109. Optical Activity in Remotely Perturbed Exocyclic s-*cis*-Butadienes. Preparation and Circular Dichroïsm of Enantiomerically Pure 5,6-Dimethylidene-2-norbornyl Derivatives[1])

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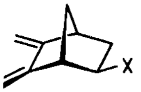
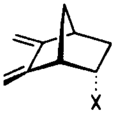
Summary

Optically pure 5,6-dimethylidene-*exo*-2-norbornanol ((+)-**1**), acetate ((+)-**2**), *p*-bromobenzenesulfonate ((+)-**3**), 5,6-dimethylidene-*endo*-2-norbornanol ((+)-**4**), acetate ((+)-**5**), *p*-bromobenzenesulfonate ((+)-**6**) and 5,6-dimethylidene-2-norbornanone ((+)-**7**) have been prepared. Their chirality was correlated chemically with that proposed by *Mislow et al.* for (+)-benzo-5-norbornen-2-yl acetate ((+)-**14**). The solution CD. spectra of these remotely perturbed exocyclic s-*cis*-butadienes are reported and discussed briefly. Unexpectedly, the β,γ-unsaturated ketone (+)-**7**, for which transannular interaction between the ketone and diene functions was revealed by its UV. absorption spectrum, showed (in isooctane) two weak *Cotton* effects of opposite sign between 265 and 340 nm.

Introduction. - Optically pure 5,6-dimethylidene-2-norbornyl derivatives **1**-**7** are interesting systems for at least three reasons: 1) The *Diels-Alder* additions (*e.g.* of **4** and of **7**) to strong dienophiles are regio- and stereoselective [3]; thus, if enantiomerically pure, these dienes might become useful synthons for the preparation of complex, polycyclic molecules; 2) the *exo*- and *endo*-5,6-dimethylidene-2-norbornyl brosylates (**3** and **6**) are convenient starting materials for the study of the π-participation by the 'back' of an exocyclic s-*cis*-butadiene group in the S_N1-solvolyses of the esters [4]; 3) The dienes **1**-**6** as well as the keto-diene **7** are remotely perturbed exocyclic dienes (no direct substitution) maintained in a



1 X=OH
2 X=OAc
3 X=OBs



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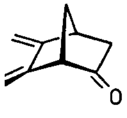
5
6



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[1] 'Interaction between non-conjugated chromophores', part 11; part 10 [1], part 9 [2].

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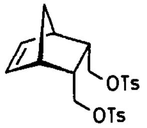
rigid geometry. Little is known about the chiroptical properties of such systems. They might be employed to test the models and rules in circular dichroïsm [5], *e.g.*: allylic chirality method [6], s-*cis*-diene helicity rule [7], couple oscillator-exciton chirality theory [8], amplified sector rule [9], general sector rule [10], electric dipole (μ)-magnetic dipole (m) coupling mechanism [11], through-bond mechanism [12] and the Generalized Octant Rule [13].

Synthesis. - When applied to the *endo*-5,6-bis(tosyloxymethyl)-2-norbornene (**8**), the asymmetric hydroboration-oxidation procedure of *Brown* [14] (diisopinocampheylborane [15] prepared from (−)-α-pinene) led to *endo*-5,6-bis(tosyloxymethyl)-*exo*-2-norbornanol which, after double elimination of *p*-toluenesulfonic acid (*t*-BuOK/THF), yielded (+)-**1** with $[\alpha]_D^{25} = +3.4°$ ($c=4$, $CHCl_3$), corresponding to 9.4% enantiomeric excess (e.e.) (see later). The same procedure applied to *trans*-5,6-bis(chloromethyl)-2-norbornene ((±)-**9**) [16], followed by double elimination of HCl (KOH/EtOH) gave impure (+)-**1** with $[\alpha]_D^{25} = +19°$ ($c=4$, $CHCl_3$, maximum value, low reproducibility, *cf* [17]) in low yield. Furthermore, its purification was difficult. When (−)-limonene was used as optical inducer, the yield and optical purity of **1** were even lower than with (−)-α-pinene [18]. Finally, using *Gerlach*'s technique [19], the readily available *exo*-alcohol (±)-**1** [20] was treated with optically pure (−)-camphanic acid chloride in pyridine (0°, 16 h) and converted to the corresponding diastereomeric esters (+)-**10** ($[\alpha]_D^{25} = +28°$, $c=2$, $CHCl_3$) and (−)-**11** ($[\alpha]_D^{25} = -51°$, $c=2$, $CHCl_3$), which were easily separated by fractional crystallization from hexane (see exper. part).



