Asymmetric Induction in the Diels-Alder Reaction of Chiral (2*S*)-2-(*tert*-Butyl)-5-methylene-1,3-dioxolan-4-one[1)]

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Received August 1, 1988

Keywords: Asymmetric induction / Diels-Alder reaction / 1,3-Dioxolan-4-one, (2*S*)-2-(*tert*-butyl)-5-methylene-

The Diels-Alder reaction of the cyclic methylene compound **3** with cyclopentadiene at ambient temperature leads to the adducts **4** and **5** with more than 95% *face* and more than 96% *exo* selectivity. The structure of the products has been verified by chemical correlation as well as by X-ray diffraction analysis of the Diels-Alder adduct **4**. The mixture of **4** and **5** was converted to optically active (+)-norbornenone **12**. *face* Selectivity was dramatically decreased by Lewis acid catalysis with $TiCl_2(iPrO)_2$ or $AlEtCl_2$ at lower temperatures.

Asymmetrische Induktion in der Diels-Alder-Reaktion von (2*S*)-2-*tert*-Butyl-5-methylen-1,3-dioxolan-4-on[1)]

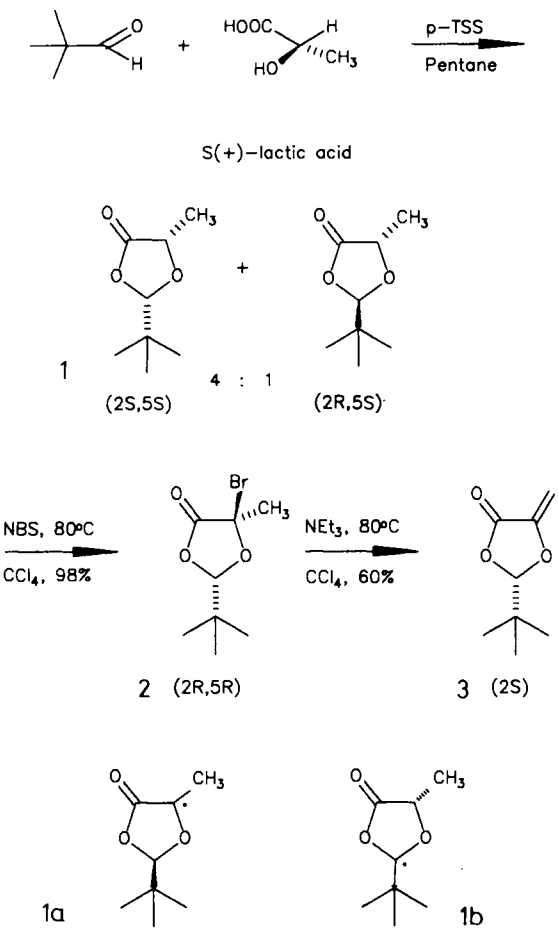
Die Diels-Alder-Reaktion der Methylenverbindung **3** mit Cyclopentadien bei Raumtemperatur führt zu den Addukten **4** und **5** mit mehr als 95proz. Seitendifferenzierung und 96proz. *exo*-Selektivität. Die Struktur der Produkte wurde sowohl durch chemische Folgereaktionen als auch durch eine Röntgenstrukturanalyse von **4** bestimmt. Eine Mischung aus **4** und **5** wurde zum optisch aktiven (+)-Norbornenon **12** abgebaut. Katalyse mit $TiCl_2(iPrO)_2$ sowie $AlEtCl_2$ bei niedrigen Temperaturen verringert dramatisch die Seitendifferenzierung.

The Diels-Alder reaction is one of the most investigated areas of asymmetric synthesis[2)]. The achievement of high asymmetric induction normally requires Lewis-acid catalysts and low temperatures[3)]. For example, the degree of asymmetric induction observed in the Diels-Alder reactions of chiral acrylates is large only when the cycloadditions are promoted by Lewis acids, while the corresponding thermal reactions occur with only modest stereoselectivities. Only very few examples are known where high asymmetric induction was achieved under thermal conditions[4)].

