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Chemo and Enantioselective Butadiene-functionalized Dienes Cyclodimerization catalyzed by Nickel Complexes

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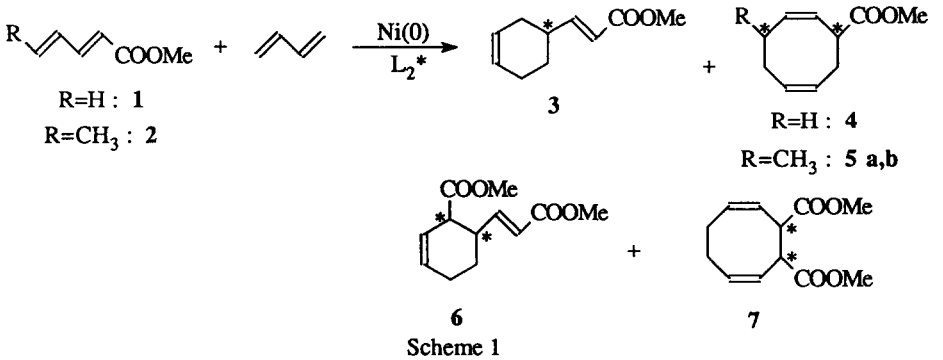
Abstract : Chiral aminophosphine-phosphinite and diphosphine ligands induce chirality during nickel catalyzed cyclodimerization of conjugated dienic esters with butadiene. The enantiomeric excesses of the cyclodimers are determined by chiral GLC and NMR methods.

The oligomerization of butadiene with conjugated dienic esters in the presence of nickel complexes leads to a great variety of co-dimers according to the ligand structure, the co-catalyst and the reaction conditions [1-6].

We have already reported that the modification of zerovalent nickel by amino-phosphinite (AMP) ligands gives rise to the production of chiral linear dimers [1]. On the other hand, cyclodimers are obtained on a catalyst formed *in situ* by reducing a nickel salt in the presence of PR_3 [2,3]. In this case, cyclooctadienic or vinylcyclohexenic compounds are formed, in which case the ratio depends on the catalyst [4] and particularly on the nature of the reductive organoaluminum species [5].

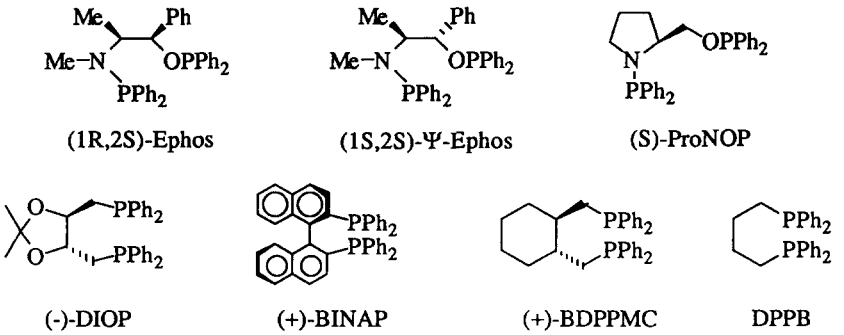
Nevertheless, up to now, no asymmetric cyclocodimerization between butadiene and conjugated dienic esters has been described in the literature. Only methyl penta-2,4-dienoate **1** cyclodimerization was reported with different chiral ligands [7,8].

In this paper, we wish to report that the asymmetric cyclodimerization of butadiene with **1** or methyl sorbate **2** can be achieved on chiral bidentate phosphine zerovalent nickel complexes as shown in scheme 1.



Scheme 1

We have used aminophosphine-phosphinite (AMPP) ligands, which have already shown their ability to give chemoselectively 4-vinylcyclohexene by cyclodimerization of butadiene on nickel [9]. These ligands were prepared according to procedures described in literature [10]. The (+)-BINAP, (-)-DIOP and (1S,2S)-(+)-*trans*-bis(diphenylphosphinomethyl)cyclohexane (BDPPMC) chiral diphosphines were also tested. The structure of these ligands are given in Scheme 2.