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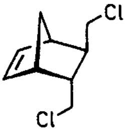
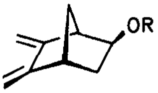
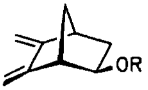
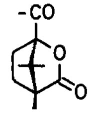


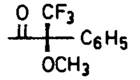
(±)-**9**





R = 

(+)-**10** (−)-**11**

R = 

12 **13**

Saponification of (+)-**10** (KOH/EtOH + H_2O) furnished (+)-**1** ($[\alpha]_D^{25} = +37°$, $c=4$, $CHCl_3$) whose enantiomeric purity was established by ^{19}F-NMR. of its α-methoxy-α-trifluoromethyl-α-phenylacetate (**12**) prepared from (1*S*)-(−)-α-methoxy-α-trifluoromethyl-α-phenylacetic acid [21] ((*S*)-MTPA) (see *Fig. 1*). Considering the signal/noise ratio S/N = 260 of the spectrum reported in *Figure 1B*, we can state that the optical purity of (+)-**1** exceeds 98%. Similarly, (−)-**11** yielded the enantiomerically pure *exo*-alcohol (−)-**1**.

Collins [22] oxidation of (+)-**1** furnished (+)-5,6-dimethylidene-2-norborbornane ((+)-**7**, which yielded the *endo*-alcohol (+)-**4** upon reduction with

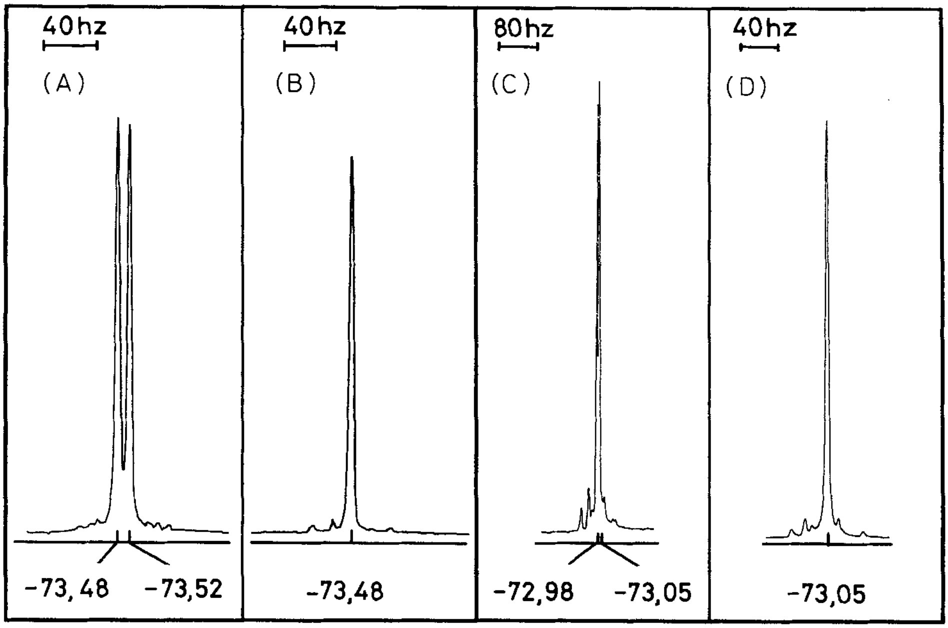
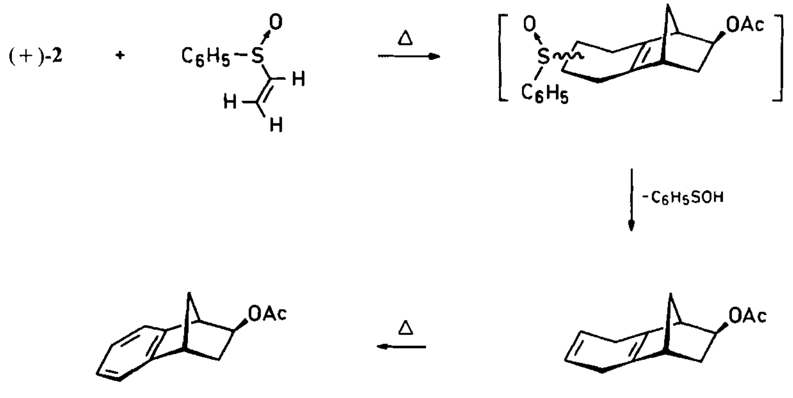


Fig. 1. *^{19}F-NMR.* (CDCl$_3$) *of the a-methoxy-a-trifluoromethyl-a-phenylacetates of* (A) (±)-**1**, (B) (+)-**1**, (C) (±)-**4** and (D) (+)-**4** (δ_F (ppm), int. ref. δ_{CFCl_3} = 0.0 ppm).

LiAlH(OMe)$_3$ [4]. ^{19}F-NMR. of the α-methoxy-α-trifluoromethyl-α-phenylacetate of (+)-**4** (see *Fig. 1C, D*) showed an e.e. >97% and demonstrated the absence of racemization during the (+)-**1**→(+)-**7**→(+)-**4** transformations. Acetylation of (+)-**1** yielded (+)-**2**. Similarly, (+)-**4** furnished (+)-**5**. The (+)-*exo*-brosylate (+)-**3** used in the solvolytic studies reported in the previous paper [4] was obtained by esterification (BsCl/pyridine) of (−)-**1**. Similarly, the (+)-*endo*-brosylate (+)-**6** was made from (+)-**4**.