We now report on a highly asymmetric Diels-Alder reaction which neither requires catalysts nor low temperatures. Starting from our concept of "Captodative Olefins in Normal and Inverse Diels-Alder Reactions"[5)] we synthesized **3** as a chiral olefin bearing the c,d-substituents in the ring. Olefin **3** was expected to undergo a π-*face* selective cycloaddition with cyclopentadiene. In contrast to chiral acrylates where Lewis acid complexation is essential to reach high ee's, conformational restriction is intrinsic to the dioxolanone moiety. Olefin **3** was also synthesized independently by Seebach and Zimmermann[6)].

Bromination of the dioxolanone **1** [from pivalaldehyd and (S)-(+)-lactic acid, separation of the main isomer by means of two recrystallizations, d.e. = 92%][7)] with NBS in refluxing CCl_4 gave **2** in nearly quantitative amounts. NMR measurements of **2** revealed that only one isomer was formed. Subsequent dehydrohalogenation under standard conditions (NEt_3, CCl_4, reflux) leads to **3** in good yields. The exclusive formation of **2** is due to the greater stability of **1a** compared to **1b**. The α-centered radical is stabilized both by the electron-donating ether group and the electron – withdrawing carboxy substituent. Similar effects have been

Scheme 1



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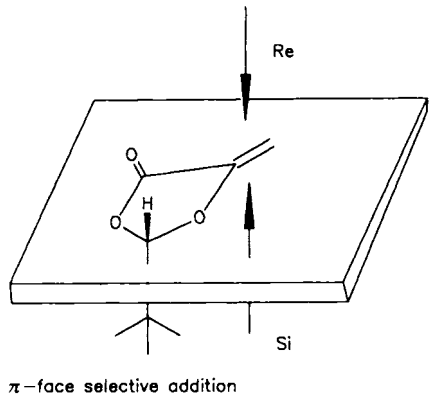
observed with the NBS bromination of amido carboxy-substituted valine derivates[8].

Cycloaddition of 3 to Cyclopentadiene

Compound **3** was treated with an excess of cyclopentadiene at room temperature. After three days at room temperature the Diels-Alder adducts were isolated in 86% yield. NMR analyses revealed that only two isomeric adducts had been formed in a ratio of 96:4 (Scheme 2). Several recrystallizations of the mixture in Et_2O/Pentane at $-30^\circ C$ leads to a small amount of pure **4** $[\alpha]_D^{25} = 148.6$ ($c = 0.88$, $CHCl_3$). The structure of **4** has been verified by X-ray analysis (Figure 1). The crystal contains two independent molecules of the same enantiomer. They differ only marginally in the conformation of the heterocyclic five-membered ring (difference of the endocyclic torsional angles $0.8-4.7^\circ$).

Scheme 2



Treatment of the crude mixture of the adducts **4** and **5** with $LiAlH_4$ (LAH) afforded the alcohols **8** and **9**. The NMR analysis revealed a 96.5:3.5 ratio of the *exo/endo*-(hydroxymethyl)norbornenes. Removal of **9** by crystallization leads to optically active (1*R*,2*R*)-2-hydroxybicyclo[2.2.1]hept-5-ene-2-methanol (**8**), $[\alpha]_D^{22} = 117.8$ ($c = 2.75$, $CHCl_3$) in 64% yield. Optical rotation, melting point, and NMR spectra are

