degenerate Cope rearrangement **1** $\rightleftarrows$ **1′**, thus providing for novel challenges to theoretical chemists.

Conclusion

The present study demonstrates for two examples that differences in the crystal lattices between the racemates (*rac*-**1**, *rac*-**3**) and single enantiomers [(1*S*)-**1**, (1*S*)-**3**] are unimportant for the molecular geometry, which, therefore, may be considered as crystal-independent molecular property. Diphenylbarbaralanedicarbonitrile **1** is characterised by uncommon features, i.e. a very long carbon−carbon bond in the cyclopropane ring, ground-state destabilisation by unfavourable steric interactions across that bond, an extremely low barrier towards the degenerate Cope rearrangement, and a temperature- and solvent-dependent long-wavelength absorption which is indicative of a sizeable fraction occupying a higher, vibronic (transition) state. The latter phenomenon is also observed in the CD spectra of (1*S*)-**1**. Thus chiral, nonracemic thermochromic barbaralanes and semibullvalenes allow the investigation of the chiroptical properties of pericyclic transition states.

Experimental Section

General Remarks: Yields, diastereomeric ratios (d.r.), melting points, and IR: Table 1. − ^{1}H NMR: Tables 2, 5−7. − ^{13}C NMR: Table 8. − MS: Table 9. − $[\alpha]_D$, CD and UV/Vis: Table 4. − Molecular formulae and masses, and elemental analyses: Table 10. − Melting points: Kofler apparatus from Reichert, Vienna, Austria. − IR: Perkin−Elmer 1420. − ^{1}H and ^{13}C NMR: Bruker AC 250 (**11**) and DMX 600. The signals were assigned on the basis of DEPT spectra, and ^{1}H,^{1}H and ^{13}C,^{1}H COSY experiments (except for **11**). − MS (70 eV): Finnigan MAT 8200. − UV/Vis: Perkin−Elmer 330; the data were transferred with the programme MS-DOS Kermit 3.15 (Trusties of Columbia University), [ε] = L mol^{-1} cm^{-1}. − Specific rotations: Perkin−Elmer polarimeter 241 MC. − CD: Jobin-Yvon dichrograph CD6; variable-temperature CD spectra were recorded with a 0.1-cm quartz cuvette equipped with a heating mantel (Hellma, D-79371 Müllheim), which was kept at constant temperatures with a thermostat (Colora K5, D-73547 Lorch). The temperature was measured in the cuvette (thermometer 16213 with a NiCr−Ni thermoelement, Bioblock Scientific, F-67403 Illkirch-Cedex). − HPLC: Bruker−Franzen LC 21-C equipped with a UV detector Knauer 87.00 (λ = 254 nm), (250 × 4.6) mm stainless-steel column packed with Ultremex 3μ silica (Phenomenex), 1.5 mL/min petroleum ether (50−70°C) (PE)/ethyl acetate (EA), 80:20, retention times t_R [min] = 4.7 [(1*S*)-**13**], 5.1 (**3**), 7.1 [(1*S*)-**1**], 8.2 (*endo*-**4**), 9.8 (*exo*-**4**); 7.2 [*exo*-(1*R*)-**9**], 10.0 [*exo*-(1*S*)-**9**]; (90:10), t_R = 17.0 [*endo*-(1*R*)-**9**], 18.8 [*endo*-(1*S*)-**9**]; (250 × 4.6)-mm stainless-steel column packed with reversed-phase silica Prodigy 5μ ODS (3) 100 Å (Phenomenex), 1.0 mL/min acetonitrile/water (62:38), t_R = 34.5 [(1*R*)-**7**], 36.0 [(1*S*)-**7**]; 1.5 mL/min (70:30), t_R = 2.7, 2.8 (**5**), 3.8 (*endo*-, *exo*-**4**), 5.1 (**3**), 9.4 [*exo*-(1*S*)-**9**], 9.9 [*endo*-(1*S*)-**9**], 10.5 [*endo*-(1*R*)-**9**], 10.6 [*exo*-(1*R*)-**9**], 28.3 (**11**); 1.5 mL/min acetonitrile, t_R [min] = 3.8 [*endo*,*endo*-(1*S*)-**12**], 4.3 [*endo*,*exo*-(1*S*)-**12**], 5.2 [*exo*,*exo*-(1*S*)-**12**]. − (1*S*)-Camphanoyl chloride (**6**) (> 98%, e.r. = 99.5:0.5) and (*R*)-(1-phenylethyl) isocyanate (**8**) (> 98%, e.r. = 98:2) were purchased from Aldrich. Diphenyl diketone *rac*-**3** was prepared according to the published procedure.[14]