Chirality. - Based on three independent, *indirect* techniques, the absolute configuration of (+)-*exo*-benzo-5-norbornen-2-yl acetate (+)-**14** has been proposed to be 1*R*, 2*S* [17]. When the *exo*-diene-acetate (+)-**2** was heated with a 2.5 fold excess of phenylvinylsulfoxide [23] in pyridine (140-150°, 40 h), (+)-**14** was obtained as main product (by TLC.) in 33% yield. Its $[\alpha]_D^{25} = +64°$ ($c=3$, MeOH), compares well with the calculated $[\alpha]_D^{25} = +69°$ ($c=6$, MeOH) for 100% e.e. [17]. Therefore, by chemical correlation and assuming that no stereospecific inversion occurred during the reaction (+)-**2**→(+)-**14**, these two acetates must have the same absolute configuration. From their mode of formation, the chirality of the other 5,6-dimethylidene-2-norbornyl derivatives is also established, *i.e.:* (+)-(1*R*,2*S*)-**1**, (+)-(1*R*,2*S*)-**2**, (+)-(1*S*,2*R*)-**3**, (+)-(1*R*)-**7**, (+)-(1*R*,2*R*)-**4**, (+)-(1*R*,2*R*)-**5** and (+)-(1*R*,2*R*)-**6**.

Circular dichroïsm. - According to *Labhart & Wagnière* [24], in β,γ-unsaturated ketones of the appropriate molecular geometry, the non-bonding electrons of the



(+)-(1*R*,2*S*)-**14**

carbonyl group interact with the π-electrons of the homoconjugated π-function (see also [25]). It follows that the forbidden $n \rightarrow \pi^*_{CO}$ transition borrows intensity from the allowed $\pi \rightarrow \pi^*_{CC}$ transition. Accordingly, the extinction coefficient of the Q←N bond near 300 nm is enhanced. This was found for various monocyclic and bicyclic β,γ-unsaturated ketones, including the keto-diene **7** [20] (see *Table 1*). These interactions between the CO and π-groups cause a relatively large optical activity which was attributed to the characteristic feature of inherently dissymetric homoconjugated chromophores [13a]. Following *Moscowitz & Mislow* [13a] and assuming the π-system of the exocyclic s-*cis*-butadiene to be comparable with the 5-norbornen-2-one [17], we expected a positive *Cotton* effect near 300 nm for (+)-**7**. The larger the extinction coefficient in the UV. absorption spectrum, the larger should be the magnitudes of the rotational strengths of the $n \rightarrow \pi^*$ transition of the β,γ-unsaturated bicyclic ketones [17]. In contrast, the CD. spectrum of (+)-**7**

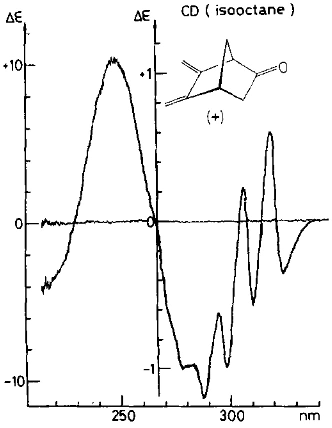


Fig. 2.
CD. spectrum of (+)-**7** *in isooctane*

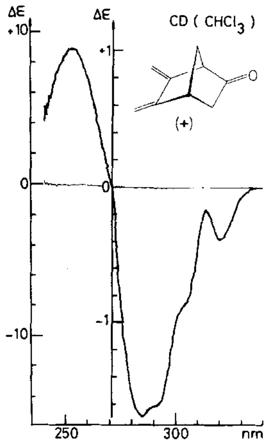


Fig. 3.
CD. spectrum of (+)-**7** *in* $CHCl_3$

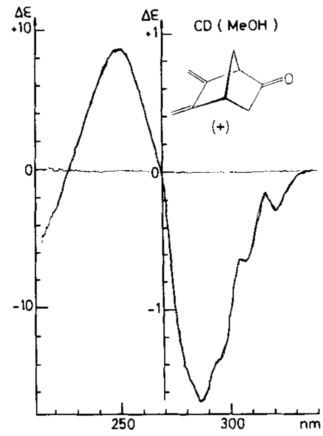


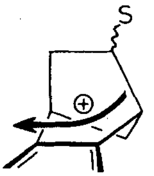
Fig. 4.
CD. spectrum of (+)-**7** *in MeOH*

measured in isooctane showed two weak *Cotton* effects of opposite sign between 265 and 340 nm (see *Table 1* and *Fig. 2*).

