Influence of *Lewis* Acids on the [4 + 2] Cycloaddition of *N,N'*-Fumaroylbis[(2*R*)-bornane-10,2-sultam] to Cyclopentadiene and Application to Various Dienes

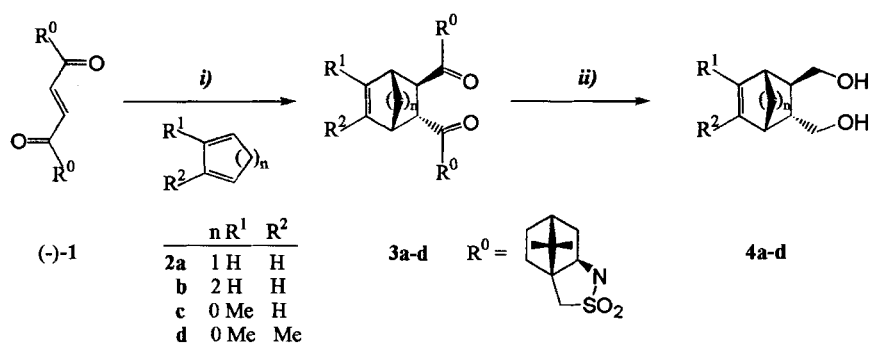
by **Tomasz Bauer**[a]), **Christian Chapuis**[b])[1])*, **Anna Kucharska**[a]), **Piotr Rzepecki**[a]), and **Janusz Jurczak**[a])[b])*

[a]) Department of Chemistry, University of Warsaw, Pasteura 1, PL-02-093 Warsaw
[b]) Institut of Organic Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, PL-01-224 Warsaw

Among seventeen different *Lewis* acids, $TiCl_4$ was found to be the best catalyst for the [4 + 2] cycloaddition of cyclopentadiene to *N,N'*-fumaroylbis[(2*R*)-bornane-10,2-sultam] ((−)-**1**). Independently of the $TiCl_4$ molar concentration, almost constant and complete (98–89% d.e.) diastereofacial π-selection was achieved in the *Diels-Alder* addition of (−)-**1** to cyclopentadiene, cyclohexadiene, isoprene, and 2,3-dimethylbuta-1,3-diene.

Introduction. – We recently reported the preparation of (−)-**1** [1] as well as its cycloaddition to cyclopentadiene **2a** [2][2]) and found that, under the cooperative influence of two prosthetic groups [5], the uncatalysed reaction occurs smoothly at −78° in CH_2Cl_2 to afford, after total conversion, the major cycloadduct (2*R*,3*R*)-**3a** in 95% yield and 89% d.e. (see *Scheme*)[3]). Complete conversion and π-facial selectivity (98–99% d.e.) were also achieved under the same conditions, independently of the $TiCl_4$ molar

Scheme



i) CH_2Cl_2, −78°, 20 h, 1.0 mol-equiv. of *Lewis* acid. *ii*) $LiAlH_4$, THF.

[1]) Present address: *Firmenich SA*, Corporate R & D Division, P.O. Box 239, CH-1211 Geneva 8.

[2]) For earlier asymmetric [4 + 2] cycloadditions of fumarates, see ref. cit. in [2]; for more recent references, see [3]; for a recent review on asymmetric intermolecular homo- and hetero-*Diels-Alder* reactions, see [4].

[3]) PM3 Calculations suggest that the four lower uncatalysed transition states, expressed in kcal/mol, are the following: C(α)-*re* bis(*anti*-s-*cis*): −133.15; C(α)-*re* *syn*-s-*cis*-s-*cis*-*anti*: −132.23; C(α)-*re* bis(*syn*-s-*cis*) −131.82; C(α)-*si* bis(*syn*-s-*cis*): −131.27 [6] [7]. Under catalysed conditions, the situation is more complicated since neither the ratio nor the relative reactivity of the respective mono-, di-, and non-coordinated species is known.

concentration (0.25–2.5 mol. equiv.). The major diastereoisomer (2*R*,3*R*)-**3a** was obtained pure in 95% yield by simple recrystallization or chromatography, and the absolute configuration was ascertained by chiroptical analysis of the known corresponding diol (2*R*,3*R*)-**4a** [8]. We wish now to report on the influence of diverse *Lewis* acids and dienes on the [4 + 2] cycloaddition to dienophile (–)-**1**.