(1*R*)- and (1*S*)-*exo*-4,*exo*-8-Diphenylbicyclo[3.3.1]nonane-2,6-dione [(1*R*)- and (1*S*)-3]

***endo*- and *exo*-6-Hydroxy-*exo*-4,*exo*-8-diphenylbicyclo[3.3.1]nonan-2-one [(*endo*- and *exo*-4)]:** Sodium borohydride (0.17 g, 4.4 mmol) was added to a stirred solution of *rac*-**3** (3.00 g, 9.9 mmol) in ethanol (750 mL) followed by stirring for 16 h at 20−25°C. The pH of the clear, yellow solution was adjusted to a value of 5 by addition of aq. HCl (1 M, 5 mL). The solvent was distilled in vacuo. Water (200 mL) was added to the residue followed by extraction of the suspension with CH_2Cl_2 (2 × 50 mL). The combined org. layers were extracted with water (50 mL) and dried with $MgSO_4$. Distillation of the solvent in vacuo gave a colourless, semi-solid residue which was dissolved in a minimum amount of ethanol. Slow crystallisation at −20°C afforded colourless crystals (*endo*- and *exo*-**4**) and a mother liquor, which contained a mixture of *endo*- and *exo*-**4** (13%) and the diastereomeric diols *rac*-**5** (87%, RP-HPLC). MPLC of the crystals with PE/EA {73:27, 62 mL/min, 13 bar, t_R [min] = 102 (*endo*-**4**), 113 (*exo*-**4**)} afforded two fractions. The solvent was distilled in vacuo, and the solid residues were recrystallised at −20°C to yield colourless prisms. The first fraction gave *endo*-**4** (1.68 g, 56%), m.p. 139−141 °C. The second fraction yielded *exo*-**4** (0.75 g, 25%), m.p. 107−108 °C. − The solvent of the first mother liquor was distilled i. vac. The colourless, semi-solid residue was recycled to *rac*-**3** by Swern oxidation (see below).

Table 5. Chemical shifts (δ values, diagonal elements) and absolute values of coupling constants ([Hz], other elements) in the 600-MHz proton spectrum of the hydroxy ketone *endo*-**4** taken from a solution in [D]trichloromethane; zigzag couplings (^4J) are printed in *italics*

	9-H'	7-H_n	9-H	7-H_x	5-H	3-H_n	1-H	3-H_x	4-H_n	8-H_n	6-H_x
9-H'	1.715		14.3		2.3		2.3				
7-H_n		1.750		14.4						6.4	12.3
9-H			2.169		3.9		3.9			*1.4*	
7-H_x				2.294	*1.4*		*1.4*			1.4	5.1
5-H					2.377		*1.4*		2.0		5.0
3-H_n						2.678		15.6	6.6		
1-H							2.717			2.2	
3-H_x								2.823	11.3		
4-H_n									3.405		
8-H_n										3.569	
6-H_x											4.248

OH: δ = 1.98 (br. s); Ph: δ = 7.2 – 7.4

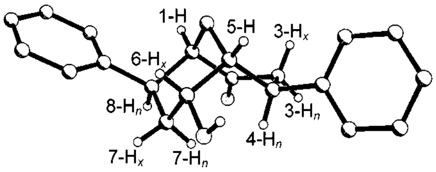


Table 6. Chemical shifts (δ values, diagonal elements) and absolute values of coupling constants ([Hz], other elements) in the 600-MHz proton spectrum of the hydroxy ketone *exo*-**4** taken from a solution in [D]trichloromethane; zigzag couplings (^4J) are printed in *italics*

	9-H'	7-H_n	7-H_x	5-H	9-H	3-H_n	1-H	3-H_x	4-H_n	8-H_n	6-H_n
9-H'	1.945			3.5	14.3		3.5				
7-H_n		2.107	15.3							6.8	4.3
7-H_x			2.197							4.2	4.2
5-H				2.218	2.6		*1.4*		2.2		3.7
9-H					2.334		2.6				
3-H_n						2.736		15.8	6.6		
1-H							2.823			2.2	
3-H_x								2.836	8.9		
4-H_n									2.968		
8-H_n										3.237	
6-H_n											4.011