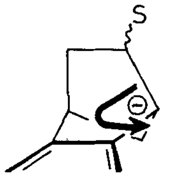
These striking observations definitively merit further experimental and theoretical investigations. Before doing so, we feel that the absolute configuration of (+)-**7** (and of the other 5,6-dimethylidene-2-norbornyl derivatives presented here) should be confirmed by a direct method. In our view, the chirality of (+)-**14** used in the chemical correlation described above has not been established unambiguously [17]. The spectra of (+)-**7** and of the other β,γ-unsaturated ketones reported in *Table 1* should be measured before discussing the theoretical implications of our observations. If the bisignate CD. curve observed for (+)-**7** between 260–340 nm is not due to solvation [26], ketone association [27] (*cf.* CD. spectrum in $CHCl_3$/MeOH, *Fig. 3* and *4*) or to vibronic couplings [28], two transitions of similar energy are responsible for the observed effects (a 'localized' $n \rightarrow \pi^*_{CO}$ with fine *Franck-Condon* contour and a broad band due to a 'delocalized' charge-transfer diene-CO transition?). *A priori*, such a situation (superposition of two transitions) could also exist in the case of the other β,γ-unsaturated ketones and might have gone undetected so far4).

The CD. spectra of the dienes (+)-**1**, (+)-**2**, (+)-**4** and (+)-**5** showed a weak *Cotton* effect for the V←N transition of the s-*cis*-butadiene *(Table 2)*. This was expected for 'quasi-planar' dienes remotely perturbed (*cf.* (+)-2,3-dimethylidenebornane and (−)-borno[2,3-b]cyclopenta-1,3-diene [31]). Substitution at C(2) affects the polarisability of the σ–C(1,2)-bond, and, accordingly, might be responsible for the observed positive *Cotton* effects, in agreement with the allylic axial chirality rule [6] [32] and the proposed absolute configurations of these 2-norbornyl derivatives, but only if the diene (A) instead of the 6-methylidene group (B) is considered as π-system (*cf.* [31]). Since these effects are relatively small, they might also be attributed to incomplete planarity (diene helicity [7]) of the exocyclic diene5). It is interesting to note, however, that a much stronger positive

A



B



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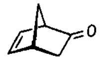
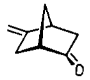
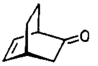
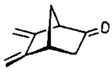
4) *Bays et al.* found that the $n \rightarrow \pi^*_{CO}$ transition enhancement increases as the $\pi \rightarrow \pi^*_{CC}$ transition energy decreases in 5-arylbornenones [29] [25]. Accordingly, we expected a larger extinction coefficient ε for the diene-ketone **7** than for 2-norborn-5-enone and benzo-2-norborn-5-enone (see *Table 1*). This was not observed! (*cf.* also UV. absorption spectra of bicyclo[2.2.2]octenones and bicyclo[2.2.2]octadienones [30]). Moreover, it was reported [29] that the intensity gained by the $n \rightarrow \pi^*_{CO}$ transition is lost by the $\pi \rightarrow \pi^*_{CC}$ transition in 5-arylnorbornenones and the sign of the *Cotton* effects ($\Delta\varepsilon$, CD. spectra) for the $n \rightarrow \pi^*_{CO}$ and $\pi \rightarrow \pi^*_{CC}$ are opposite and their magnitudes are nearly the same. Our data *(Table 1)* definitively show that the β,γ-unsaturated ketone **7** cannot be compared directly with the 5-arylbornenones, 2-norborn-5-enones and benzo-2-norborn-5-enones.

5) MINDO/3 calculations gave 'minimized' geometries where the s-*cis*-butadienes deviate slightly from planarity. Assuming the (1*R*)-configuration, the two double bonds were skewed (by 0.1° in **1**, 0.8° in **2**, 1.9° in **4** and 2.6° in **5**) in a right-handed helix [33], supposed to lead to a positive *Cotton* effect for the V←N transition.

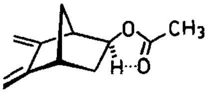
Table 1. *UV. and CD. characteristics of bicyclic ketones* (n→π^*_{CO} transition)

	UV. (isooctane)		CD. (isooctane)		
	λ_{max} [nm]	ε_{max}	λ (peak)	$\Delta\varepsilon$	
(−)-(1*R*)- 	293	26.2	307	+ 0.77	[36]
(+)-(1*R*)- 	307	195	309	+ 14.8	[36] [37]
(−)-(1*S*)- 	294[a])	23	308[a])	+ 0.89	[36][c])
(+)-(1*R*)- 	297[b])	85.4	298	+ 2.0	[36] [13b]
(+)-(1*R*)- 	298	110	298	+ 15.75	[38]
(+)-(1*R*)- 	308	796	307.5	+ 18.8	[17]
(+)-(1*R*)- 	320.5	275	318	+ 0.59	
	309	470			
	298	470	287.5	− 1.20	[c])

[a]) In cyclopentane. [b]) In isopentane. [c]) 6-Methylidene-2-norbornanone [39] is missing in this *Table*. This obviously interesting system has not yet been prepared in its optically active form.