Results and Discussion. – The first screening was performed, as previously reported for $TiCl_4$, at –78° for 4 h in the presence of 1.0 mol-equiv. of *Lewis* acid in CH_2Cl_2. The conversion and diastereoselectivity were directly determined by integration of the olefinic signals in the ^{1}H-NMR spectra of the crude reaction mixture of (–)-**1** and cycloadducts (2*R*,3*R*)-**3a**/(2*S*,3*S*)-**3a** [2]. First of all, the isosteric analogous *Lewis* acid $SnCl_4$ gave complete conversion with a slightly lower selectivity (92.5% d.e., see *Table 1*, *Entry a*) as compared to $TiCl_4$. Since $TiCl_2(O^iPr)_2$ was earlier used to minimize the diene polymerization [9], we then compared a series of titanium-isopropoxide-derived catalysts of decreasing *Lewis* acidity and chelating properties (*Entries b–e*), which resulted in average in a consequent decrease of the diastereoselectivity, reaching even lower values (82–86% d.e., *Entries d* and *e*) than that observed for the noncatalysed reaction. This may tentatively be rationalized by favoured SO_2/C=O *anti*, C=O mono-coordinated species, or even C=O/C=C s-*trans* conformations[3]). A similar π-face selectivity was observed with $TiCl_2(OEt)_2$ (*Entry f*).

The complex with $AlCl_3$ was not fully dissolved and formed a suspension in CH_2Cl_2, leading to a conversion and π-facial differentiation comparable with $SnCl_4$ (*Entry g*). The

Table 1. *Cycloaddition of (–)-***1** *to Cyclopenta-1,3-diene* (**2a**) *at* –78° (4 h) *in the Presence of 1 mol-equiv. of* Lewis *Acid*

Entry	*Lewis* acid	Solvent	Conversion [%]	d.e. [%]
a	$SnCl_4$	CH_2Cl_2	100	92.5
b	$TiCl_3(O^iPr)$	CH_2Cl_2	88.1	90.2
c	$TiCl_2(O^iPr)_2$	CH_2Cl_2	100	90.2
d	$TiCl(O^iPr)_3$	CH_2Cl_2	76.5	82.3
e	$Ti(O^iPr)_4$	CH_2Cl_2	100	86.0
f	$TiCl_2(OEt)_2$	CH_2Cl_2	100	86.0
g	$AlCl_3$	CH_2Cl_2[a])	100	92.1
h	$AlCl_3$	THF	100	85.0
i	$AlCl_2Me$	CH_2Cl_2	100	97.8
j	$AlCl_2Et$	CH_2Cl_2	100	84.9
k	$AlClMe_2$	CH_2Cl_2	100	94.6
l	$AlClEt_2$	CH_2Cl_2	100	84.1
m	$AlMe_3$	CH_2Cl_2	100	91.5
n	$AlEt_3$	CH_2Cl_2	100	90.0
o	$ZnCl_2$	CH_2Cl_2[a])	83.0	73.3
p	$ZnCl_2$	THF	56.5	60.0
q	$ZnBr_2$	CH_2Cl_2[a])	53.0	89.1
r	$ZnBr_2$	THF	34.0	80.0
s	$BF_3 \cdot OEt_2$	CH_2Cl_2	100	87.0
t	BCl_3	MeOH	100	84.1

[a]) Suspension of the complex.

complex was soluble in THF, but this resulted in a drop of diastereoselectivity (*Entry h*, 85% d.e.)[4]). Previously, $AlCl_2Et$ was preferred over $TiCl_4$ for the cycloadditions of (2*R*)-*N*-acryloylbornane-10,2-sultam to **2a** and buta-1,3-diene [11]. In our case, comparison of several alkylchloroaluminium catalysts (*Entries i–n*) suggests that the size of the aluminium substituents may play a role in the dienophile conformational equilibrium, or may sterically interact with the incoming diene. In all cases, the diastereoselectivity was lower when compared with $TiCl_4$ or even with the uncatalysed reaction; it reached a maximum of 97.8% d.e. with $AlCl_2Me$. $ZnCl_2$ and $ZnBr_2$ formed also a partially insoluble complex, resulting in lower conversion and diastereoselectivity (*Entries o* and *q*). The use of THF diminished even more drastically the chemical and optical yields, supposedly by additional or competitive coordination to the metal. Finally, under non-chelating boron-derived *Lewis* acid conditions (*Entries s* and *t*), we observed, similarly to *N*-acryloyl- and *N*-crotonoylbornane-10,2-sultams [11], a worse diastereoselectivity, even lower as that obtained under uncatalysed conditions.