OH: δ = 1.85 (br. s), δ = Ph: 7.2 – 7.5

Diastereomeric (1*S*)-Camphanoates (1*R*)- and (1*S*)-7: Under N_2, a solution of *endo*-**4** (91.9 mg, 0.30 mmol), **6** (83.3 mg, 0.38 mmol), and 4-(dimethylamino)pyridine (45.8 mg, 0.38 mmol) in CH_2Cl_2 (1.5 mL) was stirred for 16 h at 20−25°C. The colourless solution was extracted with aq. HCl (1 M, 2 × 1 mL). The combined aq. layers were extracted with CH_2Cl_2. The combined org. layers were extracted with water and dried with $MgSO_4$. Distillation of the solvent in vacuo gave a colourless semi-solid residue (146 mg, 98%, d.r. = 1:1, RP-HPLC), which was recrystallised from EA by allowing the solution to cool from 60 to 20−25°C during 15 h. Colourless fine needles (38 mg, 52%, m.p. 204−206°C) were obtained which consisted exclusively of the faster eluted diastereomer (1*R*)-**7**. The mother liquor was concentrated in vacuo. Seeding with a crystal of (1*R*)-**7** yielded a small second crop of colourless needles, (1*R*)-/(1*S*)-**7** = 87:13. The mother liquor contained (1*R*)- and (1*S*)-**7** in the ratio 29:71.

Diastereomeric *N*-(1-Phenylethyl)carbamates *endo*- and *exo*-9: A stirred solution of *endo*- or *exo*-**4** (3.00 g, 9.8 mmol), **8** (1.51 g, 10.3 mmol) and 4-(dimethylamino)pyridine (1.25 g, 10.3 mmol) in tetrahydrofuran was heated under reflux for 18 h. Distillation of the solvent in vacuo gave a light-brown oil, which was dissolved in CH_2Cl_2 (100 mL). The solution was extracted with aq. HCl (1 M, 50 mL). The aq. layer was extracted with CH_2Cl_2. The combined org. layers were extracted with water (50 mL) and dried with $MgSO_4$. Distillation of the solvent in vacuo yielded light-brown oils which were purified or separated by flash chromatography with PE/EA (7:3).

***endo*-(1*R*)- and *endo*-(1*S*)-9:** Flash chromatography yielded a colourless solid [d.r. = 1:1 (HPLC)]. Cyclic MPLC with PE/EA {80:20, 80 mL/min, t_R [min] = 131 [*endo*-(1*R*)-**9**], 135 [*endo*-(1*S*)-**9**]} gave two fractions (Figure 2). The first afforded colourless crystals (2.15 g, 96%), m.p. 163−164°C [*endo*-(1*R*)-**9**, d.r. = 100:0]. Recrystallisation from ethanol/water (7:3) at 60°C yielded crystals that were suitable for an X-ray diffraction analysis. − The second fraction afforded a colourless semi-solid material (2.13 g, 96%), softening at 62−69°C, [*endo*-(1*S*)-**9**, d.r. = 99:1]. Attempts at crystallisation from ethanol or EA met with failure.

***exo*-(1*R*)- and *exo*-(1*S*)-9:** Flash chromatography yielded two fractions with d.r. > 97:< 3 (HPLC). The separation was completed for each fraction by MPLC with PE/EA {73:27, 60 mL/min, 10 bar, t_R [min] = 76 [*exo*-(1*R*)-**9**], 98 [*exo*-(1*S*)-**9**]}. The first fraction afforded a colourless, semi-solid material (1.95 g, 88%), softening at 48−52°C [*exo*-(1*R*)-**9**, d.r. = 100:0]. Attempts at crystallisation from ethanol or EA met with failure. − The second fraction afforded colourless crystals (1.89 g, 86%), m.p. 118−119°C [*exo*-(1*S*)-**9**, d.r. = 99:1]. Recrystallisation from ethanol/water (1:1) yielded crystals that were suitable for an X-ray diffraction analysis.