Cotton effect is found in the CD. spectrum of the keto-diene (+)-**7** for its V←N transition ($\Delta\varepsilon_{248}$ + 10.3, λ_{max} 248 nm (ε 8050)). This might be attributed to the $n_{CO} \leftrightarrow \sigma C(1,2) \leftrightarrow \pi_{CC}$ electron delocalization [33] (*cf.* also [12]).

The *exo*-acetate (+)-**2** showed a weak negative *Cotton* effect near 215 nm ($\Delta\varepsilon_{213} = -0.4$, $c = 0.025$, isooctane, 25°) which could be assigned to the acetate function maintained in a preferred conformation [34]. The corresponding *Cotton* effect led to a trough in the CD. spectrum of the *endo*-acetate (+)-**5** ($\varepsilon_{213} = +0.9$) due to the overlap of the relatively large *Cotton* effect (of opposite sign) associated with the V←N transition of the diene ($\Delta\varepsilon_{243} = +2.9$).



(+)-**2**

The *exo*-brosylate (+)-(1*S*,2*R*)-**3** showed a positive *Cotton* effect $\Delta\varepsilon_{232} = +3.6$ ($c = 0.016$, isooctane, 25°) whereas, the *endo* isomer (+)-(1*R*,2*R*)-**6** displayed two

Table 2. *UV. and CD.* (isooctane) *characteristics of the $V \leftarrow N$ transitions of the s-*cis*-butadienes in 5,6-dimethylidene-2-norbornyl derivatives* (+)-**1**-(+)-**7**

Diene	(+)-(1*R*,2*S*)-**1**	(+)-(1*R*,2*R*)-**4**	(+)-(1*R*,2*S*)-**2**	(+)-(1*R*,2*R*)-**5**	(+)-(1*S*,2*R*)-**3**	(+)-(1*R*,2*R*)-**6**	(+)-(1*R*)-**7**
UV. [nm]	245.5	244.5	244	243.5	234[a])	235.5[a])	247.5
ε	10,000	9,300	9,200	8,750	24,000	25,000	8,070
CD. λ	248	245	242	243	232	260; 228	248
$\Delta\varepsilon$	+0.33	+1.8	+0.6	+2.9	+3.6	−0.4; +1.6	+10.3

[a]) In ethanol 96%.

Cotton effects of opposite sign $\Delta\varepsilon_{260} = -0.4$ and $\Delta\varepsilon_{228} = +1.6$ *(Table 2)* as expected from the exciton chirality method [8] [35]. The UV. absorption spectrum of **6** [4] showed one broad band at 235.5 nm (ε 25000) due to the superposition of the two allowed $\pi \rightarrow \pi^*$ transitions of the diene (240-250 nm) and of the arylsulfonate (230-240 nm). These two chromophores are close to each other in the *endo*-brosylate **6** only and, consequently, are expected to give a typical exciton split double extrema in the CD. spectrum of **6** only. At present, we are hesitant to use this observation as a proof for the proposed absolute configuration of (+)-**6** since it is difficult to ascertain the average conformation of the *endo*-brosyloxy substituent (steric effects with the norbornane skeleton, solvent effects, etc.) which defines the direction of the electric dipole moment of the transition localized on the brosylate group. Furthermore, we think that the diene helicity in (+)-**3** and (+)-**6** cannot be disregarded.

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Experimental Part

General remarks, see [4]. CD. spectra (λ [nm]), *Roussel-Jouan* Dichrograph III *(Jobin-Yvon)* ($\Delta\varepsilon_\lambda$, tr. = trough, sh. = shoulder; no specification = a positive or negative peak, except for $\Delta\varepsilon_\lambda = 0$). ^{19}F-NMR. spectra *Bruker* HX-90 (84.67 MHz, FT. mode, $CDCl_3$ as solvent and deuterium lock-signal, $CFCl_3$ as internal reference $\delta_F = 0.0$ ppm).