Convinced that $TiCl_4$ was the best chelating agent[5]), we then studied the influence of its molar concentration on the cycloaddition to diverse dienes (see *Table 2*). First of all, the least reactive cyclohexa-1,3-diene (**2b**) was studied, and the desired ratios were determined by ^{1}H-NMR analysis[6]). The diastereoselectivity was constant and very high (> 95% d.e.), independent of the $TiCl_4$ concentration. The conversion was low for 0.25 mol-equiv. of $TiCl_4$ and increased gradually to reach almost complete conversion within 20 h for 1.0 mol-equiv. of *Lewis* acid. The major diastereoisomer (2*R*,3*R*)-**3b** could be obtained pure by chromatography (98%) of the totally converted material (2.0 mol-equiv. of $TiCl_4$). The situation was nearly identical with isoprene (**2c**), which shows virtually complete conversion and diastereoselectivity for 1.0 mol-equiv. of $TiCl_4$[7]). Chromatography of crude **3c** (2.0 mol-equiv. of $TiCl_4$) afforded pure (1*R*,2*R*)-**3c**

Table 2. *Cycladdition of (–)-***1** *to Diverse Dienes at –78° in CH_2Cl_2* (20 h) *in the Presence of Increasing Amounts of $TiCl_4$*

$TiCl_4$ [mol. equiv.]	Cyclohexa-1,3-diene (**2b**)		Isoprene (**2c**)		2,3-Dimethylbuta-1,3-diene (**2d**)	
	Conversion [%]	d.e. [%]	Conversion [%]	d.e. [%]	Conversion [%]	d.e. [%]
0.25	5	95	36	95	100	84
0.50	10	95	52	95	100	85
0.75	21	95	73	95	100	89
1.00	95	96	95	96	100	87
1.25	97	96	97	96	100	85
1.50	98	97	99	97	100	82
1.75	99	97	100	97	100	82
2.00	100	98	100	98	100	82
2.25	100	98	100	98	100	82
2.50	100	98	100	98	100	82

[4]) For a study of the solvent effect on the diastereoselectivity of chiral dienophiles, see [10].

[5]) For an X-ray analysis of $TiCl_4$ chelated to (2*R*)-*N*-crotonoylbornane-10,2-sultam, see [12].

[6]) The major diastereoisomer (2*R*,3*R*)-**3b** exhibits two well-resolved signals resonating at 6.06 and 6.48 ppm, while the minor diastereoisomer (2*S*,3*S*)-**3b** shows two sets of signals at 6.28 and 6.45 ppm.

[7]) The major diastereoisomer (1*R*,2*R*)-**3c** exhibits a signal resonating at 1.15 ppm, while the minor diastereoisomer (1*S*,2*S*)-**3c** shows a signal at 1.20 ppm.

in 98% yield. The more reactive 2,3-dimethylbuta-1,3-diene (**2d**) gave constantly full conversion, even at low concentrations of catalyst. The diastereoselectivity was also constant at 82% d.e., with an optimum for 0.75–1.0 mol-equiv. of $TiCl_4$ (89–87% d.e.)[8]). Under these optimal conditions, pure (1*R*,2*R*)-**3d** (93%) and (1*S*,2*S*)-**3d** (5%) could be separated by chromatography.

In all cases, the absolute configuration of the main diastereoisomer was ascertained by reduction to the known corresponding diols (2*R*,3*R*)-**4b** [13], **4c** [14], and **4d** [15], respectively, with non-destructive removal of the chiral auxiliary, isolated in 92 to 98% yield by chromatography.