Cleavage of the *N*-(1-Phenylethyl)carbamate *endo*-(1*R*)-9 with Trichlorosilane in the Presence of Triethylamine: Under Ar, trichlorosilane (3.72 g, 27.6 mmol) was added to a stirred solution of *endo*-(1*R*)-**9** (1.00 g, 2.2 mmol) and triethylamine (5.6 g, 55 mmol) in CH_2Cl_2. After stirring for 24 h, *endo*-(1*R*)-**9** had disappeared almost completely (RP-HPLC). The brown mixture was poored cautiously upon ice (25 g). The white solid was removed by filtration and washed with CH_2Cl_2 (50 mL). The colourless aq. layer was extracted with CH_2Cl_2. The combined org. layers were dried with $MgSO_4$. Distillation of the solvent i. vac. gave a light-brown solid which consisted of equal amounts of *endo*-(1*R*)-**4** and a second product with a long retention time on RP-HPLC. Flash chromatography with PE/EA (7:3) separated the solid into two fractions. The first afforded a light-brown solid (0.20 g, 22%, **11**), melting range 182−187°C, which was almost pure (RP-HPLC). − ^1H

Table 7. Chemical shifts (δ values) and absolute values of coupling constants ([Hz]) in 600-MHz proton spectra recorded for solutions in [D]trichloromethane; an asterisk (*) indicates that the couplings can be observed in the ^{1}H,^{1}H-COSY spectrum but the values of the coupling constants cannot be determined[22]

Cpd.	1-H 5-H	3-H$_x$ 3-H$_n$	4-H 8-H	6-H	7-H$_x$ 7-H$_n$	9-H 9-H'	Ph (m)	Carbamate NH	 1-H	 1-Me
x-(1*R*)-**9**	2.94	2.85	3.16	4.92	2.39	2.32	7.2 – 7.3	4.42	4.72	1.37
	m	[a]	tm	m	dm	dt		m	dq	d
	2.23	2.82	3.26		2.11	2.00				
	m		tm		ddd	dt				
x-(1*S*)-**9**	2.92	2.85	3.20	4.95	2.31	2.28	7.1 – 7.4	4.43	4.78	1.40
	m	[a]	tm	m	dm	dm		br. d	dq	d
	2.30	2.82	3.24		2.10	2.00				
	m		m		ddd	dm				
n-(1*R*)-**9**	2.73	2.86	3.34	5.26	2.42	2.17	7.2 – 7.5	4.97	4.81	1.43
	m	dd	tm	dt	dm	dm		br. d	dq	d
	2.64	2.70	3.61		1.81	1.73				
	m	dd	dm		ddd	dm				
n-(1*S*)-**9**	2.70	2.84	3.34	5.28	2.46	2.13	7.2 – 7.5	5.00	4.82	1.49
	m	dd	tm	dt	ddm	dm		br. d	dq	d
	2.57	2.70	3.63		1.85	1.71				
	m	dd	m		ddd	dm				
								Camphanoate 5-H$_x$ 5-H$_n$	 6-H$_x$ 6-H$_n$	 Me
(1*R*)-**7**	2.80	2.88	3.43	5.53	2.52	2.27	7.2 – 7.5	1.92	2.39	0.75
	m	dd	ddd	dt	ddq	dtd		ddd	ddd	1.04
	2.55	2.73	3.69		1.92	1.79		1.70	2.01	1.11
	m	dd	dm		ddd	dt		ddd	ddd	s

Cpd.	$^2J_{3n,3x}$ $^2J_{7n,7x}$	$^2J_{9,9'}$	$^3J_{1,8}$ $^3J_{4,5}$	$^3J_{1,9}$ = $^3J_{5,9}$	$^3J_{1,9'}$ = $^3J_{5,9'}$	$^3J_{3n,4}$ $^3J_{7n,8}$	$^3J_{3x,4}$ $^3J_{7x,8}$	$^3J_{5,6}$ $^3J_{6,7n}$	$^3J_{6,7x}$	$^4J_{1,5}$ $^4J_{8,9}$	$^4J_{1,7x}$ $^4J_{5,7x}$
x-(1*R*)-**9**	16.3	14.2	*	2.4	3.0	7.2	7.2	*		*	
	15.3					6.2	6.0	4.0	*		
x-(1*S*)-**9**	16.3	13.7	*	*	*	7.2	7.2	*		*	
	15.5		*			6.5	*	4.1	*		
n-(1*R*)-**9**	15.4	14.7	*	*	*	6.3	11.4	5.4		*	*
	13.7		*			6.6	*	13.7	5.4	*	*
n-(1*S*)-**9**	15.5	14.5	*	*	*	6.2	10.9	5.0		*	*
	13.4		*			6.6	*	13.4	5.0	*	*
(1*R*)-**7**	15.5	14.2	2.2	4.0	2.2	6.5	11.6	4.9		1.4	1.4
	14.5		1.9			5.6	1.4	12.3	5.2	1.4	1.4

[a] The protons 3-H$_x$, 3-H$_n$, and 4-H form an ABX system.