*5,6-Dimethylidene-*exo*-2-norbornyl camphanates* (+)-**10**, (−)-**11**. (−)-Camphanic acid chloride (*Fluka*, $[\alpha]_{546}^{20} = -23 \pm 2°$, $c = 2$, CCl_4) (18 g, 0.083 mol) was added portionwise to a solution of (+)-5,6-dimethylidene-*exo*-2-norbornanol [20] (8.9 g, 0.065 mol) in anh. pyridine (130 ml) cooled to 0°. After stirring at RT. for 16 h, the mixture was poured into ice (500 g) under vigorous stirring. The precipitate was filtered off, washed with cold water and dried in air. Yield: 19 g (92%) of a mixture of (+)-**10** and (+)-**11**. This crystalline substance was dissolved in hexane (200 ml) and was heated under reflux for 5 min with charcoal (0.3 g). After hot filtration, the solution was allowed to cool slowly to RT.: (−)-**11** crystallized first (prismatic crystals) and was filtered off at the appearance of the first needles of (+)-**10**. The crude (−)-**11** was washed with hexane/CH_2Cl_2 9:1 (dissolution of (+)-**10**). Mother liquor and washing solutions were mixed and concentrated to 150 ml by distillation under reflux. After slow cooling to RT., (+)-**10** (needles) crystallized and was filtered off at the appearance of (−)-**11** (prisms). The mother liquor was concentrated again by distillation under reflux to 80 ml. Cooling to RT. yielded (−)-**11** contaminated with some crystals of (+)-**10** which were washed out with hexane/CH_2Cl_2 95:5 directly on the filter. All the solutions were mixed and concentrated to 100 ml and furnished more (−)-**11** and (+)-**10**, successively. All the fractions of crystalline (+)-**10** were combined and recrystallized from hexane to constant rotation. Similarly, (−)-**11** was recrystallized from hexane to constant rotation (3 to 5 recrystallizations). When the mother liquor reached 50 ml (last crystallization), it was evaporated to dryness; the residue was washed with cold water and used with another batch for the fractional crystallization of (+)-**10** and (−)-**11**. Yield of one cycle of fractional crystallization: (+)-**10**, 6 g (29%), colourless needles, m.p. 129-131°, $[\alpha]_D^{25} = +28°$ ($c = 2$, $CHCl_3$); (−)-**11**, 6.8 g (33%), colourless prisms, m.p. 144-147°, $[\alpha]_D^{25} = -51°$ ($c = 2$, $CHCl_3$).

*(+)-(1*R*,2*S*)-5,6-Dimethylidene-*exo*-2-norbornanol* ((+)-**1**). The camphanate (+)-**10** (5 g, 0.0158 mol) was heated under reflux in ethanol (150 ml) and aq. KOH 3N (100 ml) for 1 h. After cooling to RT., the solution was concentrated to 80 ml by evaporation i.V. and extracted with ether

(4× 100 ml). The ethereal extract was washed with water (3× 50 ml) and dried ($MgSO_4$). After evaporation of the solvent i.V., the residue was distilled. Yield: 1.95 g (90%), colourless liquid, b.p. 70°/0.01 Torr. $[\alpha]_{D}^{25} = +37°$ ($c = 4$, $CHCl_3$); $[\alpha]_{578}^{25} = +39°$; $[\alpha]_{546}^{25} = +44°$; $[\alpha]_{436}^{25} = +79°$; $[\alpha]_{365}^{25} = +130°$. Same UV., IR., ^{1}H-NMR. than (±)-**1** [20]. – CD. ($c = 0.032$, isooctane, 25°, *Table 2*): $\Delta\varepsilon_{270} = 0$; $\Delta\varepsilon_{248} = +0.33$; $\Delta\varepsilon_{237} = 0$; $\Delta\varepsilon_{215} = -1.5$. – CD. ($c = 0.032$, methanol, 25°); $\Delta\varepsilon_{265} = 0$; $\Delta\varepsilon_{252} = +0.1$; $\Delta\varepsilon_{246} = 0$; $\Delta\varepsilon_{222} = -0.7$; $\Delta\varepsilon_{209} = 0$; $\Delta\varepsilon_{201} = +3.3$.

$C_9H_{12}O$ (136.2) Calc. C 79.37 H 8.88% Found C 79.29 H 8.89%

(–)-*(1*S*, 2*R*)-5, 6-Dimethylidene*-exo-*2-norbornanol* ((–)-**1**) was obtained following the same procedure used in the preparation of (–)-**11**. $[\alpha]_{D}^{25} = -37°$ ($c = 4$, $CHCl_3$).

(+)-*(1*R*, 2*S*)-5, 6-Dimethylidene*-exo-*2-norbornyl acetate* ((+)-**2**) was prepared from (+)-**1** according to [4]. Yield: 92%, colourless liquid, b.p. 90°/1 Torr. $[\alpha]_{D}^{25} = +45°$ ($c = 4.5$, $CHCl_3$); $[\alpha]_{578}^{25} = +47.5°$; $[\alpha]_{546}^{25} = +54°$; $[\alpha]_{436}^{25} = +98°$; $[\alpha]_{365}^{25} = +164°$. – CD. ($c = 0.025$, isooctane, 25°): $\Delta\varepsilon_{265} = 0$; $\Delta\varepsilon_{242} = +0.6$; $\Delta\varepsilon_{227} = 0$; $\Delta\varepsilon_{213} = -0.4$; $\Delta\varepsilon_{208} = 0$; $\Delta\varepsilon_{195} = +5.12$. – CD. ($c = 0.025$, methanol, 25°): $\Delta\varepsilon_{265} = 0$; $\Delta\varepsilon_{243} = +0.4$; $\Delta\varepsilon_{227} = 0$; $\Delta\varepsilon_{215} = -0.2$; $\Delta\varepsilon_{211} = 0$; $\Delta\varepsilon_{205} = +1.26$.

