52. First Direct Synthesis of Optically Active 3-Methylcyclopentene

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Summary

(−)-(*S*)- and (+)-(*R*)-3-methylcyclopentene (**1**) has been prepared in a stereochemically unambiguous synthesis. The (*S*)-configuration for (−)-**1** was confirmed by correlation with (−)-(*S*)-1-methylindane.

1. Introduction. – 3-Methylcyclopentene (**1**) can be considered a model compound for the understanding of both vibrational [1][2] and electronical [3][4] optical activity of the chirally perturbed ethylene chromophore. It is a pure hydrocarbon with a restricted number of attainable conformations [5] and, therefore, more convenient to be investigated spectroscopically than analogous open chain molecules (*cf.* [6]).

Several attempts have been described to obtain optically active **1,** but all methods listed in *Table 1* are not suitable to synthesize **1** free of isomers. The elimination reactions shown in *Table 1* lead to a nearly constant mixture of about 60% of **1** and 40% of 4-methylcyclopentene (**3**), even by varying widely the reaction conditions. Only by time-consuming and sophisticated preparative gas chromatography the achiral isomer **3** can be separated from the optically active **1** [13][17]. For this reason, the UV-CD and VROA[3]) spectra of (+)-**1** so far presented [1–4] had been measured of the material which was considerably contaminated with **3.** This isomer, even though achiral, makes, without doubt, the correct assignment of the CD transitions and optically active vibration modes more difficult.

The (*R*)-configuration attributed to (+)-**1** seems to be firmly established, since most syntheses of (+)-**1** start with (+)-3-methylcyclopentanone, whose (*R*)-configuration has been confirmed by several authors [18–22].

On the other hand, there is at least one published contradiction in the configurational relationships with respect to (+)-**1.** *Semmler* [7] isolated (+)-2-methylglutaric acid ((+)-**5**), whose absolute configuration is (*S*), after oxidative degradation of (+)-**1.** This result was later contested by other authors [11], who failed to detect any acid **5** in repeating *Semmler*'s experiment. Nevertheless, these contradictions could weaken the

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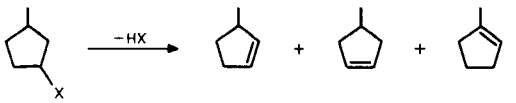
[3]) *V*ibrational *R*aman *O*ptical *A*ctivity [5].

Table 1. *Formation of 3-Methylcyclopentene* (**1**) *and By-products* **3** *and* **4** *from the Precursor* **2** *under Various Conditions*



2 **1** **3** **4**

Entry	X in **2**	Reaction conditions[a])		Composition [%]				**1**		Ref.
				1	**3**	**4**	Analytical method	$[\alpha]^{b}$)	n_d[a])	
1	OH	$ZnCl_2$	120°					+		[7]
2	OH	Oxalic acid	110°					$[\alpha]_D = +21.83$	1.4201	[8]
3	OH	Phthalic anhydrid	284°					rac	1.4272 (19°)	[9] [10]
4	OH	H_2SO_4	100°	≈ 60	≈ 40		n_D	$[\alpha]_{579} = +77.9$	1.4233 (16°)	[9] [10]
5	OH	H_2SO_4	160°					rac	1.4250 (16°)	[11]
6	OH	Al_2O_3	290°					rac	1.4215 (16°)	[11]
7	OH	Al_2O_3	400°	60	40		n_D, IR	rac	1.4251 (17°)	[12]
8	OH	H_3PO_4	145°					$[\alpha]_D = +125$	–	[13]
9	OH	H_3PO_4	145°	45	40	15	GC	?	–	[14]
10	OH	P_2O_5	115°	≈ 60	≈ 40		n_D	rac	1.4248	[15]
11	I	NaOH	100°					$[\alpha]_D = +59.07$	1.4222 (18°)	[8]
12	OAc	Pyrolysis	530°	61	39	?	GC	$[\alpha]^{20}_{589} = +174.5$	–	[13]
13	Cl	Kieselguhr	114°					rac	–	[11]
14	OH	HMPT	240°	?	?			rac	–	[16]
15	OH	DMSO	170°	60	40		NMR	$[\alpha]^{25}_{589} = +108.8$	–	[c])

[a]) Temp. in °C; HMPT = hexamethylphosphoric triamide, DMSO = dimethyl sulfoxide.
[b]) rac = Reaction with racemic material.
[c]) This work.

