Short communication

Diels-Alder Reactions of Styrylcyclohexenones: an Efficient Procedure for the Synthesis of Substituted Dehydrodecaline Derivatives

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Abstract

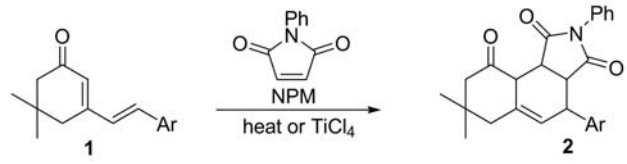
The Diels-Alder reaction of styrylcyclohex-2-enone derivatives **1** with *N*-phenylmaleimide was shown to be an efficient pathway for the synthesis of substituted dehydrodecaline derivatives. At elevated temperatures, mixtures of *endo*/*exo* adducts were formed, while in the presence of $TiCl_4$ exclusive formation of the *endo* stereoisomer was observed. Spectroscopic analysis and X-ray crystallography confirmed the formation of the *endo* adducts.

Keywords: Styrylcyclohexenone dienes, Diels-Alder reaction, Lewis acid catalysis, dehydrodecalines, cycloaddition

1. Introduction

The Diels-Alder (DA) cycloaddition[1] is considered to be one of the key reactions in synthetic organic chemistry[2] due to its ability to simultaneously yield two carbon-carbon bonds, a six-membered ring, and up to four stereogenic centers with predictable stereoselectivity in a single step reaction.[3] The reactivity and selectivity features of DA cycloadditions have been enhanced significantly in recent years with the use of chiral Lewis acids,[4] self-assembling reactants,[5] enantioselective catalysts,[6] and transiently tethered trienes.[7] Further enhancement is also achieved by the application of intramolecular and transannular DA reactions of appropriate trienes in the synthesis of complex multicyclic[8] and natural product[9] molecules.

The dehydrodecaline skeleton constitutes a structural fraction of several natural products and industrially significant perfumes.[10] In the framework of our investigations on Lewis acid catalyzed carbonyl group chemistry,[11] we recently reported the synthesis of novel styrylcyclohex-2-enone derivatives **1**[12] which could be explored for their DA reactivity. Through the positive results, we were encouraged to investigate the cycloaddition reactions of precursors of type **1** to examine their potential for assembling dehydrodecaline systems. Hereby, we report the synthesis and structural elucidation of the novel products obtained from the [4+2] cycloadditions of **1** with *N*-phenylmaleimide (NPM) under both thermal and $TiCl_4$-mediated conditions (Scheme 1).



Scheme 1

2. Results and Discussion

Initially, we attempted thermal cycloaddition of **1a** with NPM (Table 1). A 1:1 solution of the diene and the

dienophile in refluxing toluene completely converted to [4+2] cycloadducts within 10 hours. ^{1}H NMR analysis of the reaction mixture suggested formation of both adducts in a 9:1 ratio (entry 1). The structure of the major product, **2a**, isolated by column chromatography, was assigned as *endo* in which the newly formed π bond had rearranged to the more stable tetrasubstituted enone position. The stereochemical assignment was based on the ^{1}H NMR signal at the position 3a which splits the proton 4 to exhibit a medium coupling constant of about 7 Hz (Figure 1). This coupling constant is in accordance with the *endo* structure as opposed to the *exo* stereoisomer, which is expected to exhibit a large $^3J_{H,H}$ for the same proton.

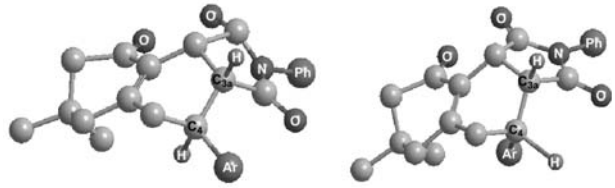


Figure 1. Diagnostic H-H coupling constants of adducts. For simplicity, only two hydrogen atoms at C_{3a} and C_4 are shown.

Table 1: Thermal DA reactions of **1a**-**g** with NPM.