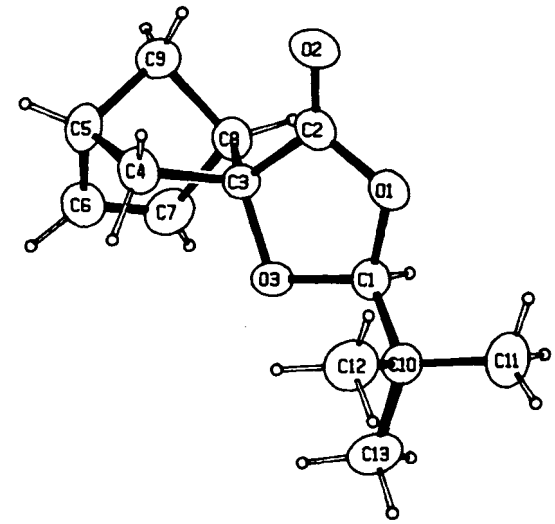
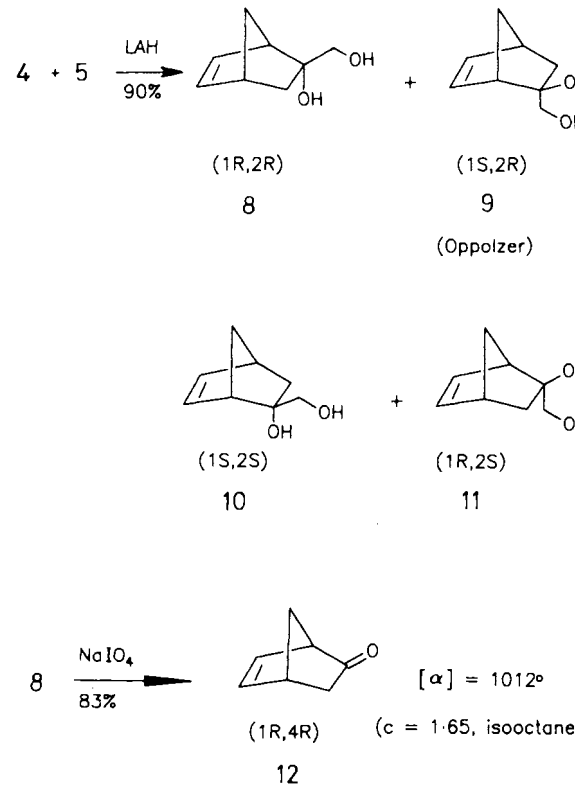


Figure 1. ORTEP plot of one independent molecule of **4**. (The size of the ellipsoids represents a 33% probability.) The absolute configuration was assigned by chemical correlation

different from the (1*S*,2*R*)-isomer described by Oppolzer et al.[3a]. The stereochemical identity of the alcohol was confirmed by conversion of **8** into the corresponding norbornenone **12** of known absolute configuration. Oxidative cleavage with buffered $NaIO_4$[9] gave the (+)-enantiomer of ketone **12** having $[\alpha]_D^{22} = 1012$ ($c = 1.65$, isooctane). The rotation value indicates about 90% enantiomeric excess[10], which, considering the optical purity of the starting material, points to a selectivity in excess of 95% for the Diels-Alder reaction.

Scheme 3



In order to examine the influence of Lewis acid catalysis were carried out the experiments with $TiCl_2(iPrO)_2$ as catalyst at −20°C. The cycloaddition showed an increace in *endo/exo* selectivity but a dramatic decrease in *π-face* selectivity. Workup furnished adducts **4**, **5**, and **6** in a ratio of 59:1:40 (62% yield). Reduction of this mixture with LAH afforded the alcohols **8** + **10**:**9** (ratio 98.5:1.5 as determined by NMR and GC) in 90% isolated yield (Scheme 3). Similar results were obtained with $AlEtCl_2$ at −20°C as catalyst.

The influence of high temperatures was demonstrated by performing the cycloaddition of **3** and cyclopentadiene at 140°C in a sealed ampoule. After 4 h a 87:8:5 mixture (65%) of adducts **4**, **5**, and **6** is obtained. These results are summarized in Table 1.

Table 1. Additions of **3** to cyclopentadiene

Entry	Catalyst	*T*/°C	*t*/h	Yield/%	4:5:6[a]
1	none	25	72	86	96 4 –
2	none	140	4	65	87 8 5
3	$TiCl_2(iPrO)_2$[b]	−20	24	62	59 1 40
4	$EtAlCl_2$[c]	−20	16	34	63 3 34

[a] Ratios were determined by ^1H or ^{13}C NMR. – [b] 1.5 equiv. of catalyst was used with respect to **3**. – [c] 1 equiv. of catalyst was used with respect to **3**.

