

12. Complete π -Facial Stereoselectivity in the TiCl_4 -Mediated [4 + 2] Cycloaddition of Cyclopentadiene to *N,N'*-Fumaroyldi[(2*R*)-bornane-10,2-sultam]

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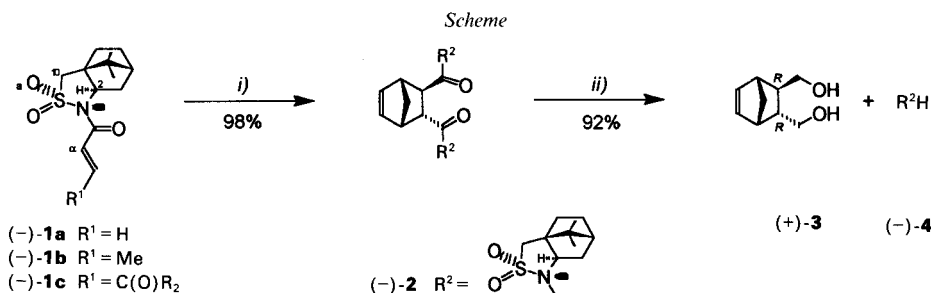
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Under the co-operative influence of two prosthetic groups, and independent of the TiCl_4 concentration, complete and constant diastereofacial π -selection was achieved during the [4 + 2] cycloaddition of cyclopentadiene to *N,N'*-fumaroyl-di[(2*R*)-bornane-10,2-sultam] ((-)-**1c**); reactive conformations are discussed.

Introduction. – Among asymmetric *Diels-Alder* reactions, fumaric-acid-derived dienophiles²⁾ are characterized by their high reactivity as well as their C_2 symmetry. Furthermore, the *Tolbert* and *Ali* [4] co-operating concept has elevated them to ideal substrates for uncatalyzed [5] as well as for *Lewis*-acid-mediated cycloadditions [6]. They have also been employed in the presence of a chiral solvent [6i], a chiral diene [7], or a chiral catalyst [8]³⁾. The resulting cycloadducts have subsequently served as corner stones for the syntheses of numerous natural products [11] or analogues [12], chiral cryptands [13], and prostaglandin receptor antagonists [14]. Recently, we reported the preparation of (-)-**1c** [15] (*Scheme*), a precursor of (2*R*)-*N*-glyoxyloylbornane-10,2-sultam⁴⁾ in a formal synthesis of mevinolin and compactin [18].



i) TiCl_4 , cyclopentadiene, CH_2Cl_2 , -78° . ii) LiAlH_4 , THF, 21° .

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²⁾ For chiral substituted and unsubstituted methylidenemalononic-acid-derived dienophiles, see [1]; for chiral 1,3-dicarboxylic-allene-derived dienophiles, see [2a, b]; for unsymmetrical maleates, see [2c]; for chiral 1,1-ethene disulfoxides, see [3a, b]; for 2-methylideneimidazolidines, see [3c, d].

³⁾ For chiral nonsymmetric fumaric-acid-derived dienophiles, see [9]; for the reactions of achiral dienophiles of this type in the presence of chiral catalysts, see [10].

⁴⁾ For a *N*-(acylnitroso)sultam-derived heterodienophile and its complete π -facial stereoselectivity, see [16]; for spirocyclization of 2-substituted tryptamines using (-)-**1c** as starting material, see [17].