Entry	Diene	Major product	*Endo*/*Exo*[a]	Yield (%)[b]
1	**1a**	**2a**	9:1	92
2	**1b**	**2b**	9:1	88
3	**1c**	**2c**	9:1	91
4	**1d**	**2d**	8:2	87
5	**1e**	**2e**	7:3	86
6	**1f**	**2f**	7:3	91
7	**1g**	**2g**	9:1	92

[a] Determined by ^{1}H NMR analysis of the crude mixtures. [b] Isolated yields.

Next, we examined the DA reactions of some other dienes (**1b**-**g**) with NPM. As a result, formation of *endo*-**2b**-**g** derivatives was observed as the major products in the reaction mixtures (Table 2, entries 2–7). In all cases *endo* products were isolated by column chromatography and their structures were assigned in the same way by spectroscopic methods, as described for *endo*-**2a**. In order to verify the structure of the stereoadducts, a single crystal of *endo*-**2c** was prepared and analyzed by X-ray crystallography. The result, depicted in Figure 2, clearly indicates the formation of *endo* stereoisomer as the major DA adduct.

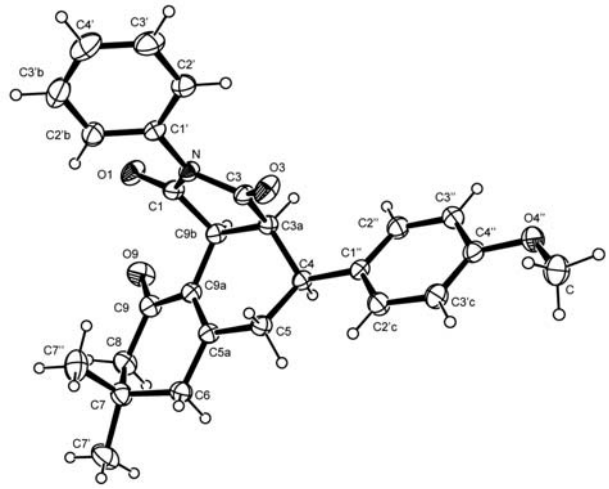


Figure 2. Crystal structure of *endo*-**2c**. Displacement ellipsoids are at 50% probability level.

Due to usually observed rate and selectivity enhancements associated with Lewis acid (LA) mediated DA cycloadditions,[13] we next examined the use of various Lewis acids ($LiClO_4$, $MgBr_2.OEt_2$, $SnCl_4$, and $TiCl_4$) to boost the DA reactions of **1** with NPM. The best conditions were obtained when $TiCl_4$ was used and *endo* adducts were the sole products within 1 hour of reaction (Table 2).

Table 2: *Endo* selective $TiCl_4$-mediated DA reactions of **1a**-**g** with NPM.

Entry	Diene	Product	Yield (%)[a]
1	**1a**	**2a**	92
2	**1b**	**2b**	90
1	**1c**	**2c**	95
4	**1d**	**2d**	89
5	**1e**	**2e**	90
6	**1f**	**2f**	93
7	**1g**	**2g**	95

[a] Isolated yields of *endo* adducts

As shown in Table 2, the LA-catalyzed reactions proceed much faster than the corresponding thermal reactions, which is usually observed for DA cycloadditions mediated with Lewis acids.[13] The exclusive high yield formation of the *endo* adducts can be attributed to the $TiCL_4$-mediated catalysis of the process which is already observed for similar [4+2] reactions with NPM as dienophile.[2]

3. Experimental

3. 1. General

The progress of the reactions was monitored by TLC using silica-gel coated plates (stationary phase) and ethyl acetate/hexane solution (1:2, mobile phase). Melting points are uncorrected. FT-IR spectra were recorded using KBr disks on a Bruker Vector-22 IR spectrometer. ^1H and ^{13}C NMR spectra were obtained on a FT-NMR Bruker Ultra Shield^{TM} (500 MHz) instrument as $CDCl_3$ solutions. Chemical shifts are expressed relative to the Me_4Si as the internal standard.

Mass spectra were obtained using a Finnigan Mat 8430 apparatus operating with an ionization potential of 70 eV. Elemental analyses were performed using a Thermo Finnigan Flash EA 1112 instrument. Dienes **1a**-**d** and **1g** were synthesized as reported in our recent work[12] and a similar procedure was used for the synthesis of the two new dienes (**1e** and **1f**). All other reagents were purchased from commercial sources and were used fresh after being purified by standard procedures.