Conclusion. – $TiCl_4$ as chelating agent shows the best chemical as well as stereochemical efficiencies for the cycloaddition of dienophile (–)-**1** to cyclopenta-1,3-diene (**2a**). In the presence of 1 mol-equiv. of $TiCl_4$, high conversion (95–100%) and high diastereoselectivity (89–98%) was achieved for the [4 + 2] cycloaddition of (–)-**1** to cyclohexa-1,3-diene (**2b**), isoprene (**2c**), and 2,3-dimethylbuta-1,3-diene (**2d**) in CH_2Cl_2 at –78° for 20 h. The absolute configurations of the main cycloadducts may be rationalized by attack of the dienes on the C(α)-*re* face of the mono- or di-chelated bis-SO_2/C=O *syn*,bis-C=O/C=C s-*cis* conformer of (–)-**1**, as previously proposed for simple *N*-acryloyl and *N*-crotonoylbornane-10,2-sultams [2] [11]. The cycloadditions of dienophiles derived from nonsymmetrical *O*-alkylfumaroyl-*N*-bornane-10,2-sultams will be presented in due course.

Financial support from the *Polish Academy of Sciences* and from the University of Warsaw (BST562/18/97) is gratefully acknowledged.

Experimental Part

General. See [16]. Standard deviation for ^{1}H-NMR determination: 2%.

*(–)-*N,N'*-Fumaroylbis[(2*R*)-bornane-10,2-sultam]* (= *(–)-1,1'-[(*E*)-1,4-Dioxobut-2-ene-1,4-diyl]bis[(3a*S*,6*R*,7a*R*)-1,4,5,6,7,7a-hexahydro-8,8-dimethyl-3*H*-3a,6-methano[2,1]benzisothiazole] 2,2,2',2'-Tetraoxide*; (–)-**1**). To a suspension of NaH (50% in mineral oil; 300 mg, 6.25 mmol) in dry toluene (50 ml) under Ar at –5°, a soln. of (2*R*)-bornane-10,2-sultam (1.3 g, 6.05 mmol) in toluene (15 ml) was added slowly. After 30 min, a soln. of fumaroyl chloride (0.33 ml, 3.05 mmol) in toluene (15 ml) was added dropwise within 1 h, and the resulting mixture was stirred overnight at 20°. MeOH (5 ml) and then H_2O (20 ml) were added, and the aq. phase was extracted with toluene (2 × 10 ml). The org. phase was washed successively with H_2O (20 ml) and $NaHCO_3$ (20 ml) soln., dried, and evaporated. The crude material was crystallized from CH_2Cl_2/hexane: pure (–)-**1** (66%). M.p. 247–248°. $[\alpha]_D^{20} = -135.6$ (*c* = 1.18, $CHCl_3$). IR: 2990, 1710, 1340, 1140, 1050. ^{1}H-NMR: 0.98 (*s*, 6 H); 1.15 (*s*, 6 H); 1.13–1.50 (*m*, 4 H); 1.82–2.0 (*m*, 6 H); 2.08–2.18 (*m*, 4 H); 3.49 (*AB*, *J* = 13.8, 4 H); 3.95 (*t*, *J* = 6.8, 2 H); 7.63 (*s*, 2 H). ^{13}C-NMR: 19.7 (C(9)); 20.6 (C(8)); 26.2 (C(5)); 32.7 (C(6)); 38.1 (C(3)); 44.6 (C(4)); 47.8 (C(7)); 48.7 (C(1)); 52.9 (C(10)); 65.1 (C(2)); 132.5 (C=C); 162.2 (CO). HR-MS: 510.1855 ($C_{24}H_{34}N_2O_6S_2^+$, $M^{+\cdot}$; calc. 510.1858), 446.2239 ($C_{24}H_{34}N_2O_4S^+$, $[M - SO_2]^+$; calc. 446.2239).

General Procedure for the Cycloadditions. To a soln. of (–)-**1** (51 mg, 0.1 mmol) in CH_2Cl_2 (2 ml), 1M *Lewis* acid soln. (0.025–0.25 ml, 0.025–0.25 mmol) was added. The mixture was cooled to –78° and 5M precooled diene soln. (2 ml, 1 mmol) was added dropwise and slowly along the inside cold wall of the reaction flask. After 4–20 h, the reaction was quenched with NH_4F and equilibrated. After addition of H_2O, the mixture was extracted with CH_2Cl_2 and the extract dried ($MgSO_4$) and evaporated under medium, then high vacuum. Conversion was measured by ^{1}H-NMR analysis. Pure material was obtained after chromatography (SiO_2, hexane/AcOEt 7:3 to 6:4).

