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Nickel zero catalysed Cyclodimerization of 2,4-pentadienoic acid methyl ester. A remarkable directing effect of Et_2AlOEt.

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Abstract : The presence of organoaluminic compounds has a decisive influence on the selectivity of Ni(0) catalysed cyclodimerization of functionalized dienes.

The transition metal catalysed oligomerization and cyclooligomerization of conjugated diene is an important reaction both from the industrial and theoretical point of view (1). In such reactions,catalysed by Nickel , the active species is considered to be zerovalent nickel (2). Wilke and his group, have clearly shown that the nature of the catalyst : naked nickel and liganded nickel, as well as the metal ligand in the later case, have a decisive influence on the selectivity of the cyclooligomerization process (3). .It had been considered until now that the manner in which the catalyst was generated had no significant influence on the outcome of such reactions. This conclusion was based upon the observation of similar efficiencies (catalytic activity, turnover, product distribution) for nickel zero catalysts, generated either from $Ni(COD)_2$ or by reduction of Nickel II by alkylaluminum derivatives (4).However our results clearly demonstrate the fact that the mode of preparation of the zerovalent nickel catalyst does have a definite influence on the cyclooligomerization process. In particular, the presence or the absence of organoaluminum derivatives dramatically affects the course of the cyclooligomerization reaction.

The formation of 1,2-dicarbomethoxy 3,7-cyclooctadiene 2 from methyl 2,4-pentadienoate 1 proceeds with high yields and total selectivity when $Ni(acac)_2$-PPh_3/Et_2AlOEt catalysts are used (5) (see entry 7, Table) . Instead the selectivity drops markedly with the $Ni(COD)_2,P(C_6H_{11})_3$ catalyst (which also provides a liganded nickel species) (see entry 1, Table) (6). Several explanations could be advanced in order to rationalize this striking difference in behaviour:

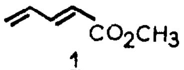
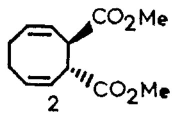
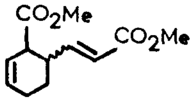
1) occurence of different effective catalytic nickel species

2) complexation of the polar groups of the functionnalized diene 1 with the alkylaluminum derivative (7)

3) similar kind of complexation but now occuring on the phosphine (either on the phosphorus, or on the aromatic nucleus in the case of triphenylphosphine) which would modify its basicity, a factor known to have

a decisive influence of this type of reaction (3,8)

TABLE

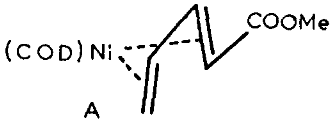
entry	diene	catalyst			products	
	 1	→			 2	+  3
1^a		$Ni(COD)_2$	$P(C_6H_{11})_3$	77%	2.5	$\overbrace{67.3, 2.3, 17.0, 6.9}^{93.5}$
2^a		$Ni(COD)_2$	$P(Ph)_3$	77%	31	69
3		—	—		starting diene 1	
4		$Ni(acac)_2$	$P(Ph)_3$		"	
5^c	Et_2AlOEt	—	—		"	
6^b	Et_2AlOEt +	$Ni(COD)_2$	$P(Ph)_3$	50%	90	0
7^b	"	$Ni(acac)_2$	$P(Ph)_3$	83%	100	0
8^b	"	$Ni(acac)_2$	$P(C_6H_{11})_3$	68%	81	19

a:molar ratio:diene 1/Ni/L:20/1/1;b:molar ratio:diene 1/Et_2AlOEt/Ni/L:20/2/1/1;c:molar ratio:diene 1/Et_2AlOEt:20/2
All reactions have been carried out in benzene at 60°C for 24 hours;except for entry 1(see ref. 6)