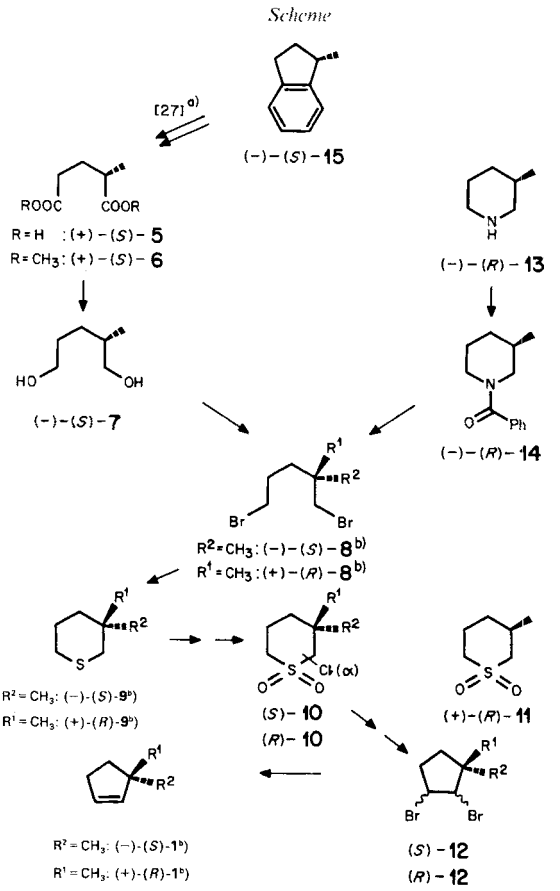
configurational assignment of (+)-**1** and, thus, of many compounds in the cyclopentene and indane series (*cf.* [23–30]).

For these reasons we developed a new synthesis for optically active **1** (see the *Scheme*) which correlates (+)-(*S*)-**5** unequivocally with (−)-**1** as well as with (−)-1-methylindane ((−)-**15**) [27][28] and which, in addition, allows the preparation of specifically deuterated species of **1** for VROA measurements. In this way we also removed all possible doubts, based on *Semmler*'s work [7], on the (*R*)-configuration of (+)-**1.**

2. Synthesis and Configuration of (−)- and (+)-3-Methylcyclopentene. – The oxidative degradation of **15** and probably of **1** leads to the acid **5** [27][7] *(Scheme)*. We, therefore, chose this acid as starting material for the synthesis of **1.** A first attempt to accomplish this synthesis by an intramolecular coupling reaction of a diphosphorane derived from 2-methyl-1,5-dibromopentane (**8**) according to *Bestmann et al.* [31] failed. Even under intensified reaction conditions no diphosphonium salt of **8** was formed (see *Exper. Part*). We then achieved the synthesis of **1** *via* **8** by relying on an intramolecular *Ramberg-Bäcklund* reaction.

Reduction of the dimethylester (+)-**6** with $LiAlH_4$ in ether gave the diol (−)-**7** which was transformed into the dibromide (−)-**8** by standard methods. Reaction of (−)-**8** with sodium sulfide led to the formation of (−)-(*S*)-3-methylthiacyclohexane ((−)-**9**) (*cf.* [32]

Scheme



a) The chemical correlation was, in fact, carried out in the (*R*)-series. All signs of rotation refer to the sodium D-line.

b) Only the substituent $R^{1,2} \neq H$ is indicated.

for the reaction with racemic material). Chlorination of (−)-**9** with *N*-chlorosuccinimide followed by treatment with *m*-chloroperbenzoic acid yielded the α-chlorosulfone (*S*)-**10**[4]). Eventual ring contraction of (*S*)-**10** with KO*t*Bu in ether gave (−)-**1**.

Solvent-free (−)- or (+)-**1** (see *below*) was obtained by direct addition of Br_2 to 3-methylcyclopentene (**1**) in the etheral solution. The dibromide **12** was separated by distillation and chromatography on silica gel. The pure dibromide was then decomposed with Zn in H_2O [33] to give **1**. After removal of the co-distilled H_2O (−)- or (+)-**1** (b.p. 65°) was further purified by distillation. Optically active **1** thus obtained was free of 4-methylcyclopentene (**3**; established by ^{13}C-NMR spectroscopy).