3. 2. Typical Procedure for Thermal DA Reactions

A solution of a diene (2 mmol) and NPM (363 mg, 2.1 mmol) in toluene (2 mL) was refluxed for 8–10 hours in an atmosphere of argon. When TLC showed completion of the reaction, the mixture was cooled to room temperature and concentrated under vacuum. The *endo*-**2a**-**g** was obtained by column chromatography of the residues over silica-gel using EtOAc/hexane solution (1:2).

3. 3. Typical Procedure for $TiCl_4$ Mediated DA Reactions

A mixture of a diene (2 mmol), NPM (363 mg, 2.1 mmol), and $TiCl_4$ (110 μL, 1 mmol) in CH_2Cl_2 (4 mL) was stirred at room temperature for about 1 hour in an inert atmosphere of argon. When TLC showed completion of the reaction, the mixture was diluted with CH_2Cl_2 (10 mL) and washed with saturated aqueous solution of $NaHCO_3$ (2 × 10 mL). Organic layer was passed through a short column of Na_2SO_4 and concentrated under vacuum. The *endo*-**2a**-**g** were obtained by column chromatography of the residues over silica-gel using EtOAc/hexane solution (1:2).

3. 4. Spectral Data of New Compounds

(*E*)-3-(3-Bromostyryl)-5,5-dimethylcyclohex-2-enone (**1e**). IR (KBr) ν 3025, 1643 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.65 (s, 1H), 7.46–7.42 (m, 2H), 7.25 (dd, *J* = 7.9 and 7.8 Hz, 1H), 6.92 (s, 2H), 6.11 (s, 1H), 2.48 (s, 2H), 2.34 (s, 2H), 1.13 (s, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 200.5, 154.4, 138.6, 133.6, 132.2, 131.4, 130.8, 130.4, 128.3, 126.2, 51.8, 39.5, 33.8, 28.9; MS (70 eV) m/z: 304 (M^+), 286, 141, 115. Calcd. for $C_{16}H_{17}BrO$: C 62.96, H 5.61. Found: C 63.02, H 5.63.

(*E*)-5,5-Dimethyl-3-(2-(naphthalen-2-yl)vinyl)cyclohex-2-enone (**1f**). Mp = 114-115 °C; IR (KBr) ν 1648, 1605, 1300 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 8.19 (d, *J* = 8.2 Hz, 1H), 7.91 (d, *J* = 7.2 Hz, 1H), 7.88 (d, *J* = 8.2 Hz, 1H), 7.82 (d, *J* = 15.9 Hz), 7.77 (d, 1H, *J* = 7.2 Hz), 7.63–7.50 (m, 3H), 7.00 (d, *J* = 15.9 Hz, 1H), 6.17 (s, 1H), 2.62 (s, 2H), 2.38 (s, 2H), 1.20 (s, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 200.6, 155.2, 134.2, 133.8, 132.8, 132.1, 131.7, 129.9, 129.3, 127.8, 127.0, 126.5, 126.1, 124.7, 123.7, 51.9, 39.7, 33.8, 29.0; MS (70 eV) m/z: 276 (M^+), 191, 165, 152. Calcd. for $C_{20}H_{20}O$: C 86.92, H 7.29. Found: C 86.59, H 7.28.

(*3aS,4S,9bS*)-7,7-Dimethyl-2,4-diphenyl-4,5,6,7,8,9b-hexahydro-1*H*-benzo[e]isoindole-1,3,9(2*H*,3a*H*)-trione (*endo*-**2a**). White crystals were obtained in 92% yield. Mp = 114–116 °C; IR (KBr) ν 1716, 1670, 1380 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.44–7.27 (m, 7H), 7.23–7.17 (m, 2H), 6.64 (d, *J* = 7. 5 Hz, 1H), 4.45 (d, *J* = 7.8 Hz, 1H), 3.63–3.60 (m, 1H), 3.55 (dd, *J* = 7.8, 7 Hz, 1H), 2.76 (dd, *J* = 18.5, 4.8 Hz, 1H), 2.68–2.63 (m, 2H), 2.52 (d, *J* = 18.2 Hz, 1H), 2.42 (d, *J* = 15.8 Hz, 1H), 2.35 (d, *J* = 18.2 Hz, 1H), 1.21 (s, 3H), 1.11 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 196.9, 176.2, 174.1, 156.9, 140.3, 131.8, 129.2, 129.1, 128.7, 128.1, 126.7, 126.5, 51.7, 46.2, 44.8, 39.4, 38.6, 35.8, 33.9, 29.3, 28.2; MS (70 eV) m/z: 399 (M^+), 274, 196, 167, 141, 91, 43. Calcd. for $C_{26}H_{25}NO_3$: C 78.17, H 6.31. Found: C 78.35, H 6.13.