Scheme 2

All reactions were carried out in a nitrogen atmosphere. In a typical experiment, bis(cycloocta-1,5-diene)nickel (0.4 mmol, 110 mg) and 0.4 mmol of ligand were dissolved in 8 ml of dry toluene in a glass reactor closed with a teflon stopper. The ester (16 mmol) and liquid butadiene (32 mmol, 1.7 g) were added. The mixture was stirred and heated to the desired temperature. The reaction was followed by GC for conversion and selectivities by using *n*-heptane as internal standard. The enantiomeric excess of **3** was determined by GC analysis (FS-cyclodex beta-I/P, 25m) and by the LIS NMR technic using chiral Europium salts ($Eu(hfc)_3$). The **5a** and **5b** diastereoisomers were separated by gas preparative chromatography on a Carbowax column (10% CW 20M CSorb WAW 80/100 mesh, 4m*1/4"*4mm) and the ee's were calculated by the NMR techniques with $Eu(hfc)_3$.

The results are reported in tables 1 and 2.

Table 1. Cyclodimerization of Butadiene with Methyl Penta-2,4-dienoate[a] **1**

Entry	Ligand	Conv. (%)[b]	Cyclodimers (yield %)				ee (%)
			3	**4**	**6**	**7**	**3**[c]
1[d]	DPPB	100	27	31	3	9	-
2[e]	(+)-BDPPMC	13	28	28	6	7	8
3	(-)-DIOP	20	81	2	5	12	3
4[f]	(+)-BINAP	38	40	0	60	0	5
5	(1S,2R)-Ephos	14	29	34	10	25	10
6	(1S,2S)-Ephos	22	20	44	17	19	14[g]
7	(S)-ProNOP	9	12	32	15	41	12

[a] Experimental conditions : see text, t=72 hours, T=40 °C [b] Methyl-2,4-pentadienoate conversion
[c] All the ligands lead to the same major enantiomer except with DIOP.
[d] t=40h, VCH=21%, COD=9% [e] VCH=31% [f] T=80°C, t=48h [g] $[\alpha]_D$=-10 ($CHCl_3$, c=2.5)

Table 2. Cyclodimerization of Butadiene with Methyl Sorbate 2 [a]

Entry	Ligand	Conv.[b]	Codimers (%)		BD dimers (%)[c]		ee (%)	
		(%)	5a	5b	VCH	COD	5a	5b
1	DPPB	83	8	65	16	11	-	-
2	(+)-BDPPMC	17	3	32	51	14	3	3
3	(-)-DIOP	32	1	40	46	13	-	3
4	(+)-BINAP	0	0	0	49	51	-	-
5	(1S,2R)-Ephos	45	10	31	19	40	3	2
6	(1S,2S)-Ephos	57	9	55	12	24	5[d]	3
7	(S)-ProNOP	40	3	26	24	47	2	<1

[a] Experimental conditions : see text, t=48 hours, T=80°C [b] Methyl-2,4-pentadienoate conversion
[c] BD=butadiene, VCH=4-vinylcyclohexene, COD=1,5-cyclooctadiene [d] $[\alpha]_D$=- 4 ($CHCl_3$, c=2.5)

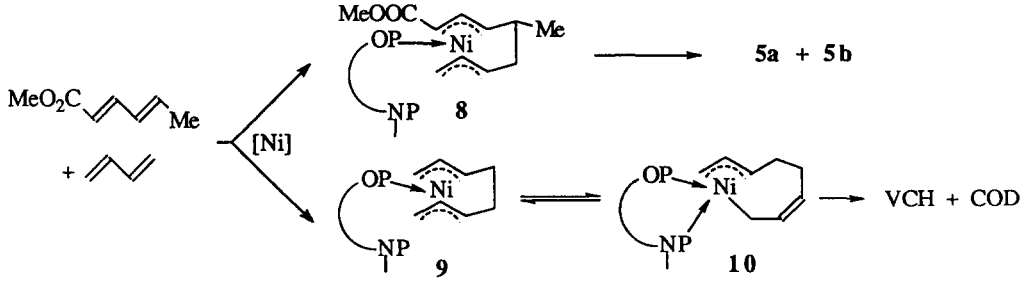
The analysis of the results leads to the following comments :

(i) The dppb ligand leads to high conversions because of its low steric hindrance.

(ii) Butadiene cyclodimerization with **1** can be achieved at 40 °C (Table 1) and gives rise to vinyl--cyclohexenic **3** and octadienic **4** esters, which ratio depends on the ligand structure. Nevertheless, this reaction does not take place at 40°C with BINAP as ligand (Table 1, entry 4), probably because of the steric hindrance of this bisphosphine. Only the C_6 rings are also obtained in this latter case. With DIOP ligand (Table 1, entry 3), a high chemoselectivity in the vinylcyclohexenic **3** compound is achieved. In contrast, with the AMPP ligands, the C_8 rings are major products.