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4) The α-chlorosulfone **10** was not characterized in detail, *i.e.* we do not know if a mixture of diastereoisomers and possibly constitutional isomers has been formed. In a separate experiment (+)-(*R*)-**9** was oxidized with *m*-chloroperbenzoic acid to yield the sulfone (+)-(*R*)-**11**.

The reported optical resolution of (±)-**5** is a tedious procedure [34]. We, therefore, looked for another way to prepare (+)-(*R*)-**8** (or (−)-(*S*)-**8**) and found (−)-3-methylpiperidine ((−)-**13**) to be a more convenient, optically active starting material, which can easily be obtained by resolution of (±)-**13** with tartaric acid (*cf.* ref. in *Table 2*, see *Exper. Part*). Since no correct [α]-values of (+)- and (−)-**13** were known, the exact rotations of optically pure **13** had first to be ascertained. ^{1}H-NMR-shift experiments with Eu(tfc)$_3$[5]) confirmed the [α]-value given by *Masamune et al.* [39] for optically pure material (see *Table 2*). This value was furthermore corroborated chemically since (+)-**5** and (−)-**13** provided the optically active dibromide **8** with identical absolute rotations (*cf. Exper. Part*). The dibromide (+)-**8** was prepared from (−)-**13** in a *von Braun* reaction of the corresponding *N*-benzoyl derivative (−)-**14** (*cf.* [38][40]).

The configurational relationship of (−)-**1** with the indane (−)-(*S*)-**15** *via* (+)-(*S*)-**5** and the absolute configuration of the new optically active tetrahydrothiopyrane (−)-**9** are thus unequivocally established by the described syntheses.

For chemical reasons we had to base our synthesis on the *Ramberg-Bäcklund* reaction [41]. While this reaction is very well suited to prepare cyclobutenes (*cf.* [42–46]), it is obviously less used in the synthesis of cyclopentenes which, in general, are formed only in low yields [46]. This is also true for the synthesis of (−)- and (+)-**1** which were formed in about 10% yield. However, this disadvantage is counterbalanced by the fact that (+)-[1,2-^{2}H$_2$]-**1** can easily be prepared following the same synthetic scheme when the α-protons in the α-chlorosulfone (*R*)-**10** are exchanged by deuterons (deuterium source D_2O) prior to the *Ramberg-Bäcklund* reaction (see [47]). In a similar manner (+)-(*R*)-3-(*methyl*-[^{2}H$_3$])cyclopentene was synthesized starting with ethyl (−)-(*R*)-piperidine-3-carboxylate which was reduced in two steps to yield (−)-(*R*)-(*methyl*-[^{2}H$_3$])-**13** (see [47])[6]).

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Experimental Part

General. See [27][28].

1. (+)-3-Methylcyclopentene ((+)-1) from (3*R*)-3-Methylcyclopentan-1-ol ((*R*)-2). – 1.1. *(3R)-3-Methylcyclopentan-1-ol* ((*R*)-**2**). Following a procedure in [49], 3-methylcyclopentanone (*Aldrich* or prepared according to [48]) was reduced to (*R*)-**2**, $\alpha_{589}^{25} = -6.1$ (neat), n_D^{28}: 1.4441, *i.e.* the *cis*-isomer was formed predominately [49].

1.2. *(+)-3-Methylcyclopentene* ((+)-**1**) *and 4-Methylcyclopentene* (**3**). At 175°, 2.7 g (27 mmol) of (*R*)-**2** were dehydrated with 10.5 g of DMSO during 64 h (*cf.* [50]). The H_2O-free distilled product was purified by column chromatography (CC) (silica gel/3% $AgNO_3$, CCl_3F, −20°). Prep. GC led to 350 µl (15%) of a pure hydrocarbon fraction. ^{13}C- and ^{1}H-NMR showed it to be a mixture of 60% **1** and 40% **3** (see *Table 1*). This mixture of isomers had $[\alpha]_{589}^{25} = +108.8$ and $[\alpha]_{579}^{25} = +113.3$ ($c = 0.6$, **3**) (*cf.* [9][10]). In contrast to optically active **15** [28], the ORD curve of (+)-**1** showed no solvent dependance. $[\alpha]_{589}^{25} \simeq +138$ ($c = 0.0089$, benzene and **3**), $[\alpha]_{589}^{25} \simeq +132$ ($c = 0.012$, isooctane and **3**). ^{13}C-NMR ($CDCl_3$) of (+)-**1**: 136.8 (C(2)); 129.4 (C(1)); 39.8 (C(3)); 32.1(C(5)); 31.9 (C(4)); 21.0 (CH_3); of **3**: 129.6 (C(1), C(2)); 40.8 (C(3), C(5)), 31.7 (C(4)), 21.8 (CH_3).