(*3aS,4S,9bS*)-7,7-Dimethyl-2-phenyl-4-(p-tolyl)-4,5,6,7,8,9b-hexahydro-1*H*-benzo[e]isoindole-1,3,9(2*H*,3a*H*)-trione (*endo*-**2b**). White crystals were obtained in 90% yield. Mp = 120–122 °C; IR (KBr) ν 1716, 1668, 1378 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.33–7.18 (m, 3H), 7.10 (s, 4H), 6.65–6.63 (m, 2H), 4.42 (d, *J* = 8 Hz, 1H), 3.58–3.56 (m, 1H), 3.51 (dd, *J* = 8 and 6.7 Hz, 1H), 2.74 (dd, *J* = 18.5, 5.1 Hz, 1H), 2.66–2.59 (m, 2H), 2.49 (d, *J* = 16 Hz, 1H), 2.43 (d, *J* = 16 Hz, 1H), 2.33 (s, 3H), 2.20 (d, *J* = 16 Hz, 1H), 1.20 (s, 3H), 1.11 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 196.8, 176.3, 174.1, 156.8, 137.8, 137.1, 134.6, 131.9, 129.8, 129.1, 128.5, 126.7, 126.5, 51.7, 46.2, 44.8, 39.1, 38.5, 36.0, 33.9, 29.3, 28.2, 21.4; MS (70 eV) m/z: 413 (M^+), 210, 167, 105, 91, 43. Calcd. for $C_{27}H_{27}NO_3$: C 78.42, H 6.58. Found: C 78.83, H 6.50.

(*3aS,4S,9bS*)-4-(4-Methoxyphenyl)-7,7-dimethyl-2-phenyl-4,5,6,7,8,9b-hexahydro-1*H*-benzo[e]isoindole-1,3,9(2*H*,3a*H*)-trione (*endo*-**2c**). White crystals were obtained in 95% yield. Mp = 196–197 °C; IR (KBr) ν 1714, 1668, 1380 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.32–7.26 (m, 3H), 7.14 (d, *J* =7.8 Hz, 2H), 6.84 (d, *J* =7.8 Hz, 2H), 6.71–6.68 (m, 2H), 4.42 (d, *J* = 7.9 Hz, 1H), 3.79 (s, 3H), 3.61–3.58 (m, 1H), 3.52 (dd, *J* = 8, 6.5 Hz, 1H), 2.76 (dd, *J* = 18.7, 5.1 Hz, 1H), 2.67 (d, *J* = 15.7 Hz, 1H), 2.62 (dd, *J* = 18.7, 4.2 Hz, 1H), 2.52 (d, *J* = 18.2 Hz, 1H), 2.42 (d, *J* = 15.7 Hz, 1H), 2.35 (d, *J* = 18.2 Hz, 1H), 1.22 (s, 3H), 1.12 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 198.3, 177.9, 175.5, 161.0, 158.2, 133.5, 133.3, 131.2, 130.5, 130.1, 128.1, 128.0, 116.0, 57.2, 53.2, 47.7, 46.3, 40.1, 39.9, 37.6, 35.4, 30.9, 29.6; MS (70 eV) m/z: 429 (M^+), 281, 226, 121. Calcd. for $C_{27}H_{27}NO_4$: C 75.50, H 6.34. Found: C 75.34, H 6.27.