General Procedure for the Reduction. A soln. of diastereoisomerically pure cycloadduct **3** (0.25 mmol) in THF (1 ml) was added to a suspension of $LiAlH_4$ (19 mg, 0.5 mmol) in THF (1 ml). After 1 h at 20°, the reaction was

[8]) The major diastereoisomer (1*R*,2*R*)-**3d** exhibits a signal resonating at 1.15 ppm, while the minor diastereoisomer (1*S*,2*S*)-**3d** shows a signal at 1.20 ppm.

quenched with NH_4Cl, the mixture filtered over *Celite*, and the filtrate evaporated and purified by chromatography (SiO_2, hexane/AcOEt 7:3 to 6:4): **4** besides (2*R*)-bornane-10,2-sultam.

*1,1'-{[(2*R*,3*R*)-Bicyclo[2.2.2]oct-5-ene-2,3-diyl]dicarbonyl}bis[(3a*S*,6*R*,7a*R*)-1,4,5,6,7,7a-hexahydro-8,8-dimethyl-3*H*-3a,6-methano[2.1]benzisothiazole] 2,2,2',2'-Tetraoxide* ((2*R*,3*R*)-**3b**). Obtained in 98% yield from (−)-**1**, using 2.0 mol-equiv. of $TiCl_4$. M.p. 311–313° (CH_2Cl_2/hexane). $[\alpha]_D^{20} = -165.53$ ($c = 1.01$, $CHCl_3$). IR: 2958, 2880, 1691, 1460, 1414, 1334, 1211, 1135, 1068, 999, 780, 687, 547, 535, 501, 437. ^{1}H-NMR: 0.97 (*s*, 6 H); 1.10 (*m*, 2 H); 1.17 (*s*, 3 H); 1.18 (*s*, 3 H); 1.25–1.40 (*m*, 6 H); 1.48 (*m*, 2 H); 1.80–1.95 (*m*, 6 H); 1.95–2.15 (*m*, 4 H); 3.09 (*m*, 2 H); 3.45 (*m*, 4 H); 3.72 (*m*, 1 H); 3.85–3.95 (*m*, 1 H); 6.06 (*t*, $J = 7$, 1 H); 6.49 (*t*, $J = 7$, 1 H). ^{13}C-NMR: 19.1 (*q*); 19.9 (*q*); 20.7 (*q*); 20.8 (*q*); 24.8 (2*t*); 26.4 (2*t*); 32.7 (*t*); 33.7 (*t*); 34.7 (2*d*); 38.4 (*t*); 38.7 (*t*); 44.5 (*d*); 44.6 (*d*); 45.0 (*d*); 45.8 (*d*); 47.7 (2*s*); 48.2 (2*s*); 53.1 (2*t*); 65.15 (*d*); 65.2 (*d*); 130.7 (*d*); 135.2 (*d*); 171.9 (*s*); 172.5 (*s*). HR-MS: 590.248805 ($C_{30}H_{42}N_2O_6S_2^+$, $M^{+\cdot}$; calc. 590.24842). MS: 590 (1.5, $M^{+\cdot}$), 526 (1), 511 (27), 375 (33), 348 (72), 311 (10), 296 (100), 284 (5), 270 (17), 233 (17), 150 (18), 135 (88), 107 (22), 93 (19), 79 (15).