(iii) It is also noteworthy that butadiene cyclodimers are always minor products in the presence of **1** although butadiene was in used excess. Moreover, in the case of AMPP ligands, there are no butadiene dimers. The presence of an electron-withdrawing group favours the substituted bis(π-allyl)-C_8 or (σ,π-allyl)-C_8 esters intermediates to the detriment of the non substituted ones [11].

(iv) During butadiene-methyl sorbate **2** cyclocodimerization, a temperature of 80 °C is necessary to obtain good conversions. No sorbate cyclodimers are formed as reported in the literature [3,5]. Only cyclooctadienic esters **5a** and **5b** are obtained, which arise from the substituted bis(π-allyl) intermediate **8**. This latter is in competition with the π,π **9** or σ,π **10** - octadienediyl species, which lead respectively to 1,5-cyclooctadiene (COD) or 4-vinylcyclohexene (VCH) cyclodimers (Scheme 3) [12]. This competition is more important as in the case of **1** because of the steric constrain due to the methyl substituent.



Scheme 3

(v) From the point of view of enantioselectivity, the optical yields remain low. Nevertheless, a 14 % ee is obtained on **3** with the (1S,2S)-Ephos ligand, which had already given a good ee on VCH (21%) [9]. This is the first cyclocodimerization reaction where an enantiomeric excess is obtained at the C_6 cyclic compound in which three functionnal groups are present.

NMR characteristics of the oligomers

The cyclodimers structures were determined using ^1H and ^{13}C NMR spectroscopies on a Brüker AC-300 spectrometer (solvent : $CDCl_3$).

4-(methylcarboxylate)vinylcyclohexene **3** : ^{1}H NMR : 1.75-1.9 (m, 2H), 2.1-2.3 (m, 4H), 2.4-2.5 (m, 1H), 3.75 (s, 3H), 5.6-5.7 (m, 2H), 5.8 (dd, 1H, $^3J_{trans}$=15.7 and ^4J=1.3), 6.95 (dd, ^3J=7.1) ; ^{13}C NMR : 24.4, 27.5, 30.1, 36.4, 51.5, 119.2, 125.3, 127, 153.6, 164.4 (conjugated CO)

Methyl-2,6-cyclooctadienecarboxylate **4** : ^{1}H NMR : 2.2-2.7 (m, 6H); 3.84 (s, 3H), 3.9 (s, 1H), 5.5-5.8 (m, 4H) ; ^{13}C NMR : 27.5, 27.9, 36.3, 48, 52, 126.5, 127, 129.4, 130.4, 174.9

Methyl(4-methyl-2,6-cyclooctadiene)carboxylate **5a** (minor diastereoisomer) : ^{1}H NMR : 1.04 (d, 3H), 2.17-2.21 (m, 2H), 2.36-2.44 (m, 1H), 2.68-2.91 (m, 2H), 3.5 (m, 1H), 3.69 (s, 3H), 5.43-5.62 (m, 4H) ; ^{13}C NMR : 22.2, 30.9, 33.4, 36.7, 44.9, 52, 124, 126.5, 129.9, 137.1, 175

Methyl(4-methyl-2,6-cyclooctadiene)carboxylate **5b** (major diastereoisomer) : ^{1}H NMR : 0.98 (d, 3H), 1.76-1.86 (m, 2H), 2.24-2.34 (m, 1H), 2.74-2.86 (m, 2H), 3.64 (s, 3H), 3.77 (m, 1H), 5.28-5.55 (m, 4H) ; ^{13}C NMR : 22.5, 31.5, 33, 35.8, 44.3, 52, 124.8, 126.5, 128.4, 136.6, 175.3

3-methylcarboxylate-4-(methylcarboxylate)vinylcyclohexene **6** : ^{1}H NMR : 1.6 (m, 2H), 2.1 (m, 2H), 2.6 (m, 1H), 3.1 (m, 1H), 3.7 (s, 3H), 5.6 (m, 1H, J_{trans}=10), 5.9 (m, 1H), 5.8 (dd, 1H, J_{trans}=15.8), 6.9 (dd, 1H, ^3J=8) ; ^{13}C NMR : 23.5, 25.9, 38, 46.4, 51.5, 52, 122.8, 149, 166.8, 172.6

Dimethyl-3,7-cyclooctadiene-1,2-dicarboxylate **7** : ^{1}H NMR : 2.1-2.3 (m, 2H), 3.6 (s, 3H), 4.2 (m, 1H), 5.6 (m, 2H) ; ^{13}C NMR : 27.6, 52, 125.2, 129.6, 173.7

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