NMR (250 MHz, [D]trichloromethane): δ = 1.60 (d, J = 7 Hz), 4.87 (q), 2.47 (s) ($H_3C-CH-N-CH_3$), 1.41 (dt, J = 13.3, 2.8 Hz, 9-H'), 1.68 (dtd, J = 13.3, 3.2, 0.9 Hz, 9-H), 1.97 (m, 1-H), 2.06 (td, J = 11.9, 6.0 Hz, 3-H$_{endo}$), 2.23 (br. s, OH), 2.24 (ddm, J = 12, 5 Hz, 3-H$_{exo}$), 2.98 (m, 5-H), 3.38 (dm, J = 6 Hz, 4-H), 3.81 (d, J = 4.0 Hz, 8-H), 4.21 (dt, J = 12.2, 4.7 Hz, 2-H), 4.73 (d, J = 4.0 Hz, 7-H), 7.13–7.48 (m, 3 Ph). – ^{13}C NMR (63 MHz, [D]trichloromethane): δ = 16.8, 55.3, 33.0 ($H_3C-CH-N-CH_3$), 21.9 (CH$_2$-9), 30.5 (CH$_2$-3), 35.2, 38.1, 42.4, 43.1 (CH), 69.4 (CHOH), 105.6, 149.2 (CH=C–N), 125.63, 125.73, 126.76, 127.20, 127.42, 127.57, 128.07, 128.23, 128.39 (Ar–CH), 142.1, 144.0, 147.9 (*ipso*-C). – IR (CCl$_4$): $\tilde{\nu}$ = 3590 cm^{-1} (OH). – The second fraction yielded pale yellow crystals [0.31 g, 46%, *endo*-(1*R*)-**4**], m.p. 137–139°C, which were identified by comparison with *rac-endo*-**4** (HPLC).

Reduction of the Diastereomeric *N*-(1-Phenylethyl)carbamates 9: Lithium aluminium hydride (0.25 g, 6.6 mmol) was added in portions to a stirred solution of a single diastereomer of **9** (1.00 g, 2.2 mmol) in tetrahydrofuran (5 mL) followed by heating under reflux for 6 h. The mixture was allowed to cool to 20–25°C. According to a recommended procedure,[36] water (0.25 mL), aq. NaOH (15%, 0.25 mL), and water (0.75 mL) were added. The grey solid was removed by filtration and washed with tetrahydrofuran. CH$_2$Cl$_2$ (100 mL) was added to the filtrate, and the mixture was extracted with aq. HCl (1 M, 50 mL). The aq. layer was extracted with CH$_2$Cl$_2$ (3 × 25 mL). The combined org. layers were dried with MgSO$_4$. Distillation of the solvent i.vac. yielded a colourless, semi-solid material (**5**). The crude product was immediately oxidised according to Swern.[20]

Swern Oxidation of the Diastereomeric Diols 5: Trifluoroacetic anhydride (1.73 g, 8.3 mmol) was added dropwise under Ar to a stirred, cooled (–75°C) solution of dimethyl sulphoxide (0.85 g, 11.0 mmol) in CH$_2$Cl$_2$ (12 mL) A colourless precipitate formed immediately. After stirring for 10 min at –75°C, a solution of **5**, obtained from **9** (2.2 mmol), in CH$_2$Cl$_2$ (70 mL) was added dropwise during 20 min. Stirring at –75°C was continued for 40 min followed by dropwise addition of triethylamine (1.61 g, 16.0 mmol). The stirred mixture was allowed to attain 20–25°C overnight. The

Table 8. Chemical shifts (δ values) in 151-MHz carbon-13 spectra recorded for solutions in [D]trichloromethane; figures that are printed in *italics* may be exchanged