Initially, the observed diastereoselectivity for the *Lewis*-acid-catalyzed [4 + 2] cycloaddition of (2*R*)-*N*-enoylbornane-10,2-sultams was rationalized by considering the steric interaction of the norbornane skeleton, which directs attack of the 1,3-diene on the bottom C(α)-*re*-face of the C=C bond, rigidified in a *s-cis*-conformation with respect to the chelated SO₂/C(O) groups [19]. However, under uncatalyzed conditions, the apparent top C(α)-*re*-face attack was not trivial to explain on the basis of this hypothesis [20]. Curran *et al.* [21] and Oppolzer *et al.* [20b] [22] [23] have also proposed that the lone pair of the pyramidalized N-atom could be of substantial importance for stereoelectronic control of the uncatalyzed process. More recently, Kim and Curran then minimized this aspect⁵), preferring a generalized steric model based on a disguised 2,5-dimethylpyrrolidine system [26], while Oppolzer has suggested a twisted model, stressing the importance of the enoyl O=C–C=C dihedral angle [27]. To rationalize the thermal cycloaddition of nitrile oxides to **1a**, Kim *et al.* [28] conclude that *Coulombic* repulsions between the S=O(a) group and the incoming reagent are more important than steric interactions⁶); furthermore, a recent puzzling report, based on MMX calculations⁷) and ¹H-NOE measurements, proposes an *anti*-SO₂/C(O) and a *s-trans*-conformation of the C=C bond to explain the uncatalyzed cycloaddition of vinyl-indols to **1a** [31]⁸). Finally, the case of methacryloyl sultam is noteworthy, since the stereoselectivity of the catalyzed *endo*-attack of cyclopentadiene [33] is unexpectedly resulting from a presumably strongly twisted *quasi-s-cis*-conformation [22]⁹).

Results and Discussion. – Since the pioneering work of Kahn and Hehre [36a–c], it is known that π -facial stereoselectivity is strongly influenced by electrostatic interactions [36d–f]. Furthermore, the π -facial stereoelectronic influence has been demonstrated for both dienes [37] and dienophiles [38]¹⁰). Based on the X-ray analysis of the 1:1 TiCl₄/(-)-**1b** complex [20b] and in accord with the previous rationalizations [22] [26], the C=C bond of (-)-**1c** should be forced into a *s-cis*/*s-cis*-conformation with respect to both C=O groups, independent of the TiCl₄ concentration, and thus attack on the C(α)-*re*-face should be preferred. In this hypothesis, the nitrogen lone pairs are pointing in opposite directions for the mono-coordinated species¹¹). We were interested to determine whether or not a stereoelectronic perturbation could be perceptible by variation of the TiCl₄ molarity¹²). Addition of cyclopentadiene (10 mol-equiv., CH₂Cl₂, 21°, 1 h) to (-)-**1c** readily gave (-)-**2** in quantitative yield and 85% d.e. (*Scheme*).

⁵) For through-bond and through-space lone-pair interactions, see [24]; for the dependence of the nature of the attacking reagent on stereoselectivity, see [25].

⁶) For a heterosubstituted diene C(α)-*re*-face attack under exceptionally polar conditions, see [29].

⁷) We are indebted to Prof. U. Pindur for providing us with the dihedral angles of his transition state: S–N–C=O = –177°, O=C–C=C = 163°. MMX Calculations [30] are mainly based on steric interactions and do not take into account all of the electronic parameters.

⁸) For a thermal non-diastereoselective cycloaddition to **1a**, see [32].

⁹) For X-ray analyses of *quasi-s-trans* non-coordinated *N*-tigloyl- and *N*-methacryloylsultam, see [22] [34]; for a recent proposal of *s-cis*-methacryloylsultam in a chelated transition state, see [35].

¹⁰) For steric vs. electronic effects in *Diels-Alder* π -facial selection, see [39].

¹¹) This remark is also valid for the S=O(a) groups [28], but we consider that *Coulombic* interactions should be weaker for a neutral non-heterosubstituted diene in comparison with nitrile oxides.

¹²) Although we were aware that, for a given molarity, neither the ratio, nor the relative reactivity of the respective mono-, di- and non-coordinated species is known, only an observed perturbing effect would be of conclusive interest.

The diastereoselectivity was directly determined by integration of the olefinic signals in the $^1\text{H-NMR}$ analysis of the crude cycloadduct¹³). Indeed, the major diastereoisomer exhibits two well resolved signals resonating at 5.90 and 6.41 ppm, while the minor diastereoisomer shows two sets of signals at 6.19 and 6.28 ppm. The major diastereoisomer, easily purified either by a single crystallization (yield 80–95%, > 99% d.e.) or by chromatography on SiO_2 (88–96%, > 99% d.e.), was reduced (LiAlH_4 , 2 mol-equiv., THF, 98%), and the chiral auxiliary (–)-4 was separated (93%) from the known diol (+)-(2*R*,3*R*)-3 (92%) [40] by chromatography. We were gratified to find that, even at -78° , the uncatalyzed cycloaddition occurs smoothly (95%, 89% d.e.), and that more than 98% d.e. was quantitatively obtained in the presence of TiCl_4 , independent of its molarity (Fig.).

