COOLIGOMERIZATION OF ALLYL ACETATE WITH NORBORNADIENE

AND ITS DERIVATIVES CATALYZED BY NICKEL COMPLEXES

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Recently it has been shown possible to introduce the methylenecyclobutane fragment selectively into hydrocarbons in the norbornene series by cyclocodimerizing them with allyl esters in the presence of low-valency Ni complexes [1]. The reaction is general and enables derivatives of 3-methylene-tricyclo[4.2.1.0²,⁵]nonane to be obtained in one stage from norbornenes and allyl acetate.

In order to extend the field of application of this reaction, as well as to develop methods for synthesizing new types of polycyclic hydrocarbons, we have studied the reaction of norbornadiene (NBD) and its derivatives with allyl acetate when catalyzed by low-valency Ni complexes.

In contrast to norbornene (NB) [1] the reaction of NBD with allyl acetate (1:1) in the presence of the system $Ni(acac)_2-(i-PrO)_3P-Et_3A1$ (1:4:3) takes place in a more complex way and is accompanied by the formation of the three isomeric products



The ratio of the isomers (I)-(III) is determined by the temperature of the reaction (Table 1) and depends to a lesser extent on the conditions under which the catalytic system is prepared. For example, if the reduction of Ni(acac)₂ by the action of Er_3Al is carried out at -15 to -20°C and the reaction of NBD with allyl acetate at 20-40°C then the reaction mixture usually contains appreciably less of the isomer (II) (see Table 1, experiments 1-4) than in the case where the catalyst is prepared at -5°C (experiments la-4a). This difference disappears for higher temperatures (experiments 5, 6, 5a, 6a).

If the reaction of NBD is carried out with a twofold molar excess of allyl acetate $(20^{\circ}C, NBD:Ni(acac)_{2} = 10$ to 15:1 then in addition to (III) the product (IV) appears in the reaction mixture, the formation of which can be represented as the addition to NBD of 2 moles of allyl acetate. The yield of (IV) is $\sim 54\%$ in virtually all the experiments. It



can be obtained with high selectivity (yield 72%) in the codimerization of (I) with allyl acetate under the conditions described above.

Institute of Chemistry, Bashkir Branch of the Academy of Sciences of the USSR, Ufa. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 1, pp. 154-160, January, 1987. Original article submitted May 13, 1985. TABLE 1. Dependence of the Yield and Composition of the Reaction Products from the Codimerization of NBD with Allyl Acetate on the Reaction Temperature and the Catalyst Preparation Conditions (Catalyst Ni(acac)₂-(1-PrO)₃P-Et₃Al (1:4:3); solvent, toluenei-PrOH (1:2), NBD:allyl acetate = 1:1, NBD: Ni(acac)₂ = 25:1)

Expt.	T., ℃	Time for complete	Yield of	Composition %				
No.*		conversion of NBD, h	(I)—(III), %	· (I)	(II)	(III)		
1	20	40	78	87	0	. 13		
- 1a	$2\check{0}$	4.0	78	82	5	13		
2	· 25	3.5	78)	76	1	23		
3	30	2,0	75	68	2	30		
3a	30	2.0	75	63	8	29		
4	40	0.5	71	68	3	29		
4a	40	0.5	71	62	. 9	29		
5	60	0.25	71	38	27	35		
5a	60	0.25	-71	37	27	36		
6	80	0,08	65	31	35	34		
6a	80	0,08	65	31	35	34		

*A catalyst prepared at -5° C, at -15 to -20° C in remaining experiments.

TABLE 2. Dependence of the Yield and Isomeric Composition of Products from the Cyclocodimerization of NBD with Allyl Acetate in the Ratio $i-(PrO)_3P$: Ni(acac)₂ (catalyst Ni(acac)₂-(i-PrO)₃P:Et₃Al, Ni(acac)₂:Et₃Al, 1:3, solvent toluene - i-PrOH(1:2), 20°C, 4 h)