Cpd.	C-2	C-1 C-5	C-4 C-8	C-6	C-3 C-7	C-9	*i*-C	*o*-C, *m*-C		*p*-C	Camphanoate 1-C=O 3-C=O	 C-1 C-4	 C-5 C-6	4-Me	CMe$_2$
rac-endo-**4**	215.6	47.5	35.0	69.0	45.8	23.3	142.1	126.89	128.53	126.24					
		42.6	41.7		30.4		147.2	127.29	128.94	126.46					
rac-exo-**4**	215.5	47.7	42.1	71.8	44.2	18.9	144.03	126.74	128.57	126.25					
		42.8	39.9		31.0		145.78	127.25	128.86	126.69					
(1*R*)-**7**	214.5	47.7	36.2	73.7	45.6	23.3	141.08	127.19	128.73	126.47	167.0	*54.74*	28.9	9.6	16.62
		39.7	41.7		27.0		145.97	126.76	128.92	126.66	177.8	*54.16*	30.6		16.81
											O=C–NH–CH–CH$_3$				
endo-(1*R*)-**9**	215.2	48.1	36.0	72.3	45.6	23.2	141.60	126.33	128.71[a]	126.01	154.8	50.5	22.2		
		39.5	41.8		27.4		143.17	126.95	128.65	126.56					
							146.59	127.41		128.91					
endo-(1*S*)-**9**	215.3	48.2	35.9	72.2	45.5	23.1	141.61	126.33	128.64[a]	125.80	154.8	50.5	22.4		
		39.5	41.8		27.5		143.35	126.71	128.90	126.49					
							146.48	127.40		127.27					
exo-(1*R*)-**9**	215.0	47.0	41.8	73.9	43.5	19.9	143.39	125.88	128.58	126.67	154.7	50.4	22.3		
		40.2	39.1		28.9		144.18	126.72	128.81[a]	126.79					
							145.41	128.40		127.29					
exo-(1*S*)-**9**	215.0	47.4	41.9	73.9	43.4	19.9	143.34	125.90	128.30	125.97	154.7	50.4	22.4		
		40.2	39.2		28.8		144.00	126.69	128.60	126.83					
							145.44	126.72	128.82	127.36					

[a] The signal has double intensity.

Table 9. Masses of molecular ions and fragment ions (m/z), and relative intensities [% of the base peak (= 100%)] in 70-eV mass spectra recorded for the hydroxy ketones **4** and their derivatives

Cpd. m/z =	306	288	247	201	172	171	156	155	147	142	132	131	117	105	91
rac-n-**4**	51[a]	77	24	7	8	38	35	41	7	82	7	40	76	41	100
rac-x-**4**	84[a]	54	4	34	34	40	28	34	8	19	9	44	55	58	100
(1*R*)-**7**[b]	1	100	23	1	6	22	38	60	2	72	6	28	42	43	75
n-(1*R*)-**9**[c]	19	100	22	3	5	20	20	24	27	44	58	18	33	41	39
n-(1*S*)-**9**[c]	9	100	21	1	4	17	16	20	13	39	28	14	27	38	31
x-(1*R*)-**9**[b]	19	100	18	7	8	19	18	23	19	27	41	18	25	42	37
x-(1*S*)-**9**[b]	44	100	16	16	17	26	21	27	38	26	81	24	31	49	47

[a] Molecular ion. – [b] Relative intensity of the molecular ion = 3%. – [c] Relative intensity of the molecular ion = 0.05%.

Table 10. Molecular formulae and masses, and elemental analyses

Cpd.		Molecular mass		Elemental analyses C	H	N
rac-endo-**4**	$C_{21}H_{22}O_2$	306.4	calcd.	82.32	7.24	
			found	81.84	7.40	
rac-exo-**4**			found	81.93	7.38	
(1*R*)-**7**	$C_{31}H_{34}O_5$	486.6	calcd.	76.52	7.04	
			found	75.53	7.31	
endo-(1*R*)-**9**	$C_{30}H_{31}NO_3$	453.6	calcd.	79.44	6.89	3.09
			found	79.13	7.23	3.20
endo-(1*S*)-**9**			found	79.58	6.60	3.10
exo-(1*R*)-**9**			found	79.53	6.72	3.09
exo-(1*S*)-**9**			found	79.06	7.07	3.17

pale yellow solution was extracted with aq. HCl (1 M, 40 mL), sat. aq. $NaHCO_3$ (40 mL) and water (40 mL) and dried with $MgSO_4$. Distillation of the solvent in vacuo gave a light-brown solid which was dissolved at 20–25°C in a minimum amount of ethanol (ca. 10 mL). Crystallisation at −20°C afforded colourless crystals; results: Table 1.