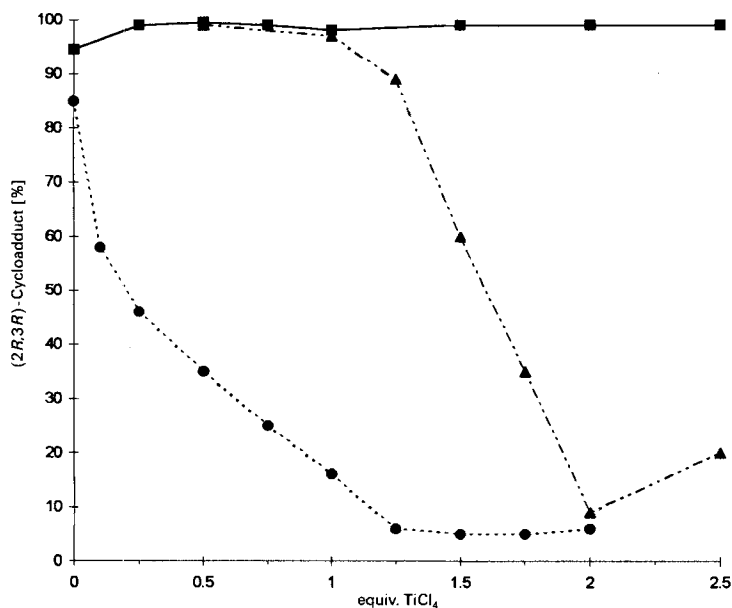


Figure. TiCl_4 -Concentration dependence on the π -facial stereoselectivity for the cyclopentadiene cycloaddition to di(fumaroyl)-derived dienophiles in CH_2Cl_2 . —■—: -78° , (–)-1c; - - -●- - : -40° , *O,O'*-fumaroyl di[(*S*)-ethyl lactate] [41]; - · - · -▲- : -40° , *N,N'*-fumaroyl di[(*S*)-proline benzyl ester] [42].

Helmchen and coworkers using the di(fumaroyl)ethyl (*S*)-lactate [41] as well as Waldmann and Drager, using the 'di(fumaroyl) ((*S*)-proline benzyl ester) amide' [42] (HPLC results reported in the Fig. for comparison), rationalized the observed change of the sense of induction by a *s-cis*/*s-trans*-interconversion of the fumaroyl moiety. However, in our case, we cannot exclude the absence of such a phenomenon. Indeed, according to Pindur *et al.* [31], both the non-coordinated *s-trans*/*s-trans*- and the mono-chelated *s-cis*/*s-trans*-species should direct attack onto the $\text{C}(\alpha)$ -*re*-face. It is noteworthy that, in this hypothesis, both nitrogen lone pairs are always orientated on the $\text{C}(\alpha)$ -*si*-face of the

¹³) Bruker AM-500 (500 MHz).

C=C bond, opposite to the attack¹⁴). Accordingly, despite a possible stereoelectronic control, no perturbation should be expected as a function of the Lewis-acid concentration^{12,15}). The uniformly high yield [%] of the (2*R*,3*R*)-cycloadduct (–)-**2** (see Fig.) can be rationalized by previous hypotheses [22] [26] [31], although it neither favors nor disfavors one of them in particular.

Further developments concerning the [4 + 2] cycloaddition of (–)-**1c** are currently in progress and will be presented in due course.

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Experimental Part

General. See [8b]. HR-MS: on AMD 604 apparatus.