The results reported demonstrate that preparatively easily accessible methylenedioxolanone can be effectively used in thermal asymmetric Diels-Alder reactions. Neither Lewis acid nor low temperatures are required to obtain high diastereoselectivities.

Financial support by the *Deutsche Forschungsgemeinschaft* and the *Fonds der Chemischen Industrie* is gratefully acknowledged. J. Me. thanks the *Land Nordrhein-Westfalen* for a predoctoral fellowship (Graduiertenförderung). We are indebted to Dr. *J. Runsink* for the NMR analyses of the products and we also thank the *Bayer AG* for generous contributions of materials and experimental equipment as well as the *Ruhrchemie AG* (Oberhausen) for pivalaldehyde.

Experimental

All temperatures quoted are uncorrected. – IR spectra: Perkin-Elmer 1700. – NMR spectra: Varian VXR 300 (TMS as internal standard). – MS: Varian Mat 212, 70 eV, 250°C. – GC: Siemens Sichromat 3, integrator Spectra Physics 4290, capillary column HP ultra 2. – Column chromatography: SiO_2 (Merck, Kieselgel 60). – Optical rotations: Perkin-Elmer 241 polarimeter.

X-ray Crystal Structure Analysis of the Spirocyclic Compound **4**: Crystal data: $C_{13}H_{18}O_3$, molecular mass 222.3, monoclinic, space group $P2_1$, a = 12.800(3), b = 6.193(3), c = 16.130(5) Å, β = 100.51(3)°, Z = 4 (two independent molecules), $d_{calc.}$ = 1.17 g · cm^{-3}, μ (Mo-K_α) = 0.8 cm^{-1}.

Data collection: crystal size 0.5 × 0.6 × 0.5 mm; Enraf-Nonius diffractometer, monochromatized Mo-K_α radiation, 1941 independent reflexions in the range of 2.00 ≤ Θ ≤ 23.00°, Θ/2Θ-scan, scan width (0.90 + 0.35 tanΘ)°, scan speed 1.67 to 4.0° min^{-1}.

Structure analysis and refinement[11]: Structure solution by direct methods, refinement by a full-matrix least-squares method. H atoms were included in refinement with a fixed B (9.0 for methyl H's, 6.0 for all others): 1728 reflexions with $I > 2\sigma(I)$, 397 variables, R = 0.039, $R_w = (\Sigma\Delta^2 F/\Sigma F_o^2)^{1/2}$ = 0.036, maximum shift/error rate 0.11.

Further details of the structure are deposited at the Fachinformationszentrum Energie Physik Mathematik, D-7514 Eggenstein-Leopoldshafen 2. These data are available with quotation of the registry number CSD-53269, the authors, and the reference to this publication.

Table 2. Positional parameters and U_{eq} values of the heavy atoms in **4**. Standard deviations are given in parentheses