(1*S*)-4,8-Diphenylbarbaralane-2,6-dicarbonitrile [(1*S*)-1]

(1*S*)-*exo*-4,*exo*-8-Diphenylbicyclo[3.3.1]nona-2,6-diene-2,6-dicarbonitrile [(1*S*)-13]: Trimethylsilyl cyanide (2.92 g, 29.4 mmol) was added under Ar to a stirred solution of (1*S*)-**3** (2.0 g, 6.6 mmol) and KCN/18-crown-6 (1.09 g, 3.3 mmol) in CH_2Cl_2 (25 mL). The solution, which was pale yellow at the beginning, turned colourless under warming. After stirring of the solution for 2 h at 20–25°C, sat. aq. KH_2PO_4 (60 mL) was added causing evolution of HCN (***Caution!***). The layers were separated, and the aq. layer was extracted with CH_2Cl_2 (2 × 30 mL). The combined org. layers were extracted with a mixture of aq. sat. KH_2PO_4 (30 mL) and water (30 mL). The aq. layer was extracted with CH_2Cl_2 (30 mL). The combined org. layers were dried with $MgSO_4$. The solvent was distilled in vacuo until the volume was about 20 mL. The dark yellow solution was filtered through a short column (5 × 2.5 cm) packed with silica gel, which was rinsed with CH_2Cl_2 (100 mL). Distillation of the solvent in vacuo gave a colourless, semi-solid product (3.0 g, 91%) consisting of *endo*,*endo*-, *endo*,*exo*-, and *exo*,*exo*-(1*S*)-**12** (41:45:14, RP-HPLC).[4] The crude product was dissolved under Ar in freshly distilled phosphoryl chloride (11 mL, 120 mmol). To the cooled (0°C), stirred solution, a solution of HF in pyridine (0.7 mL, 65%, 26 mmol) was added cautiously, followed by stirring for 1 h at 20–25°C. Dry pyridine (33 mL, 0.41 mol) was added at 0°C, and the mixture was heated at 85°C for 2.5 h. CH_2Cl_2 (100 mL) was added at 0°C followed by slow, cautious addition of cold aq. H_2SO_4 (1 M, 210 mL). The layers were separated, and the aq. layer was extracted with CH_2Cl_2 (2 × 50 mL). The combined org. layers were extracted with sat. aq. K_2CO_3 (100 mL) and dried with $MgSO_4$. Distillation of the solvent in vacuo and flash chromatography of the brown residue with PE/EA (85:15) yielded colourless crystals (1.06 g, 51%), m.p. 229–231°C.

Table 11. Experimental details and results of the X-ray diffraction analyses

Cpd.	*rac-endo*-**4**	(1*R*)-**7**	*endo*-(1*R*)-**9**	*exo*-(1*S*)-**9**	(1*S*)-**3**	(1*S*)-**1**
Molecular formula	$C_{21}H_{22}O_2$	$C_{31}H_{34}O_5$	$C_{30}H_{31}NO_3$	$C_{30}H_{31}NO_3$	$C_{21}H_{20}O_2$	$C_{23}H_{16}N_2$
Molecular mass	306.43	486.65	453.58	453.58	304.39	320.39
Crystal system	monoclinic	orthorhombic	monoclinic	monoclinic	orthorhombic	orthorhombic
Space group	Pc	$P2_12_12_1$	$P2_1$	$P2_1$	$P2_12_12_1$	$P2_12_12_1$
a [pm]	969.7(1)	665.7(2)	1210.8(2)	1277.2(2)	665.8(1)	706.4(2)
b [pm]	599.9(1)	1118.6(1)	566.5(1)	579.8(2)	1525.1(3)	1518.8(3)
c [pm]	1411.2(1)	3575.3(3)	1883.9(3)	1632.6(2)	1605.6(3)	1611.3(3)
α [°]						
β [°]	96.123(5)		100.20(1)	94.15(1)		
γ [°]						
V [$10^{-6} \cdot pm^3$]	817.4(9)	2662.3(3)	1271.9(5)	1205.7(6)	1603.5(3)	1728.6(7)
Z	2	4	2	2	4	4
d(calcd.) [g cm^{-3}]	1.245	1.214	1.184	1.249	1.240	1.231
Size of crystal [mm]	0.45 × 0.55 × 0.15	0.15 × 0.5 × 1.65	0.4 × 0.7 × 0.1	0.1 × 0.15 × 3.2	0.1 × 0.3 × 1.7	0.1 × 0.2 × 1.8
Range h	$0 \rightarrow 12$	$-1 \rightarrow 7$	$-1 \rightarrow 15$	$0 \rightarrow 16$	$-1 \rightarrow 8$	$-8 \rightarrow 1$
k	$0 \rightarrow 7$	$-1 \rightarrow 12$	$-7 \rightarrow 7$	$-7 \rightarrow 7$	$-1 \rightarrow 19$	$-18 \rightarrow 1$
l	$-18 \rightarrow 18$	$-1 \rightarrow 38$	$-24 \rightarrow 24$	$-21 \rightarrow 21$	$-20 \rightarrow 20$	$-19 \rightarrow 19$
No. of measured reflections	2180	5472	6709	4552	5218	4002
symmetry-independent refl.	1992	3550	5869	4363	3743	2869
Observed refl. $F > 3\sigma(F)$	1869	3495	4074	3111	2438	2356
Lin. absorpt. coeff. [mm^{-1}]	0.08	0.07	0.08	0.08	0.08	0.07
Absorption correction	ψ-scan	ψ-scan	ψ-scan	ψ-scan	ψ-scan	ψ-scan
Ratio F_{obs}/parameters	8.86	10.72	13.14	10.04	11.67	10.38
R	0.048	0.056	0.072	0.068	0.069	0.052
R_W	0.047	0.063	0.068	0.067	0.055	0.046
Diff. Four. $\Delta\rho_{max}$[a] [eÅ^{-3}]	0.21	0.35	0.32	0.31	0.29	0.45
$\Delta\rho_{min}$[b]	0.20	0.31	0.35	0.36	0.33	0.28