*1,1'-{[(1*R*,2*R*)-4-Methylcyclohex-4-ene-1,2-diyl]dicarbonyl}bis[(3a*S*,6*R*,7a*R*)-1,4,5,6,7,7a-hexahydro-8,8-dimethyl-3*H*-3a,6-methano[2.1]benzisothiazole] 2,2,2',2'-Tetraoxide* ((1*R*,2*R*)-**3c**). Obtained in 98% yield from (−)-**1**, using 2.0 mol-equiv. of $TiCl_4$. M.p. 249–251° (CH_2Cl_2/hexane). $[\alpha]_D^{20} = -157.64$ ($c = 1.01$, $CHCl_3$). IR: 2960, 2882, 1695, 1483, 1457, 1414, 1333, 1266, 1210, 1136, 1115, 1069, 996, 813, 764, 609, 550, 536, 500, 435. ^{1}H-NMR: 0.95 (*s*, 3 H); 0.96 (*s*, 3 H); 1.13 (*s*, 3 H); 1.155 (*s*, 3 H); 1.25–1.40 (*m*, 4 H); 1.64 (*s*, 2 H); 1.66 (*s*, 3 H); 1.8–1.9 (*m*, 6 H); 1.95–2.15 (*m*, 6 H); 2.52 (*dd*, $J = 4.5$, 15, 1 H); 2.65 (*m*, 1 H); 3.5–3.59 (*m*, 4 H); 3.93 (*ddd*, $J = 4.5$, 8.5, 12.5, 2 H); 5.37 (*d*, $J = 5$, 1 H). ^{13}C-NMR: 19.9 (*q*); 19.91 (*q*); 20.86 (*q*); 20.93 (*q*); 23.0 (*q*); 26.44 (2*t*); 29.23 (*t*); 32.8 (2*t*); 33.6 (*t*); 38.5 (2*t*); 42.7 (*d*); 43.1 (*d*); 44.6 (2*d*); 47.7 (2*s*); 48.3 (2*s*); 53.1 (2*t*); 65.0 (*d*); 65.1 (*d*); 119.3 (*d*); 132.4 (*s*); 174.0 (*s*); 174.1 (*s*). HR-MS: 578.248529 ($C_{29}H_{42}N_2O_6S_2^+$, $M^{+\cdot}$; calc. 578.24842). MS: 578 (0.5, $M^{+\cdot}$), 363 (100), 335 (54), 271 (17), 244 (48), 165 (25), 152 (41), 135 (72), 121 (28), 107 (17), 93 (36).

*1,1'-{[(1*R*,2*R*)-4,5-Dimethylcyclohex-4-ene-1,2-diyl]dicarbonyl}bis[(3a*S*,6*R*,7a*R*)-1,4,5,6,7,7a-hexahydro-8,8-dimethyl-3*H*-3a,6-methano[2.1]benzisothiazole] 2,2,2',2'-Tetraoxide* ((1*R*,2*R*)-**3d**). The major diastereoisomer was obtained in 93% yield from (−)-**1**, using 0.75 mol-equiv. of $TiCl_4$. M.p. 158–160°. $[\alpha]_D^{20} = -173.82$ ($c = 1.02$, $CHCl_3$). IR: 2960, 2883, 1693, 1334, 1211, 1136, 1114, 990, 760, 547, 534. ^{1}H-NMR: 0.96 (*s*, 6 H); 1.155 (*s*, 6 H); 1.25–1.40 (*m*, 4 H); 1.60 (*s*, 6 H); 1.80–1.90 (*m*, 6 H); 2.0–2.12 (*m*, 6 H); 2.50 (*d*, $J = 8$, 2 H); 3.47 (*s*, 6 H); 3.93 (*dd*, $J = 2.5$, 4, 2 H). ^{13}C-NMR: 18.7 (*q*); 19.9 (*q*); 20.9 (*q*); 26.4 (*t*); 32.7 (*t*); 35.0 (*t*); 38.4 (*t*); 43.3 (*d*); 44.6 (*d*); 47.7 (*s*); 48.3 (*s*); 53.0 (*t*); 65.0 (*d*); 124.1 (*s*); 173.9 (*s*). HR-MS: 592.25421 ($C_{30}H_{44}N_2O_6S_2^+$, $M^{+\cdot}$; calc. 592.26408). MS: 592 (1, $M^{+\cdot}$), 528 (1), 377 (75), 349 (60), 244 (19), 179 (20), 152 (21), 135 (69), 106 (100), 93 (25).