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[5]) Tris[3-(trifluoromethyl-hydroxymethylene)-*d*-camphorato]europium.

[6]) In March 1981, on Friday the 13th, a tremendous fire burst out in the Institute of Organic Chemistry in Fribourg and damaged the sophisticated instrument for VROA measurements, constructed by Prof. *Werner Hug*, in the Institute of Physical Chemistry. This made the measurements of VROA spectra of our pure compounds impossible (see [1] [2]).

2. Attempts to Form a Diphosphonium Salt from (±)-2-Methyl-1,5-dibromopentane ((±)-8). – In a sealed tube, 6.44 g (26.6 mmol) of (±)-**8** (see *3.3*) were heated with 17.31 g (66 mmol) Ph_3P at 150° for 15 h. No crystalline diphosphonium salt could be isolated after the addition of Et_2O. Further attempts by changing the conditions (180°/72 h, 250–270°/55 h) failed too (*cf.* [47]).

3. (–)-(*S*)-3-Methylcyclopentene ((–)-(*S*)-1) from (+)-(*S*)-2-Methylglutaric acid ((+)-(*S*)-5). – 3.1. *(+)-(S)-2-Methylglutaric Acid* ((+)-(*S*)-**5**). According to [34], 87.4 g (0.6 mol) (±)-**5** were resolved with 200 g (0.6 mol) of strychnine. Then, 10.1 g (+)-**5** were esterified with CH_2N_2 to yield 12.1 g of *dimethyl (+)-(S)-2-methylglutarate* ((+)-(*S*)-**6**), a_{589}^{20} = +24.49 (neat), $[a]_{589}^{20}$ = +23.17 (neat, d_4^{20} = 1.057), *i.e.* p = 0.95 ($[a]_{589}^{20}$ = +24.46 (neat, p = 1.0 [34])).

3.2. *(–)-(S)-2-Methylpentane-1,5-diol* ((–)-(*S*)-**7**). $LiAlH_4$ in Et_2O reduced 12 g of (+)-**6** to 6.58 g (81%) of (–)-**7**, $[a]_{589}^{25}$ = –10.0 (c = 0.025, Et_2O) (*cf.* [38][51]).

3.3. *(–)-(S)-2-Methyl-1,5-dibromopentane* ((–)-(*S*)-**8**). According to [52], 6.58 g (–)-**7** were brominated with $Ph_3P \cdot Br_2$ in CH_3CN. The formed dibromide (10.19 g, 72%) showed a_{589}^{25} = –6.1 (neat), p = 0.95 (see *3.1*), *i.e.* $[a]_{589}^{25}$ = –4.0 (neat) for p = 1.0 with d_4^{20} = 1.598 [53]. For optically active **8** different values for density and rotation are found (*cf.* [38][51][54]). The a-value reported here is confirmed in *4.4*.

3.4. *(–)-(S)-3-Methylthiacyclohexane* ((–)-(*S*)-**9**). As described for the racemate in [32][54], 10.19 g (41.7 mmol) of (–)-**8** were cyclized with 15.03 g (62.5 mmol) of $Na_2S \cdot 9H_2O$ to yield 1.65 g (34%, see *4.5*) (–)-**9**, a_{589}^{25} = –7.1 (neat), $[a]_{589}^{25}$ = –7.6 (neat, d_4^{25}: 0.9430 [54]), *i.e.* p = 0.94 (see *4.5*).

3.5. *(3S)-a-Chloro-3-methylthiacyclohexane 1,1-Dioxide* ((*S*)-**10**). For 1 h, 1.65 g (14.2 mmol) of (–)-**9** and 1.90 (14.2 mmol) of *N*-chlorosuccinimide were heated in 90 ml CCl_4 and filtered after cooling (*cf.* [55]). After evaporation of the solvent, the residue was dissolved in 25 ml of abs. Et_2O and treated with 4.9 g of *m*-chloroperbenzoic acid for 12 h. The Et_2O-solution was washed 3 times with 5 ml of sat. aq. Na_2CO_3 and afforded, after drying at 25°/0.05 Torr, 2.26 g (86%) of (*S*)-**10** as a colourless liquid, which solidified at about 5°. IR: 1315, 1290, 1130 (R–SO_2–R). MS: 185 and 183 (M^+), 147 (100%), 117, 81.