[a] Maximum and [b] minimum of the remaining electron density in the final differential Fourier synthesis.

(1*S*)-4,8-Diphenylbarbaralane-2,6-dicarbonitrile [(1*S*)-1]: According to the procedure for *rac*-**1**,[4] (1*S*)-**13** (0.98 g, 3.0 mmol) was treated with hexachloroethane (2.16 g, 9.1 mmol) in a vigorously stirrred mixture consisting of CH_2Cl_2 (15 mL), aq. tetrabutylammonium hydroxide (0.7 mL, 40%) and aq. NaOH (8 mL, 50%). Workup as described, distillation of the solvent in vacuo, and flash chromatography of the dark-red, solid residue with PE/EA (8:2) afforded brick-red needles (0.64 g, 65%), m.p. 224–225°C. Recrystallisation from PE/EA (1:1) yielded crystals that were suitable for an X-ray diffraction analysis.

X-ray Diffraction Analyses were performed on transparent, colourless [*rac*-*endo*-**4**, (1*R*)-**7**, *endo*-(1*R*)-**9**, *exo*-(1*S*)-**9**, (1*S*)-**3**] or brick-red [(1*S*)-**1**] crystals. The cell parameters were determined on the basis of 70 reflections. The number of reflections reported in Table 11 were obtained with Mo-K_α radiation and $2\ \Theta_{max} = 55°$ [*rac*-*endo*-**4**, *endo*-(1*R*)-**9**, *exo*-(1*S*)-**9**, (1*S*)-**3**, (1*S*)-**1**] or Cu-K_α radiation and $2\ \Theta_{max} = 110°$ [(1*R*)-**7**] (graphite monochromator, ω scan). Measurements were carried out with a system Siemens P4. The programme SHELXTL PLUS[37] was employed. The structure was solved by direct methods and refined anisotropically by the least-squares method. The weighting scheme for R_w is $1/\sigma^2$. The positions of the hydrogen atoms were calculated by the riding model and included with isotropic descriptions.[38]

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[22] Deviating from IUPAC rules of nomenclature for sake of consistency, we use the numbering for the bicyclo[3.3.1]nonane skeleton of the hydroxy ketones **4** also for their derivatives, viz. the camphanoates *endo*-**7** and the *N*-(1-phenylethyl)carbamates *endo*- and *exo*-**9**.

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[38] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-113997 (*rac*-*endo*-**4**), -113998 [(1*R*)-**7**], -113999 [*endo*-(1*R*)-**9**], -114000 [*exo*-(1*S*)-**9**], -114001 [(1*S*)-**3**], and -114002 [(1*S*)-**1**]. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: int. code + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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