*Cycloadduct (1*S*,2*S*)-***3d***.* The minor diastereoisomer was obtained in 5% yield from (−)-**1**, using 1.0 mol-equiv. of $TiCl_4$. M.p. 326–328°. $[\alpha]_D^{20} = +5.83$ ($c = 1.02$, $CHCl_3$). IR: 2990, 2960, 2886, 1688, 1454, 1411, 1394, 1333, 1135, 990, 762, 545, 534. ^{1}H-NMR: 0.965 (*s*, 6 H); 1.20 (*s*, 6 H); 1.25–1.45 (*m*, 6 H); 1.61 (*s*, 6 H); 1.18 (*m*, 2 H); 1.85–1.95 (*m*, 4 H); 2.0–2.1 (*m*, 4 H); 2.1–2.2 (*m*, 2 H); 2.54 (*d*, $J = 8.5$, 2 H); 3.40 (*d*, $J = 7$, 2 H); 3.50 (*d*, $J = 7$, 2 H); 3.85 (*dd*, $J = 3.5$, 4, 2 H). ^{13}C-NMR: 18.6 (*q*); 19.9 (*q*); 20.6 (*q*); 26.3 (*t*); 32.8 (*t*); 34.3 (*t*); 38.5 (*t*); 44.5 (*d*); 44.7 (*d*); 47.76 (*s*); 48.5 (*s*); 52.9 (*t*); 65.2 (*d*); 123.8 (*s*); 174.2 (*s*). HR-MS: 592.2636 ($C_{30}H_{44}N_2O_6S_2^+$; calc. 592.26408). MS: 592 (1, $M^{+\cdot}$), 377 (36), 349 (55), 285 (15), 244 (19), 152 (17), 135 (53), 106 (100), 93 (21).

*(2*R*,3*R*)-Bicyclo[2.2.2]oct-5-ene-2,3-dimethanol* ((2*R*,3*R*)-**4b**). Obtained in 98% yield from (2*R*,3*R*)-**3b**. $[\alpha]_D^{20} = +81.1$ ($c = 0.845$, $CHCl_3$) ([13]: $[\alpha]_D^{20} = -93.8$ ($c = 0.56$, $CHCl_3$) for the enantiomer). Analyses fully identical with those reported in [13].

*(1*R*,2*R*)-4-Methylcyclohex-4-ene-1,2-dimethanol* ((1*R*,2*R*)-**4c**). Obtained in 97% yield from (1*R*,2*R*)-**3c**. $[\alpha]_D^{20} = -78.13$ ($c = 0.32$, $CHCl_3$) ([15]: $\alpha_D^{20} = -78.8$). IR: 3296, 2965, 2915, 2887, 2827, 1474, 1452, 1439, 1378, 1153, 1129, 1075, 1047, 1003, 959, 778, 725, 665, 503, 477. ^{1}H-NMR: 1.25 (*m*, 2 H); 1.65 (*s*, 3 H); 1.66 (*m*, 2 H); 1.83 (*m*, 2 H); 3.00 (br. *s*, 2 H, OH); 3.59 (*ddd*, $J = 1.5$, 7.0, 11.0, 2 H); 3.73 (*ddd*, $J = 3.5$, 6.0, 10.0, 2 H); 5.35 (*d*, $J = 3.5$, 1 H). ^{13}C-NMR: 23.3 (*Me*–C(4)); 28.8 (C(6)); 33.5 (C(3)); 39.7 (C(1) or C(2)); 40.2 (C(2) or C(1)); 66.3 (OCH_2–C(1) or –(2)); 66.4 (OCH_2–C(2) or –C(1)); 120.0 (C(5)); 133.2 (C(4)). HR-MS: 138.204465 ($C_9H_{14}O^+$; $[M - H_2O]^+$; calc. 138.21133). MS: 138 (15, $M^{+\cdot}$), 120 (14), 107 (100), 91 (42), 79 (30), 67 (12), 55 (8), 41 (9).

*(1*R*,2*R*)-4,5-Dimethylcyclohex-4-ene-1,2-dimethanol* ((1*R*,2*R*)-**4d**). Obtained in 95% yield from (1*R*,2*R*)-**3d**. $[\alpha]_D^{20} = -67.7$ ($c = 0.4$, $CHCl_3$) ([15]: $\alpha_D^{22} = -67.5$). Analyses fully identical with those reported in [15].

REFERENCES

[1] T. Bauer, C. Chapuis, J. Kozak, J. Jurczak, *Helv. Chim. Acta* **1989**, *72*, 482.

[2] C. Chapuis, P. Rzepecki, T. Bauer, J. Jurczak, *Helv. Chim. Acta* **1995**, *78*, 145.