(*3aS,4S,9bS*)-4-(4-Chlorophenyl)-7,7-dimethyl-2-phenyl-4,5,6,7,8,9b-hexahydro-1*H*-benzo[e]isoindole-1,3,9(2*H*,3a*H*)-trione (*endo*-**2d**). White crystals were obtained in 89% yield. Mp = 209-211 °C; IR (KBr) ν 1713, 1659, 1380 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.36–7.33 (m, 3H), 7.31 (d, *J* = 8.5 Hz, 2H), 7.18 (d, *J* = 8.5 Hz, 2H), 6.77–6.75 (m, 2H), 4.50 (d, *J* = 7.2 Hz, 1H), 3.58–3.54 (m, 2H), 2.72 (dd, *J* = 18 and 4.2 Hz, 1H), 2.67–2.64 (m, 2H), 2.50 (d, *J* = 18 Hz, 1H), 2.42 (d, *J* = 16 Hz, 1H), 2.36 (d, *J* = 18 Hz, 1H), 1.21 (s, 3H), 1.13 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 196.7, 175.9, 173.9, 156.6, 138.6, 134.0, 131.7, 130.0, 129.3, 128.8, 126.9, 126.5, 51.6, 46.2, 47.7, 39.0, 38.7, 35.3, 33.8, 29.1, 28.4; MS (70 eV) m/z: 433 (M^+), 230, 119, 91, 57. Calcd. for $C_{26}H_{24}ClNO_3$: C 71.97, H 5.57. Found: C 71.58, H 5.61.

(*3aS,4S,9bS*)-4-(3-Bromophenyl)-7,7-dimethyl-2-phenyl-4,5,6,7,8,9b-hexahydro-1*H*-benzo[e]isoindole-1,3,9(2*H*,3a*H*)-trione (*endo*-**2e**). White crystals were obtained in 90% yield. Mp = 109–111°C; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.44–7.43 (m, 2H), 7.37–7.29 (m, 3H), 7.21–7.16 (m, 2H), 6.88–6.86 (m, 2H), 4.51(d, *J* = 8.3 Hz, 1H), 3.59 (dd, *J* = 8.3 and 6.3 Hz, 1H), 3.49–3.47 (m, 1H), 2.68–2.66 (m, 2H), 2.61 (d, *J* = 16 Hz, 1H), 2.48 (d, *J* = 18.4 Hz, 1H), 2.43–2.36 (m, 2H), 1.19 (s, 3H), 1.12 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 196.7, 175.8, 173.9, 156.7, 142.5, 131.8, 131.1, 130.6, 129.3, 128.8, 127.1, 127.0, 126.5, 123.1, 51.6, 46.3, 44.8, 39.4, 39.1, 34.8, 33.7, 28.8, 28.7; MS (70 eV) m/z: 477 (M^+), 274, 165, 152, 119. Calcd. for $C_{26}H_{24}BrNO_3$: C 65.28, H 5.06. Found: C 65.67, H 4.70.

(*3aS,4S,9bS*)-7,7-Dimethyl-4-(naphthalen-2-yl)-2-phenyl-4,5,6,7,8,9b-hexahydro-1*H*-benzo[e]isoindole-1,3,9(2*H*,3a*H*)-trione (*endo*-**2f**). White crystals were obtained in 93% yield. Mp = 139–140 °C; IR (KBr) ν 1716, 1663, 1375 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 8.09 (d, *J* = 8.5 Hz, 1H), 7.95 (d, *J* = 8 Hz, 1H), 7.85 (d, *J* = 8.3 Hz, 1H),

7.62 (dd, *J* = 7.3 and 7.2 Hz, 1H), 7.56 (dd, *J* = 7.6 and 7.2 Hz, 1H), 7.48 (dd, *J* = 7.9 and 7.5 Hz, 1H), 7.42 (d, *J* = 7.2 Hz, 1H), 7.38–7.29 (m, 3H), 7.00 (d, *J* = 7.5 Hz, 2H), 4.77 (d, *J* = 8.7 Hz, 1H), 4.11–4.07 (m, 1H), 3.90–3.87 (m, 1H), 2.97 (dd, *J* = 17 and 11 Hz, 1H), 2.63–2.58 (m ,2H), 2.49–2.44 (m, 3H), 1.17 (s, 3H), 1.16 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 196.7, 175.3, 174.6, 158.9, 135.8, 134.3, 132.1, 131.5, 129.8, 129.3, 128.7, 128.5, 127.9, 126.9, 126.5, 126.1, 125.7, 125.4, 122.8, 51.5, 46.6, 44.0, 40.1, 36.4, 34.6, 33.6, 29.4, 28.0; MS (70eV) m/z: 449 (M^+), 202, 152, 119, 91. Calcd. for $C_{30}H_{27}NO_3$: C 80.15, H 6.05. Found: C 80.01, H 6.19.