$C_{11}H_{14}O_2$ (178.24) Calc. C 74.12 H 7.92% Found C 74.24 H 7.97%

(+)-*(1*S*, 2*R*)-5, 6-Dimethylidene*-exo-*2-norbornyl brosylate* ((+)-**3**) was prepared from (–)-**1** according to [4]. Yield: 82%, white solid, m.p. 55–57°. $[\alpha]_{D}^{25} = +1.2°$ ($c = 2.17$, $CHCl_3$); $[\alpha]_{365}^{25} = +23.5°$. – CD. ($c = 0.016$, isooctane, 25°): $\Delta\varepsilon_{260} = 0$; $\Delta\varepsilon_{232} = +3.6$; $\Delta\varepsilon_{205} = +1$.

(–)-*(1*S*, 2*R*)-5, 6-Dimethylidene*-exo-*2-norbornanyl α-methoxy-α-phenyl-α-trifluoromethylacetate* (**12**). Anh. pyridine (0.6 ml), (–)-MTPA-Cl (prepared from (–)-α-methoxy-α-phenyl-α-trifluoromethylacetic acid, *Fluka*, $[\alpha]_{D}^{20} = -85°$ ($c = 2$, MeOH) [21]), CCl_4 (0.6 ml) and the *exo*-alcohol (+)-**1** (23 mg) in CCl_4 (0.2 ml) were added successively by a syringe through a septum into a flask purged with dry N_2. After standing overnight at RT., 3-diethylaminopropylamine (50 µl) was added. After stirring for 5 min, ether (10 ml) was added and the organic solution was washed successively with aq. HCl 3N (3× 3 ml) and sat. aq. $NaHCO_3$-solution. After drying ($MgSO_4$), the solvent was removed i.V. The residue was analyzed directly by ^{19}F-NMR.: $\delta_F = 73.48$ ppm *(cf. Fig. 1)*.

(+)-*(1*R*)-5,6-Dimethylidene-5-norbornanone* ((+)-**7**) was prepared from (+)-**1** according to [4]. Yield: 74%, colourless liquid, b.p. 80°/2 Torr. $[\alpha]_{D}^{25} = +63°$ ($c = 3.8$, $CHCl_3$); $[\alpha]_{578}^{25} = +65.5°$; $[\alpha]_{546}^{25} = +76°$; $[\alpha]_{436}^{25} = +134°$; $[\alpha]_{365}^{25} = +169°$. – CD. ($c = 0.035$, isooctane, 25°, *cf. Fig. 2*): $\Delta\varepsilon_{338} = 0$; $\Delta\varepsilon_{324} = -0.36$; $\Delta\varepsilon_{322} = 0$; $\Delta\varepsilon_{318} = +0.59$; $\Delta\varepsilon_{314} = 0$; $\Delta\varepsilon_{310.5} = -0.58$; $\Delta\varepsilon_{317.5} = 0$; $\Delta\varepsilon_{305.5} = +0.26$; $\Delta\varepsilon_{304} = 0$; $\Delta\varepsilon_{298} = -0.97$; $\Delta\varepsilon_{294.5} = -0.63$ (tr.); $\Delta\varepsilon_{287.5} = -1.2$; $\Delta\varepsilon_{273.5} = -1.0$ (sh.); $\Delta\varepsilon_{267} = 0$. – CD. ($c = 0.0019$, isooctane, 25°): $\Delta\varepsilon_{248} = +10.3$; $\Delta\varepsilon_{230} = 0$; $\Delta\varepsilon_{210} = -4.1$. – CD. ($c = 0.033$, $CHCl_3$, 25°, *cf. Fig. 3*): $\Delta\varepsilon_{336} = 0$; $\Delta\varepsilon_{320} = -0.37$; $\Delta\varepsilon_{314} = -0.16$ (tr.), $\Delta\varepsilon_{302} = -0.88$ (sh.); $\Delta\varepsilon_{290} = -1.61$ (sh.); $\Delta\varepsilon_{285} = -1.69$; $\Delta\varepsilon_{272} = 0$. – CD. ($c = 0.0017$, $CHCl_3$, 25°): $\Delta\varepsilon_{252} = +9$; $\Delta\varepsilon_{240} = +4.7$. – CD. ($c = 0.036$, MeOH, 25°, *cf. Fig. 4*): $\Delta\varepsilon_{335} = 0$; $\Delta\varepsilon_{321} = -0.28$; $\Delta\varepsilon_{316} = -0.15$ (tr.), $\Delta\varepsilon_{307} = -0.64$ (sh.); $\Delta\varepsilon_{295} = -1.38$ (sh.), $\Delta\varepsilon_{285.5} = -1.67$; $\Delta\varepsilon_{269} = 0$. – CD. ($c = 0.0018$, MeOH, 25°): $\Delta\varepsilon_{249.5} = +8.8$; $\Delta\varepsilon_{226} = 0$; $\Delta\varepsilon_{210} = -6.3$.