[3] H. Kansui, S. Hiraoka, T. Kunieda, *J. Am. Chem. Soc.* **1996**, *118*, 5346; J. C. Adrian, T. Ovitt, *Tetrahedron: Asymmetry* **1996**, *7*, 2407; T. Saito, H. Fujii, S. Hayashibe, T. Matsushita, H. Kato, K. Kobayashi, *J. Chem. Soc., Perkin Trans. 1* **1996**, 1897; J. Aub, S. Ghosh, M. Tanol, *J. Am. Chem. Soc.* **1994**, *116*, 9009; H. Waldmann, M. Weigerding, C. Dreisbach, C. Wandrey, *Helv. Chim. Acta* **1994**, *77*, 2111.

[4] J. Jurczak, T. Bauer, C. Chapuis, 'Houben-Weyl, Stereoselective Synthesis', Eds. G. Helmchen, R. W. Hoffmann, J. Mulzer, and E. Schaumann, Thieme Verlag, Stuttgart, 1995, Vol. E21c, p. 2735, 2905.

[5] L. M. Tolbert, M. B. Ali, *J. Am. Chem. Soc.* **1981**, *103*, 2104; *ibid.* **1982**, *104*, 1742; *ibid.* **1984**, *106*, 3806; *ibid.* **1985**, *107*, 4589; K. Furuta, K. Iwanaga, H. Yamamoto, *Tetrahedron Lett.* **1986**, *27*, 4507.

[6] C. Chapuis, J. Y. de Saint Laumer, M. Marty, *Helv. Chim. Acta* **1997**, *80*, 146.

[7] G. Bernardinelli, C. Chapuis, A. J. Kingma, M. Wills, *Helv. Chim. Acta* **1997**, *80*, 1607.

[8] D. Horton, T. Machinami, *J. Chem. Soc., Chem. Commun.* **1981**, 88; D. Horton, T. Machinami, Y. Takagi, *Carbohydr. Res.* **1983**, *121*, 135; S. Takano, A. Kurotaki, K. Ogasawara, *Synthesis* **1987**, 1075; S. Saito, H. Hama, Y. Matsuura, K. Okada, T. Moriwake, *Synlett* **1991**, 819.

[9] W. Oppolzer, C. Chapuis, G. Mao Dao, D. Reichlin, T. Godel, *Tetrahedron Lett.* **1982**, *23*, 4781.

[10] C. Cataviela, J. Garcia, J. Gil, R. M. Martinez, J. A. Mayoral, L. Salvatella, J. Urieta, A. Mainar, M. Abraham, *J. Chem. Soc., Perkin Trans 2* **1997**, 653; C. Cataviela, J. I. Garcia, J. A. Mayoral, A. J. Royo, L. Salvatella, X. Assfeld, M. F. Ruiz-Lopez, *J. Phys. Org. Chem.* **1992**, *5*, 230; T. Poll, G. Helmchen, B. Bauer, *Tetrahedron Lett.* **1984**, *25*, 2191.

[11] W. Oppolzer, C. Chapuis, G. Bernardinelli, *Helv. Chim. Acta* **1984**, *67*, 1397.

[12] W. Oppolzer, I. Rodriguez, J. Blagg, G. Bernardinelli, *Helv. Chim. Acta* **1989**, *72*, 123.

[13] Y. N. Ito, X. Ariza, A. K. Beck, A. Bohac, C. Ganter, R. E. Gawley, F. N. M. Kühnle, T. Tuluja, Y. M. Wang, D. Seebach, *Helv. Chim. Acta* **1994**, *77*, 2071.

[14] J. Jurczak, *Bull. Chem. Soc. Jpn.* **1979**, *52*, 3438; H. Suzuki, K. Mochizuki, T. Hattori, N. Takahashi, O. Tajima, T. Takiguchi, *ibid.* **1988**, *61*, 1999; H. M. Walborsky, L. Barash, T. C. Davis, *Tetrahedron* **1963**, *19*, 2333.

[15] E. R. Galan, M. J. Chamizo, J. Serrano, *Tetrahedron Lett.* **1993**, *34*, 1811; K. Maruoka, M. Akakura, S. Saito, T. Ooi, H. Yamamoto, *J. Am. Chem. Soc.* **1994**, *116*, 6153.

[16] T. Bauer, C. Chapuis, J. Kiegel, J. Krajewski, K. Piechota, Z. Urbancyk-Lipkowska, J. Jurczak, *Helv. Chim. Acta* **1996**, *79*, 1059.

Received November 21, 1997