General Procedure for the Cycloaddition. To a soln. of (–)-**1c** (510 mg, 1 mmol) in CH₂Cl₂ (2.5 ml) was added TiCl₄ (1*M*, CH₂Cl₂, *n* ml, *n* mmol). The mixture was cooled to –78° and precooled cyclopentadiene (4.84*M*, CH₂Cl₂, 2.07 ml, 10 mmol) was added dropwise and slowly along the cold wall of the reaction flask. After 4 h, the reaction was quenched with sat. aq. NH₄F, equilibrated to 21°, extracted with H₂O and CH₂Cl₂, dried (MgSO₄), evaporated under medium, then high vacuum. The crude cycloadduct **2c** (99%) was submitted to ¹H-NMR analysis for d.e. determination (Fig.). Crystallization from EtOH gave the pure major cycloadduct (2*R*,3*R*)-**2c** (80–95%). Chromatography of the mother liquor (SiO₂, AcOEt/hexane 1:6) gave the pure minor (2*S*,3*S*)-**2c** (0–7%) diastereoisomer.

(–)-N,N'-[(2*R*,3*R*)-Bicyclo[2.2.1]hept-5-ene-2,3-dicarbonyl]di[(2*R*)-bornane-10,2-sultam] ((–)-(2*R*,3*R*)-**2c**). *R_f* 0.37 (hexane/AcOEt 6:4). M.p. 238–240° (EtOH). [α]_D²⁰ = –202.0 (*c* = 1.15, CHCl₃). IR: 3070, 2960, 2880, 1680, 1455, 1410, 1370, 1335, 1275, 1215, 1165, 1135, 1070, 990. ¹H-NMR: 0.97 (*s*, 6 H); 1.19 (*s*, 3 H); 1.20 (*s*, 3 H); 1.25–1.45 (*m*, 5 H); 1.77 (*m*, 2 H); 1.87 (*m*, 6 H); 2.01 (*dd*, *J* = 8, 14, 2 H); 2.06 (*d*, *J* = 7, 1 H); 3.15 (*d*, *J* = 1.5, 1 H); 3.49 (*m*, 6 H); 3.87 (*m*, 2 H); 4.18 (*t*, *J* = 4, 1 H); 5.90 (*dd*, *J* = 2.8, 5.6, 1 H); 6.41 (*dd*, *J* = 3.1, 5.6, 1 H). ¹³C-NMR: 19.83 (2*q*); 20.72 (*q*); 20.86 (*q*); 26.4 (2*t*); 32.66 (*r*); 32.72 (*r*); 38.45 (*r*); 38.47 (*r*); 44.54 (*d*); 44.56 (*d*); 46.79 (*r*); 47.50 (*d*); 47.68 (*s*); 47.70 (*d*); 47.92 (*d*); 48.22 (*s*); 48.31 (*s*); 50.21 (*d*); 53.03 (*r*); 53.08 (*r*); 53.40 (*s*); 65.21 (2*d*); 133.17 (*d*); 138.40 (*d*); 171.33 (*s*); 172.01 (*s*). MS: 576 (1.5, *M*⁺), 511 (8), 446 (2.5), 431 (3), 361 (100), 334 (48), 296 (94), 268 (6), 231 (13), 204 (7), 163 (11), 135 (73), 119 (18), 107 (30), 93 (36), 79 (17), 66 (14), 55 (6). HR-MS: C₂₉H₄₀N₂O₆S₂; calc.: 576.23278, found: 576.232396.

*Compound (–)-(2*S*,3*S*)-2.* *R_f* 0.57 (hexane/AcOEt 6:4). M.p. 236–238° (AcOEt/hexane). [α]_D²⁰ = –10.8 (*c* = 1.4, CHCl₃). IR: 2960, 2885, 1690, 1460, 1325, 1275, 1205, 1165, 1135, 990. ¹H-NMR: 0.92 (*s*, 3 H); 0.93 (*s*, 3 H); 1.07 (*s*, 3 H); 1.09 (*s*, 3 H); 1.25–1.45 (*m*, 6 H); 1.75, 1.95 (*m*, 6 H); 2.0–2.30 (*m*, 4 H); 3.04 (*dd*, *J* = 1.5, 5.0, 1 H); 3.17 (*br. s*, 1 H); 3.37 (*br. s*, 1 H); 3.43 (*s*, 4 H); 3.72 (*dd*, *J* = 3.2, 4.9, 1 H); 3.83 (*dd*, *J* = 5.0, 7.8, 1 H); 3.89 (*dd*, *J* = 5.0, 7.8, 1 H); 6.19 (*dd*, *J* = 2.8, 5.3, 1 H); 6.28 (*dd*, *J* = 3.1, 5.4, 1 H). ¹³C-NMR: 19.92 (*q*); 19.94 (*q*); 21.06 (*q*); 21.11 (*q*); 26.48 (*t*); 26.50 (*t*); 32.94 (*r*); 33.03 (*r*); 38.33 (*r*); 38.45 (*r*); 44.51 (*d*); 44.61 (*d*); 46.85 (*d*); 47.32 (*r*); 47.61 (2*s*); 48.09 (*s*); 49.27 (*d*); 49.58 (*d*); 49.69 (*d*); 53.18 (2*t*); 60.33 (*s*); 65.92 (*d*); 65.96 (*d*); 135.93 (*d*); 136.70 (*d*); 171.58 (*s*); 172.76 (*s*). MS: 576 (0.5, *M*⁺), 511 (4), 361 (42), 334 (22), 296 (71), 231 (12), 204 (9), 163 (20), 135 (100), 119 (19), 107 (28), 93 (30), 79 (15), 66 (13). HR-MS: calc.: 576.23278, found: 576.2324.