Atom	x/a	y/b	z/c	U_{eq} [Å^2]
O1	0.6572(2)	0.8537(5)	1.0389(1)	0.054(1)
O2	0.5690(2)	0.5614(6)	0.9860(2)	0.070(1)
O3	0.7066(2)	0.9893	0.9217(1)	0.054(1)
C1	0.6985(3)	1.0449(8)	1.0047(2)	0.049(1)
C2	0.6130(3)	0.7269(8)	0.9748(2)	0.050(1)
C3	0.6298(3)	0.8276(7)	0.8935(2)	0.044(1)
C4	0.6701(3)	0.6695(8)	0.8325(3)	0.060(1)
C5	0.5862(3)	0.6895(9)	0.7515(3)	0.066(1)
C6	0.5950(3)	0.9133(9)	0.7192(2)	0.064(1)
C7	0.5599(3)	1.0440(8)	0.7710(3)	0.064(1)
C8	0.5238(3)	0.9124(8)	0.8400(2)	0.052(1)
C9	0.4856(3)	0.7085(9)	0.7894(3)	0.065(1)
C10	0.8038(3)	1.1092(8)	1.0566(2)	0.053(1)
C11	0.7868(4)	1.1725(12)	1.1439(3)	0.096(2)
C12	0.8832(3)	0.9275(10)	1.0602(3)	0.081(2)
C13	0.8449(4)	1.3044(10)	1.0135(3)	0.079(2)
O1'	0.8905(2)	0.8196(6)	0.4883(2)	0.064(1)
O2'	1.0448(2)	0.7888(7)	0.5785(2)	0.088(1)
O3'	0.7844(2)	0.9257(5)	0.5775(1)	0.054(1)
C1'	0.7900(3)	0.9187(8)	0.4913(2)	0.053(1)
C2'	0.9539(3)	0.8441(9)	0.5639(3)	0.062(1)
C3'	0.8903(3)	0.9514(7)	0.6227(2)	0.048(1)
C4'	0.9044(3)	0.8534(8)	0.7110(3)	0.060(1)
C5'	0.9416(3)	1.0468(9)	0.7693(2)	0.064(1)
C6'	0.8494(3)	1.2006(9)	0.7591(2)	0.064(1)
C7'	0.8377(3)	1.2826(8)	0.6840(3)	0.059(1)
C8'	0.9242(3)	1.1908(8)	0.6416(2)	0.055(1)
C9'	1.0134(3)	1.1584(9)	0.7168(3)	0.072(1)
C10'	0.6991(3)	0.7963(8)	0.4404(2)	0.057(1)
C11'	0.7123(4)	0.7970(13)	0.3485(3)	0.100(2)
C12'	0.6948(4)	0.5692(10)	0.4721(4)	0.096(2)
C13'	0.5957(4)	0.9115(10)	0.4477(3)	0.080(2)

(2R,5R)-5-Bromo-2-tert-butyl-5-methyl-1,3-dioxolan-4-one (**2**): A solution of 25 g (158 mmol) of dioxolanone **1**[7] (diastereomeric purity 96%) and 28 g (158 mmol) of NBS in 200 ml CCl_4 was heated unter reflux for 2 h. After filtration and evaporation of the solvent a semisolid mass is obtained, which is purified by recrystallization in Et_2O/Pentane (36.7 g, 98%), m.p. 47°C, $[\alpha]_D^{27}$ = 226.4 (c = 1.51, $CHCl_3$). – IR ($CHCl_3$): 3530–3280 cm^{-1} (br.), 2980, 2940, 2920, 2880, 1820, 1485, 1370, 1260, 1215, 1140, 1070, 965, 910, 650, 635, 500. – ^1H NMR (C_6D_6): δ = 0.67 (s, 9H), 1.87 (s, 3H), 4.98 (s, 1H). – ^{13}C NMR (C_6D_6): δ = 23.0, 26.9, 33.3, 89.7, 107.7, 166.8. – MS: no M$^{+\cdot}$, *m/z* (%) = 194 (1), 192 (1), 181 (2), 179 (2), 157 (6), 129 (14), 100 (15), 87 (31), 70 (16), 57 (58), 55 (10), 43 (100), 41 (22).

$C_8H_{13}BrO_3$ (237.1) Calcd. C 40.53 H 5.53
Found C 38.73 H 5.58

(2S)-2-tert-Butyl-5-methylene-1,3-dioxolan-4-one (**3**): To 36.7 g (155 mmol) of **2** in 300 ml of CCl_4 was added 24 g (237 mmol) of NEt_3. The mixture was heated under reflux for 4 h, then filtered and evaporated. The residue was distilled and furnished **3** (14.5 g, 60%), b.p. 59–60°C/6 Torr, $[\alpha]_D^{24}$ = −14.9 (c = 1.52, $CHCl_3$). – IR ($CDCl_3$): 3010 cm^{-1}, 2975, 2940, 2880, 1800, 1670, 1485, 1305, 1130, 990. – ^1H NMR ($CDCl_3$): δ = 0.98 (s, 9H), 4.84 (d, J = 2.7 Hz, 1H), 5.09 (d, J = 2.7 Hz, 1H), 5.47 (s, 1H). – ^{13}C NMR: δ = 22.8, 35.9, 90.6, 109.5, 144.6, 162.6. – MS: *m/z* (%) = 156 (1, M$^{+\cdot}$), 86 (5), 71 (8), 57 (100), 43 (24), 42 (22), 41 (37).