3.6. *(3S)-1,2-Dibromo-3-methylcyclopentane* ((*S*)-**12**). To a solution of 2.22 g (12.22 mmol) of (*S*)-**10** in 40 ml abs. Et_2O were added 5.48 g (48.8 mmol) of KO*t*Bu in one portion at 0° under N_2 (*cf.* [42]). After 2 h stirring at 0° the solution was refluxed for 6 h. At 0°, 35 ml H_2O and 25 ml Et_2O were added, the org. phases separated, distilled, and immediately treated at –10° with a solution of Br_2 in CCl_4. Surplus Br_2 was removed with sat. aq. Na_2SO_3. The dark green residue was purified by CC (silica gel) and complete elution with hexane. Distillation afforded 0.28 g (10%) of (*S*)-**12**. MS: 244/242/240 (M^+), 164/162, 163/161, 151/159, 121/119, 81 (100%).

3.7. *(–)-(S)-3-Methylcyclopentene* ((–)-(*S*)-**1**). At 90°, 0.28 g (1.16 mmol) of (*S*)-**12** were treated with 0.23 g activated Zn-dust [56] in a micro-distillation apparatus (*cf.* [33]). The formed (–)-**1** was extracted from the distilled material (H_2O and (–)-**1**) with 100 µl of CCl_4. IR and GC were identical with those of (+)- and (±)-**1**; the ORD showed the antipodal plain curve as compared with that of (+)-**1**, see *4.9*. With respect to the small quantity, the exact concentration of (–)-**1** in the CCl_4-solution and hence the a-value could not correctly be determined.

4. (+)-(*R*)-3-Methylcyclopentene ((+)-(*R*)-1) from (–)-(*R*)-3-methylpiperidine ((–)-(*R*)-13). – 4.1. *(–)-(R)-3-Methylpiperidine* ((–)-(*R*)-**13**). 1135 g (7.56 mol) (+)-tartaric acid and 750 g (7.56 mol) of (±)-**13** were dissolved in 1200 ml H_2O. After crystallization, the hydrogentartrate was recrystallized 3 times from H_2O (1 g salt/1.2 ml H_2O; 1 g salt/1.5 ml H_2O; 1 g salt/1.5 ml H_2O). The last salt fraction was decomposed with 20% aq. NaOH at 0°. The formed amine was extracted with Et_2O in an extraction apparatus and distilled: a_{589}^{25} = –0.52 (neat), $[a]_{589}^{25}$ = –0.61 (neat), d_4^{24} = 0.8446 [57], *i.e.* p = 0.94. Four recrystallizations led to (–)-**13** with a_{589}^{20} = –0.53 (neat), $[a]_{589}^{20}$ = –0.62 (neat), d_4^{20} = 0.8489 [57], *i.e.* p = 0.97.

4.2. *Determination of the Optical Purity of 3-Methylpiperidine* ((+)- and (–)-**13**). From the mother liquors of the first recrystallization, (+)-**13** was isolated with a_{589}^{25} = +0.21 (neat). The mother liquor of the second crystallization afforded an amine fraction with a_{589}^{25} = –0.16 (neat). Eu(hfc)$_3$ caused in ^{1}H-NMR (CCl_4) enantiomeric shifts of CH_3–C(3) which allowed to determine e = 0.379 and 0.292. The a- and e-values can be considered to be linearly dependent [58], thus a_{589}^{25} = –0.55 (neat) and $[a]_{589}^{25}$ = –0.65 (neat), d_4^{24} = 0.8446 [57] was calculated for p = 1.0, see *Table 2*.

4.3. *(R)-N-Benzoyl-3-methylpiperidine* ((*R*)-**14**) [40]. Benzoyl chloride reacted with (–)-**13** to yield (*R*)-**14** (*cf.* [59]). It was used without further purification in the next step.

4.4. *(+)-(R)-2-Methyl-1,5-dibromopentane* ((+)-(*R*)-**8**). In a *von Braun* reaction (*cf.* [60]) (*R*)-**14** was cleaved with PBr_5 to yield (+)-**8** (58%). The formed benzonitrile was not completely hydrolyzed after 14 h of reflux with 40% aq. HBr, but it could be removed by distillation. (+)-**8**: a_{589}^{25} = +6.2 (neat), $[a]_{589}^{25}$ = +3.9 (neat), d_4^{20} = 1.598 [53], *i.e.* p = 0.97. Extrapolated for p = 1.0: $[a]_{589}^{25}$ = +4.0 (neat), see *3.3*.

