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FIRST SELECTIVE LINEAR BUTADIENE-FUNCTIONALIZED DIENE CODIMERIZATION CATALYZED BY NICKEL COMPLEXES

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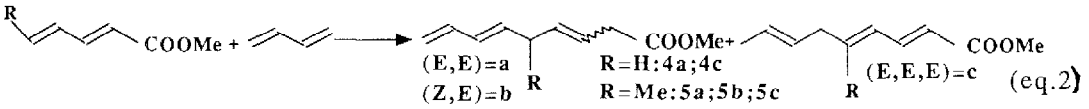
Summary : Functionalized dienes are codimerized with butadiene in the presence of Ni°-AMP catalysts to produce selectively linear trienic esters. In the case of methyl sorbate, some asymmetric induction is observed in the product.*

Butadiene-functionalized diene cyclodimerization over nickel catalysts is a well established process, by which the use of phosphines as ligands provides the synthesis of cyclooctadiene derivatives[1-3]. In each case however, the reaction rates were low. We have developed the concept of ancillary bifunctional aminophosphinite (AMP) ligand where the secondary amino group can interact with a nickel complex intermediate to produce selectively 1,3,6-octatrienes **1** under very mild conditions from butadiene [4].We wish now to report the results obtained during codimerization of methyl-2,4 pentadienoate **2** and methyl sorbate **3** with butadiene on this catalytic system. The codimerization was carried out with bis(cyclooctadiene) nickel as the source of Ni° and D-EPHOS NH, a ligand obtained by reaction between (1S,2R) ephedrine and dimethylaminodiphenylphosphine (eq.1) [4].

$$MeHNCH(Me)CH(Ph)OH + PPh_2NMe_2 \longrightarrow McHN(Me)CH(Ph)OPPh_2 \quad (eq.1)$$

In a typical experiment,$Ni(COD)_2$(110mg;0.4mg) is introduced in a Schlenk tube equiped with a Teflon tap. The ligand (140 mg;0.4 mmol) is added together with the ester in a toluene solution (7ml),followed by introduction of butadiene.The conversion are calculated by GC. The compounds structures were determined by proton and ^{13}C NMR spectroscopies as well as by IR [5]. These analyses are consistent with following general reaction :



(eq.2)

The results summarized in the table are interesting in several respects:they show first that linear trienic esters can be easily prepared by this way and hence provide

Run	Butadiene /Ni°	Ester (ester/ Ni°)	T°C	R.time (min)	Conv. (%)	Products selectivities (mol%) Codimers	1
1	50	2(50)	20	30	80	**4a**=56;4c=43	
2	50	2(50)	40	30	75	**4a**=52;4c=30	18
3	100	2(50)	40	30	62	**4a**=38;4c=23	39
4	50	3(50)	40	240	90	**5a**=36;**5b**=18;**5c**=31	14
5	100	3(50)	40	240	81	**5a**=24;**5b**=13;**5c**=15	48
6	50	3(100)	40	45	24	**5a**=40;**5b**=18;**5c**=35	6

useful starting materials for synthetic application. Secondly, they show how the use of a bifunctional ligand can enhance the chemoselectivity into linear products, even in cases where this process was unknown (methyl sorbate dimerization). It has to be noticed at last that codimers **5a** and **5b** have a prochiral carbon atom : the use of the chiral D-EPHOSNH as ligand has given some asymmetric induction in **5a** ($[\alpha]_D^{20}$ = +1.6(C=1.0,$CHCl_3$)) and **5b** ($[\alpha]_D^{20}$ = +30 (C=1.0, $CHCl_3$)).

Further experiments are under way in order to analyse the enantioselectivity observed in this chemoselective reaction.

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5 - **4a** ^{1}H NMR (60MHZ, $CDCl_3$) : 2.3-3.15(m, 4H) ; 3.7(S.3H) ; 5.3-7(m, 7H). IR : 2980, 2960, 2830, 1740, 1600, 1430, 1270, 1035, 980, 895cm^{-1} ^{13}C NMR ; 172.2 (C=0), 148.3 (C3), 135,4 (C4), 130 (C6), 132.9 (C7), 137.9 (C8), 117.7 (C9), 37.8 (C2), 31.7 (C5), 51.3 (OCH_3).**4c** ^{1}H NMR (60 MHZ, $CDCl_3$) : 2.11(m, 2H, $J_{6-5} = J_{6-7} = 5.1$) ; 3.7(S.3H) ; 1.65 (d,3H,J_{9-8} = 3.18), 5.1 - 6.51(m, 6H). IR : same as **4a** except C=0 = 1680 vs 1740 cm^{-1} ; ^{13}C NMR : 168.0 (C=0), 122.5 (C_2), 124 (C_3), 129.2 (C_4), 130.8 (C_5),128.6 (C_7), 122.9 (C_8), 35.2 (C_6), 17.73 (C_9), 51.6 (OCH_3). **5a** - ^{1}H NMR (60 MHZ, $CDCl_3$) : 1.1(d, J_{5-10} = 6.53 ; 3H) ; 2.15-2.3(m, 3H) ; 3.68 (S,3H) ; 5.1-6.7(m,7H). IR : 2980, 2960, 2830, 2820, 1734, 1600, 1430, 1310, 1270,1175,1000. ^{13}C NMR : 172.29 (C=0) ; 138.42 (C_3) ; 138 (C_4) ; 137.09 (C_6) ; 120.57 (C_7) ; 129.64 (C_8 ; 115.46 (C_9) ; 51.67 (OCH_3) ; 37.8 (C_2) ; 39.13 (C_5 ; 19.87 (C_{10}). $[\alpha]_D^{20}$ = +1.6(C 1.0 ; $CHCl_3$). **5b** - ^{1}H NMR (60 MHZ, $CDCl_3$) : 1.07 (d,J_{5-10} = 6.53 ; 3H) ; 2.95-3.05 (m,3H) ; 3.7(S,3H) ; 5-6.5 (m, 7H).IR same as **5a**. ^{13}C NMR : 172.11 (C=0) ; 138.0 (C3) ; 137.2 (C_4) ; 137 (C_6) ;120.1 (C_7) ; 129 (C_8) ; 117.58 (C_9) ; 51.33 (OCH_3) ; 35.13 (C_{12}) ; 37.52 (C_5) ; 20.7 (C_{10}) $[\alpha]_D^{20}$ = +30 (C 1.0 ;$CHCl_3$). **5c** ^{1}H NMR (60MHZ, $CDCl_3$) : 1.59 (5.3H) ; 1.86 (d, J_{8-9} = 5.15 ; 3H) ; 3.15 (d,J_{6-7} = 5.86 ; 2H) ; 3.68 (S.3H) ; 5-6.37 (m,5H). IR : Same as **5a** and **5b** except C=0 = 1700 vs 1734 cm^{-1}. ^{13}C NMR : 167.91 (C=0) ; 121.73 (C_2) ; 122.51 (C_3) ;136.71 (C_4) ; 140.11 (C_5) ; 129.10 (C7) ; 122.01 (C_8) ; 51.73 (OCH_3) ; 17.15 (C_9) ; 36.51 (C_6) ; 18.15 (C10).

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