$C_8H_{12}O_3$ (156.2) Calcd. C 61.52 H 7.74
Found C 61.61 H 7.79

Thermal Diels-Alder Reaction of **3** *to Cyclopentadiene* (*Method A*, see Table 1, Entry 1): A mixture of 0.78 g (5.0 mmol) of **3** and 1.65 g (25 mmol) of freshly distilled cyclopentadiene was stirred under Argon for 6 h at room temperature. Another portion of 1.65 g (25 mmol) cyclopentadiene was added, and stirring was continued for additional 66 h. After consumption of **3** (according to GC) dicyclopentadiene was removed by evaporation (b.p. 40 °C/0.2 Torr). The residue was purified by chromatography (30 g SiO_2, 1. 100 ml Hexane, 2. 100 ml CH_2Cl_2) to give adducts **4** and **5** (0.95 g, 86%). Isomeric ratio 96:4 according to ^{13}C NMR. Analytical data for the mixture. – IR ($CDCl_3$): 3560 cm^{-1}, 3070, 2980, 1790, 1370, 1175. – ^1H NMR (C_6D_5): δ = 0.80, 0.85 (s, 9H), 1.21 (dd, *J* = 4; 12.4 Hz, 1H), 1.37 (dm, *J* = 9 Hz, 1H), 2.02 (br. d, *J* = 9 Hz, 1H), 2.22 (dd, *J* = 3.6; 12.4 Hz, 1H), 2.55, 2.52 (br. s, 1H), 2.87, 2.72 (br. s, 1H), 4.81, 4.87 (s, 1H), 5.96, 5.92 (dd, *J* = 3.0; 5.5 Hz, 1H), 6.24, 6.15 (dd, *J* = 3.1; 5.6 Hz, 1H). – ^{13}C NMR (C_6D_6): δ = 23.2, 23.3; 34.3, 34.4; 39.7, 40.6; 42.1, 41.4; 47.0, 49.5; 48.7, 48.9; 85.4, 84.8; 107.2, 106.9; 132.9, 131.3; 139.9, 141.0; 175.7, 174.0. – MS: *m/z* (%) = 222 (1, $M^{+\cdot}$), 80 (2), 79 (2), 69 (7), 67 (5), 66 (100), 57 (4), 41 (6). $C_{13}H_{18}O_3$ (222.3) Calcd. C 70.25 H 8.16 Found C 70.00 H 8.27

A small amount of pure **4** could be obtained by successive recrystallizations of the mixture in Et_2O/Pentane at −30 °C. M.p. 53 °C, $[\alpha]_D^{24}$ = +148.6 (*c* = 0.87, $CHCl_3$).

After reduction (see below), GC and NMR showed a 96.5:3.5 mixture of alcohols **8** and **9**.

Method B (see Table 1, Entry 3): A solution of **3** (0.78 g, 5.0 mmol) in 5 ml of CH_2Cl_2 was treated with 7.5 ml of a 1 M solution of $TiCl_2(iPrO)_2$ in CH_2Cl_2 and 1.65 (25 mmol) of cyclopentadiene at −20 °C. Stirring at −20 °C was continued for 24 h. Workup gave **4**, **5**, and **6** (0.69 g, 62%). Isomeric ratio 59:1:40 (^{13}C NMR). No separation of isomers was possible by means of chromatographic methods. Isomers **4** and **5** were identified by comparison of the NMR of the adducts obtained by Method A. – NMR spectra of compound **6**: ^1H NMR (C_6D_6): δ = 0.82 (s, 9H), 1.20 (dd, *J* = 3.5; 12.5 Hz, 1H), 1.37 (dm, *J* = 9 Hz, 1H), 2.11 (br. d, *J* = 8.6 Hz, 1H), 1.96 (dd, *J* = 3.6; 12.4 Hz, 1H), 2.66 (br. s, 1H), 2.89 (br. s, 1H), 4.78 (s, 1H), 6.04 (dd, *J* = 3.0; 5.5 Hz, 1H), 6.21 (dd, *J* = 3.0; 5.6 Hz, 1H). – ^{13}C NMR (C_6D_6): δ = 23.3, 34.4, 40.0, 42.3, 47.3, 51.5, 84.6, 107.6, 133.5, 139.7, 176.1.