(*3aR,4S,9bS*)-7,7-Dimethyl-2-phenyl-4-(thiophen-2-yl) -4,5,6,7,8,9b-hexahydro-1*H*-benzo[e]isoindole-1,3,9 (2*H*,3a*H*)-trione (*endo*-**2g**). White crystals were obtained in 95% yield. Mp = 188–190 °C; IR (KBr) ν 1716, 1668, 1384 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.32–7.26 (m, 3H), 7.18 (dd, *J* = 5.1 and 1 Hz, 1H), 6.94–6.92 (m, 1H), 6.90 (d, *J* = 3 Hz, 1H), 6.70–6.68 (m, 2H), 4.34 (dd, *J* = 8.3 and 1.8 Hz, 1H), 4.06–4.04 (m, 1H), 3.50 (dd, *J* = 8.3 and 6 Hz, 1H), 2.82 (dd, *J* = 18.5 and 4.2 Hz, 1H), 2.66 (d, *J* = 15.3 Hz, 1H), 2.58 (dd, *J* = 18.5 and 3 Hz, 1H), 2.51 (d, *J* = 18.3 Hz, 1H), 2.39 (d, *J* = 15.3 Hz, 1H), 2.28 (d, *J* = 18.3 Hz, 1H), 1.21 (s, 3H), 1.07 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 197.1, 176.2, 173.6, 154.6, 141.9, 131.9, 129.2, 127.8, 127.4, 127.3, 126.9, 126.8, 125.5, 51.9, 46.4, 45.0, 38.0, 37.5, 34.9, 34.0, 30.0, 27.8; MS (70 eV) m/z: 405 (M^+), 257, 202, 119, 91. Calcd. for $C_{24}H_{23}SNO_3$: C 71.09, H 5.72. Found: C 70.97, H 5.76.

3. 5. X-Ray Data for Endo-2c

$C_{27}H_{27}NO_4$, M = 429.50 g/mol, triclinic system, space group $P\bar{1}$, *a* = 10.0376(9), *b* = 10.8919(9), *c* = 11.4595(10) Å, α = 89.219(7), β = 65.236(7), γ = 81.641(7)°, V = 1124.00(18) Å^3, Z = 2, *Dc* = 1.269 g cm^{-3}, μ(Mo–Kα) = 0,085 mm^{-1}, crystal dimension: 0.45 × 0.23 × 0.15 mm. The structure refinement and data reduction was carried out with SHELXL. The non-hydrogen atoms were refined anisotropically by full matrix least-squares on F^2 values to final R_1 = 0.0623, wR_2 = 0.1300 and S = 1.128 with 292 parameters using 6027 independent reflections (θ range = 1.96–29.33°). Hydrogen atoms were located from expected geometry and were not refined. Crystallographic data for *endo*-**2c** have been deposited and could be obtained free of charge on application at the Cambridge Crystallographic Data Centre.

4. Conclusions

In summary, the DA reactions of **1** with NPM illustrated stereoselective formation of the corresponding *endo* adducts which could be appropriate precursors for the synthesis of other substituted dehydrodecaline derivatives. Study of the reactions with singly activated dienophilic systems and attempts to perform intramolecular DA reactions are also underway.

5. Acknowledgement

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6. References

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Povzetek

V prispevku je prikazana učinkovita priprava substituiranih derivatov dehidrodekalina z Diels-Alderjevo reakcijo med derivati stirencikloheks-2-enona **1** in *N*-fenilmalenimida. Pri običajni termični reakciji se pri višji temperaturi tvori zmes *endo*/*exo* aduktov, medtem ko se v prisotnosti $TiCl_4$ kot katalizatorja tvori izključno *endo* stereoisomer. Avtorji so selektivnost reakcije potrdili s spektroskopsko in rentgensko strukturno analizo izoliranih *endo* aduktov.