(+)-(2*R*,3*R*)-Bicyclo[2.2.1]hept-5-ene-2,3-dimethanol ((+)-**3**). LiAlH₄ (70 mg, 1.84 mmol) was added to a soln. of (–)-(2*R*,3*R*)-**2** (520 mg, 0.9 mmol, obtained using 0.75 mol-equiv. of TiCl₄ and without any traces of (–)-(2*S*,3*S*)-**2** (¹H-NMR¹⁵)) in THF (15 ml). After 2 h, three drops of sat. aq. Na₂SO₄ were added, and the soln. was filtered and evaporated. The residue was chromatographed (SiO₂, hexane/AcOEt 9:1–6:4) to give the sultam

¹⁴) For a recent example of Cieplak theory applied to asymmetric Diels-Alder reactions, see [43] and ref. cit. therein.

¹⁵) Diastereoselectivity being entropic in origin [4c], Lewis-acid-concentration and temperature dependencies were observed [19] [20a] during the *endo*-cycloaddition of **1a** to cyclopentadiene at –78°: TiCl₄: 0.5 equiv., 87% yield, 97% *endo*, 66% d.e.; 1.5 equiv., 98% yield, 95% *endo*, 71% d.e.; 4.0 equiv., 97% yield, 96% *endo*, 82% d.e. For 1.5 equiv. TiCl₄: –94°, 80% yield, 97% *endo*, 77% d.e.; –130°, 89% yield, 97% *endo*, 94% d.e.

(–)-4 (93%, R_f 0.5 (cyclohexane/AcOEt 6:4)) and (+)-3 (98%, R_f 0.13 (cyclohexane/AcOEt 6:4)) further purified by bulb-to-bulb distillation (92%). B.p. 120°/1 Torr. $[\alpha]_D^{20} = +22.9$ ($c = 1.0$, CHCl_3) ($[\alpha]_D^{20} = +23.06$ ($c = 1.0$, CHCl_3)). IR: 3670, 3580, 3070, 2970, 2885, 1630, 1470, 1340, 1260, 1030. $^1\text{H-NMR}$: 1.32 (*dt*, $J = 5, 10$, 1 H); 1.45 (*br. s*, 2 H); 1.94 (*m*, 1 H); 2.59 (*br. s*, 1 H); 2.83 (*br. s*, 1 H); 2.83 (*br. s*, 2 OH); 3.04 (*t*, $J = 9$, 1 H); 3.42 (*t*, $J = 9$, 1 H); 3.67 (*dd*, $J = 5, 9$, 1 H); 3.78 (*dd*, $J = 5, 9$, 1 H); 5.98 (*dd*, $J = 3, 5$, 1 H); 6.23 (*dd*, $J = 3, 5$, 1 H). $^{13}\text{C-NMR}$: 44.6 (*d*); 44.7 (*d*); 46.9 (*d*); 47.1 (*t*); 47.9 (*d*); 66.1 (*t*); 66.6 (*t*); 133.4 (*d*); 138.0 (*d*). MS: 154 (0.5, M^+), 136 (3), 105 (4), 91 (6), 87 (5), 77 (7), 66 (100), 39 (6).

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