Reduction of this mixture (see below) furnished the two enantiomeric *exo*- and *endo*-norbornenemethanol derivates (**8** + **10**:**9**) in a 98.5:1.5 ratio, according to GC and ^{13}C NMR.

Method C (see Table 1, Entry 4): Olefin **3** was treated with 1.0 equiv. of $AlEtCl_2$ and cyclopentadiene as described above. After 16 h workup gave adducts **4**, **5**, **6** (0.38 g, 34%). The isomeric ratio (63:3:34) was determined by GC and NMR. The chemical shifts of the NMR spectra were identical with those obtained by Method B.

Method D (see Table 1, Entry 2): Heating of **3** (0.78 g, 5.0 mmol) and cyclopentadiene (3.30 g, 50 mmol) at 140 °C for 4 h in a sealed glass ampoule furnished **4**, **5**, and **6** (0.72 g, 65%). The ratio determined by NMR was 87:8:5.

Reduction of the Crude Adduct Mixtures

1. *Adducts obtained by Method A. (1R,2R)-2-Hydroxybicyclo[2.2.1]hept-5-ene-2-methanol* (**8**): The crude reaction mixture (0.97 g, 4.4 mmol) was stirred with $LiAlH_4$ (0.36 g, 9.5 mmol) in 20 ml of Et_2O at room temp. for 16 h. The reaction was quenched by addition of satd. aq. Na_2SO_4. Filtration, drying with $MgSO_4$, evaporation of the solvent, and chromatographic workup (Et_2O/EtOAc 1:1) furnished alcohols **8** and **9** in a 96.5:3.5 ratio (0.51 g, 82%). Two recrystallizations (Et_2O/Pentane) afforded pure **8** (0.39 g, 64%), m.p. 46.5 °C, $[\alpha]_D^{22}$ = 117.8 (*c* = 2.75, $CHCl_3$). – IR ($CDCl_3$): 3700 – 3100 cm^{-1} (br.), 3060, 2970, 2880, 1470, 1450, 1340, 1280, 910. – ^1H NMR ($CDCl_3$): δ = 1.04 (dd, *J* = 3.3; 12.5 Hz, 1H), 1.34 (d, *J* = 9 Hz, 1H), 1.43 (dm, *J* = 9 Hz, 1H), 1.61 (dd, *J* = 3.5; 12.5 Hz, 1H), 2.73 (br. s, 1H), 2.81 (br. s, 1H), 3.58 (d, *J* = 11.4 Hz, 1H), 3.64 (d, *J* = 11.4 Hz, 1H), 4.25 (br. s, 2H), 6.06 (dd, *J* = 3; 6 Hz, 1H), 6.29 (dd, *J* = 3; 6 Hz, 1H). – ^{13}C NMR ($CDCl_3$): δ = 40.8, 42.4, 48.6, 69.2, 81.9, 133.2, 140.0. – MS: *m/z* (%) = 140 (1, $M^{+\cdot}$), 122 (1), 109 (16), 81 (9), 79 (13), 78 (4), 77 (5), 74 (4), 67 (12), 66 (100), 65 (10).

$C_8H_{12}O_2$ (140.2) Calcd. C 68.55 H 8.63 Found C 68.57 H 8.68

2. *Adducts obtained by Method B*: The crude adducts obtained by the $TiCl_2(iPrO)_2$ promoted cycloaddition (1.00 g, 4.5 mmol) and successive reduction as described above gave a 98.5:1.5 mixture of alcohols **8** + **10**:**9** (0.57 g, 90%). The NMR data of the main isomer are identical with those described above.