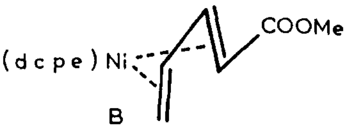
Comparison of entry 7 and 8 shows that the complexation of the aromatic ring of triphenylphosphine by the alkylaluminum is not a major process, as the selectivity in 2 only drops from 100 to 81. This should be compared with entry 1 and 2, which emphasise the influence of the basicity of the phosphine : the replacement of $P(C_6H_{11})_3$ (entry 1) by the less basic PPh_3 (entry 2) (8) increases the 2/3 ratio. This can easily be explained by the fact that $P(C_6H_{11})_3$ favours the σπ forms of the intermediate nickel complexes, leading to vinylcyclohexene derivatives. The changes in selectivity observed when going from entry 8 to 7, is more likely due to such a change in basicity.

However the comparison of the results obtained with the same phosphine (entry 1 and 8 or 2 and 7) but using either Ni(COD)$_2$ or Ni(acac)$_2$/Et$_2$AlOEt, shows that the difference in selectivity is very marked, and always in favour of compound $\underline{2}$ when the Ni(acac)$_2$/Et$_2$AlOEt couple is used. These results could be interpreted by invoking the formation of a catalyst where the nickel would be associated with aluminum via acetylacetonate bridges (9). This appears to be unlikely as similar selectivity is also observed with the Ni(COD)$_2$/Et$_2$AlOEt catalyst (entry 6). Furthermore the diene ester $\underline{1}$ remains unchanged when treated independently by Ni(acac)$_2$/PPh$_3$ (entry 4) or Et$_2$AlOEt (entry 5). Consequently the cyclodimerization is definitely induced by the zerovalent nickel, and the high selectivity in compound $\underline{2}$ must be due to the alkylaluminum used as reducing agent.

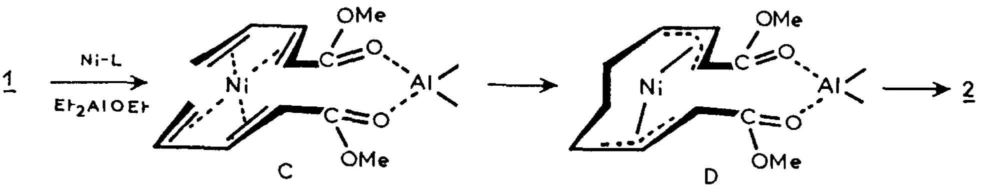
The comparison of our results with those of Wilke on butadiene (the same COD,VCH distribution is obtained either with Ni(COD)$_2$-PPh$_3$ or with Ni(acac)$_2$-PPh$_3$-Et$_2$AlOEt) suggests that the increase in selectivity in $\underline{2}$, is due to an interaction between diene ester $\underline{1}$ and the organoaluminum species leading to an intermediate such as D. This is further corroborated by the dramatic increase in selectivity observed when Et$_2$AlOEt is added to the Ni(COD)$_2$/PPh$_3$ catalyst (compare entry 2 and 6). The geometry postulated for intermediate D is in perfect agreement not only with the one of the final product $\underline{2}$ (10), but also with the structure which can be derived from the methyl 2,4-pentadienoate $\underline{1}$ and nickel liganded with bis dicyclohexyl phosphino ethane B (11).Complex A and B have been isolated by Binger and B has been characterized by X-ray cristallography (11).Accordingly ,it is quite reasonable to assume that the replacement of the ligands by an additional methyl 2,4-pentadienoate would lead to C which in turn yields D.



A



B



The regio and stereoselectivity control(which is lost (5,12) when an additional carbon is introduced between the dienic structure and the methyl ester function) is therefore likely to be due to a chelation occuring on the ester oxygens as shown in intermediate D. The present work demonstrates a remarkable directing effect of aluminum organic compound in presence of nickel zero catalysts. It also shows that in such reactions involving oxydo-reduction processes, the action of organoaluminum species used as reducing agent is not limited to this specific role (13). Further work is in progress to obtain more detailed informations on these systems.

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