Table 2. *Reported Specific Rotations of the Optically Pure 3-Methylpiperidines* (**13**)

$[\alpha]_D^T$	T [°C]	Solvent	Ref.
−3.98[a])	25	neat	[35]
−2.05	21	neat	[36]
−1.5	17	dioxane	[36]
+3.05	20	dioxane	[37]
−0.79	20	neat	[38]
−0.6	20	dioxane	[38]
+0.65	15	neat	[39]

[a]) α-value.

4.5. *(+)-(R)-3-Methylthiacyclohexane* ((+)-(*R*)-**9**) was prepared according to *3.4*. The yield could be raised to 87% by extraction of the formed sulfide with pentane in an extraction apparatus. $[\alpha]_{589}^{25} = +7.7$ (neat), $d_4^{25} = 0.9430$ [54]. ORD (25°, neat, α-values): 5.4 (650), 6.9 (600), 8.9 (550), 12.3 (500), 18.2 (450), 29.7 (400), 58.5 (350), 77.6 (334), 120.0 (313), 156.8 (302).

4.6. *(3R)-α-Chloro-3-methylthiacyclohexane 1,1-Dioxide* ((*R*)-**10**) was prepared as described in *3.5*.

4.7. *(+)-(R)-3-Methylthiacyclohexane 1,1-Dioxide* ((+)-(*R*)-**11**). At 0°, 0.3 g (2.58 mmol) of (+)-**9** in 15 ml Et_2O were treated with an Et_2O-solution of 0.89 g (5.16 mmol) of *m*-chloroperbenzoic acid. After stirring overnight the mixture was washed with a few ml of sat. aq. Na_2CO_3- and then Na_2SO_3-solution. Usual workup led to crude (+)-**11**, which was purified by bulb-to-bulb distillation at 150°/0.04 Torr yielding 0.21 g (55%) of a colourless liquid (*cf.* [54]). $[\alpha]_{589}^{25} = +3.2$ ($c = 0.019$, CH_2Cl_2), $[\alpha]_{589}^{25} = +1.5$ ($c = 0.022$, H_2O). IR: 1300, 1285, 1135 (R−SO_2−R). ORD ($c = 0.019$,CH_2Cl_2, 25°): 2.6 (650), 3.1 (600), 3.7 (550), 6.3 (450), 8.4 (400), 12.6 (350), 15.3 (334).

4.8. *(3R)-1,2-Dibromo-3-methylcyclopentane* ((*R*)-**12**) was prepared by using different solvents as described in *3.6*. In THF/Et_2O 1:1 the yield of pure (*R*)-**12** was 7%, in dioxane 10%, in pure THF 14%.

4.9. *(+)-(R)-3-Methylcyclopentene* ((+)-(*R*)-**1**). As described in *3.7*, 0.4 g (1.65 mmol) of (*R*)-**12**, $p = 0.97$, afforded after debromination 0.1 g (77%) of (+)-**1**. ^{13}C-NMR showed the absence of the isomer **3** (see *1.2*). (+)-**1**: $[\alpha]_{589}^{20} = +157.5$ and $[\alpha]_{579}^{20} = +164.0$ ($c = 0.012$, benzene) for $p = 1.0$ extrapolated from the α-values for $p = 0.97$ (*cf.* $[\alpha]_{579}^{20} = +182.9$ (neat), $d_4^{20} = 0.762$, $p = 1.0$ [13]). ORD ($c = 0.012$, benzene, for $p = 1.0$, 20°): 123.9 (650), 149.9 (600), 184.7 (550), 234.6 (500), 309.6 (450), 430.3 (400), 650.3 (350), 757.9 (334), 956.1 (313), 1096.3 (302), 1178.8 (296). IR (CCl_4): identical with a published spectrum of (±)-**1** [61] and the spectrum obtained in *3.7*. ^{1}H-NMR (CCl_4): 5.63 (*s*, 2H, H−C(1) and H−C(2)); 2.9–2.5 (*m*, 1H, H−C(3)); 2.5–1.6 (*m*, 3H, 2H−C(5) and 1H−C(4)); 1.6–1.3 (*m*, 1H, H−C(4)); 1.03 (*d*, $J = 6.9$, 3H, CH_3−C(3)).

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