(1R,4R)-Bicyclo[2.2.1]hept-5-en-2-one (**12**): $NaIO_4$ (0.93 g, 4.3 mmol) was dissolved in 10 ml of H_2O, and pH 7 buffer was added (Na_2HPO_4). To this mixture a solution of **8** (0.60 g, 4.3 mmol) in 8 ml of EtOH was given. Stirring was continued at room temp. for 3 h, then 20 ml of H_2O was added, and the solution was continously extracted with pentane for 2 days. The pentane extract was dried and distilled through a Vigreux column to remove solvent. The norbornenone was isolated by bulb-to-bulb distillation at 100 °C/50 Torr yielding 0.39 g (83%) of **12**. $[\alpha]_D^{22}$ = 1012 (*c* = 1.65, isooctane). – IR (neat): 3060 cm^{-1}, 2980, 2940, 1745, 1420, 1320, 1225, 1160, 1140, 1120, 1080, 990, 855, 770, 740, 710. – ^1H NMR ($CDCl_3$): δ = 1.83 (dd, *J* = 4.4; 16.5 Hz, 1H), 1.92 – 2.00 (m, 2H), 2.20 (m, 1H), 3.00 (m, 1H), 3.19 (br. s, 1H), 6.11 (m, 1H), 6.56 (dd, *J* = 2.5; 5.5 Hz, 1H). – ^{13}C NMR ($CDCl_3$): δ = 37.2, 40.1, 50.9, 55.8, 130.6, 143.1, 215.5.

CAS Registry Numbers

1: 81037-06-1 / **2**: 116635-37-1 / **3**: 113304-16-8 / **4**: 116635-38-2 / **5**: 116697-42-8 / **6**: 116697-43-9 / **8**: 116697-44-0 / **9**: 82729-79-1 / **10**: 82729-80-4 / **12**: 16346-63-7 / cyclopentadiene: 542-92-7

[1] Part 6 of "*Thermal Reactions of Donor-Acceptor Systems*". For part 5 see: J. Mattay, K. Buchkremer, *Heterocycles* **27** (1988) 2153.

[2] [2a] W. Oppolzer, *Angew. Chem.* **96** (1984) 840; *Angew. Chem. Int. Ed. Engl.* **23** (1984) 876. – [2b] R. J. Loncharich, T. R. Schwartz, K. N. Houk, *J. Am. Chem. Soc.* **109** (1987) 14.

[3] [3a] W. Oppolzer, C. Chapuis, D. Dupuis, M. Guo, *Helv. Chim. Acta* **68** (1985) 2100. – [3b] M. Yamauchi, T. Watanabe, *J. Chem. Soc., Chem. Commun.* **1988**, 27.

[4] [4a] R. M. Ortuno, M. Ballesteros, J. Corbera, F. Sanchez-Ferrando, J. Font, *Tetrahedron* **44** (1988) 1711. – [4b] B. L. Feringa, J. C. de Jong, *J. Org. Chem.* **53** (1988) 1127. – [4c] For Hetero Diels-Alder reactions see: L. F. Tietze in *Selectivity – A Goal for Synthetic Efficiency* (W. Bartmann, B. M. Trost, Eds.), Verlag Chemie, Weinheim 1984.

[5] J. Mertes, J. Mattay, *Helv. Chim. Acta* **71** (1988) 742.

[6] J. Zimmermann, D. Seebach, *Helv. Chim. Acta* **70** (1987) 1104.

[7] D. Seebach, R. Naef, G. Calderari, *Tetrahedron* **40** (1984) 1313.

[8] C. J. Easton, M. P. Hay, S. G. Love, *J. Chem. Soc., Perkin Trans. 1*, **1988**, 265.

[9] L. A. Paquette, C. W. Doecke, F. R. Kearney, A. F. Drake, S. F. Mason, *J. Am. Chem. Soc.* **102** (1980) 7228.

[10] D. J. Sandman, K. Mislow, *J. Org. Chem.* **33** (1968) 2924.

[11] All calculations were made with the Structure Determination Package (Enraf-Nonius, Delft) on a PDP 11/23-plus calculator.

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