$C_9H_{10}O$ (134.18) Calc. C 80.56 H 7.51% Found C 80.47 H 7.49%

(+)-*(1*R*, 2*R*)-5, 6-Dimethylidene*-endo-*2-norbornanol* ((+)-**4**) was prepared from (+)-**7** by reduction with $LiAl(OMe)_3H$/THF according to [4]. Yield: 90%, white solid, m.p. 50.5–51.5° (pentane). $[\alpha]_{D}^{25} = +78°$ ($c = 3.8$, $CHCl_3$); $[\alpha]_{578}^{25} = +82.5°$; $[\alpha]_{546}^{25} = +95.5°$; $[\alpha]_{436}^{25} = +181.5°$; $[\alpha]_{365}^{25} = +329°$. – CD. ($c = 0.0032$, isooctane, 25°): $\Delta\varepsilon_{268} = 0$; $\Delta\varepsilon_{245} = +1.8$; $\Delta\varepsilon_{223} = 0$. – CD. ($c = 0.0032$, MeOH, 25°): $\Delta\varepsilon_{268} = 0$; $\Delta\varepsilon_{246} = +1.0$; $\Delta\varepsilon_{223} = +0.2$ (tr.); $\Delta\varepsilon_{199} = +4.7$.

$C_9H_{12}O$ (136.2) Calc. C 79.37 H 8.88% Found C 79.50 H 8.78%

(+)-*(1*R*, 2*R*)-5, 6-Dimethylidene*-endo-*2-norbornyl acetate* ((+)-**5**) was prepared from (+)-**4** by acetylation with acetic anhydride in pyridine according to [4]. Yield: 88%, colourless liquid, b.p. 90°/2 Torr. $[\alpha]_{D}^{25} = +186°$ ($c = 1.34$, $CHCl_3$): $[\alpha]_{578}^{25} = +194.5°$; $[\alpha]_{546}^{25} = +224°$; $[\alpha]_{436}^{25} = +410°$; $[\alpha]_{365}^{25} = +708°$. –

CD. ($c = 0.024$, isooctane, 25°, *Table 2*): $\Delta\varepsilon_{267} = 0$; $\Delta\varepsilon_{243} = +2.9$; $\Delta\varepsilon_{213} = +0.9$ (tr.); $\Delta\varepsilon_{200} = +5.2$. - CD. ($c = 0.023$, MeOH, 25°): $\Delta\varepsilon_{265} = 0$; $\Delta\varepsilon_{244} = +1.1$; $\Delta\varepsilon_{223} = +0.55$ (tr.); $\Delta\varepsilon_{210} = +1.2$.

$C_{11}H_{14}O_2$ (178.24) Calc. C 74.12 H 7.92% Found C 74.04 H 7.97%

*(+)-(1R,2R)-5,6-Dimethylidene-*endo*-2-norbornyl brosylate* ((+)-**6**) was prepared from (+)-**4** by esterification with BsCl/pyridine according to [4]. Yield: 92%, white solid, m.p. 97.5-98.5°, $[a]_D^{25} = +54°$ ($c = 3.9$, $CHCl_3$); $[a]_{365}^{25} = +186°$. - CD. ($c = 0.016$, isooctane, 25°): $\Delta\varepsilon_{280} = 0$; $\Delta\varepsilon_{260} = -0.4$; $\Delta\varepsilon_{250} = 0$; $\Delta\varepsilon_{228} = +1.6$; $\Delta\varepsilon_{215} = 0$; $\Delta\varepsilon_{209} = +1.3$; $\Delta\varepsilon_{205} = 0$.

*(+)-(1R,2R)-5,6-Dimethylidene-*endo*-2-norbornanyl a-methoxy-a-phenyl-a-trifluoromethylacetate* was prepared as described above for the corresponding ester of (+)-**1** [21]. - ^{19}F-NMR. ($CDCl_3$): $\delta_F = -73.05$ ppm, *cf. Figure 1.*

*(+)-(1R,2S)-*exo*-Benzo-norborn-5-en-2-yl acetate* ((+)-**14**). The acetate (+)-**2** (0.185 g, 1.04 mmol), phenylvinylsulfoxide (0.4 g, 2.6 mmol) and anh. pyridine (100 µl) were heated in a pyrex sealed tube to 140-150° for 40 h. After cooling to RT., the tube was opened and extracted with CH_2Cl_2. The dark solution was evaporated i.V. to dryness. The residue was taken up in hexane, heated with charcoal and separated by TLC. (SiO_2, AcOEt/hexane 1:9). The main fraction contained (+)-**14** (extraction with CH_2Cl_2) and was purified by distillation. Yield: 70 mg (33%), colourless liquid, b.p. ~90°/0.2 Torr. $[a]_D^{25} = +64°$ ($c = 3$, MeOH) (Litt. $[a]_D^{25} = +69°$ ($c = 6$, MeOH) [17]). The other properties were identical to those reported [17].

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