Molar ratio (<i>i</i> -prO) ₃ P: : Ni(acac) ₂	NBD conver- sions %	Yield of	Compo		
		(1) - (111), %	(I)	(11)	(111)
0		No r	eaction	ñ	·
. 1 2	30 100	22 67	65 80	6	29 17
3 4	100	78 78	82 87	1	17
	82 75	73 72	86		13
	Molar ratio (t-PrO) ₃ P: : Ni(acac) ₂ 0 1 2 3 4 10 20	$\begin{array}{c c} Molar \\ ratio \\ (i-PrO)_{3}P: \\ : Ni(acac)_{2} \\ \end{array} \\ \hline \\ 0 \\ 1 \\ 3 \\ 100 \\ 3 \\ 4 \\ 100 \\ 4 \\ 100 \\ 10 \\ 82 \\ 20 \\ 75 \\ \end{array} \\ \begin{array}{c} NBD \ conversional \\ NBD \ conversional $	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	$ \begin{array}{c c c c c c c c c c c c c c c c c c c $

*For ratios $(i-PrO)_3P:Ni(acac)_2 = 0$ to 3:1 the reduction of Ni(acac)_2 was carried out in the presence of NBD.

A change in the ratio $(i-PrO)_{3}P:Ni(acac)_{2}$ has little effect on the isomeric composition of the reaction products but affects the total yield of (I)-(III) substantially (Table 2). The optimum ratios are $R_{3}P:Ni = 3:1$ and 4:1. A decrease or an increase in the concentration of the organophosphorus ligand in the catalyst composition leads to a decrease in the conversion of NBD. In the absence of an activator ligand cooligomerization products cannot be obtained, the initial monomers being recovered unchanged from the reaction under these conditions.

We have established that the most effective method which enables the selectivity of the cyclocodimerization of NBD with allyl acetate to be controlled, is to change the nature and structure of the organophosphorus activator in the composition of the catalyst (Table 3). In particular, highly active and selective catalysts for the cyclocodimerization of NBD with allyl acetate are obtained from phosphites prepared from the secondary alcohols $(i-PrO)_3P$, $(sec-BuO)_3P$, $(cyclo-C_6H_{11}O)_3P$ (see Table 3, experiments 7, 8, 13-16). The other phosphites we tested accomplish codimerization only at elevated temperatures and act less selectively. An exception is $(CH_3O)_3P$; catalysts based on it possess a fairly high selectivity with respect to the isomer (I) but the over-all yield of (I)-(III) is low here (experiment 2). TABLE 3. Effect of the Nature and Structure of the Organophosphorus Ligand on the Yield and Isomeric Composition of the Products from the Cyclocodimerization of NBD and Allyl Acetate (catalyst Ni(acac)_2:L:Et_3Al, 1:4:3, solvent toluene - i-Pr(OH) (1:2), NBD:Ni(acac)_2 = 25:1)

Expt.	, A - Minut	m 00		NBD con-Yield of version (I)-(III)		Isomeric com- position, %		
No.	ACLIVATOR L	т., ъ	11me, h	. %		(I)	(II)	(III)
1 2	(MeO)₃P	20 80	$6.0 \\ 3.0$	0 30	0 37	76		
3 4	(EtO)₃P	$\begin{array}{c} 20\\ 80 \end{array}$	6.0 0.5	0 100	0 69	$\frac{-}{56}$	- 18	26
5 6	(n-PrO) ₃ P	20 80	$\begin{array}{c} 6.0\\ 0.5\end{array}$	0 100	0 72	- 66	19	- 15
7 8	(<i>i</i> -PrO) ₃ P	20 80	4,0 0,5	100 100	78 76	87 17	0 45	13 38
9 10	(n-BuO)3P	20 80	6.0 0,5	0 100	0 76	 47	- 30	- 23
11 12	(i-BuO)₃P	20 80	6.0 0,5	. 0 100	0 70	 28	 46	26;
13 14	(sec-BuO) ₃ P	20 80	6.0 1,0	100 100	77 39	79 14	11 42	10) 44
15 16	(C ₆ H ₁₁ O) ₃ P	20 80	5.0 0.5	100 100	76 67	80 28	$\frac{4}{50}$	16 22
17 18	(PhO)₃P	20 80	6.0 1.0	0 10	0 7	 35		- 26
$\begin{array}{c} 19 \\ 20 \end{array}$	(Bu)₃P	20 80	6.0 6,0	0 100	0 17	_ 8	 68	- 24

Note. The catalytic systems based on $(t-BuO)_3P$, Ph_3P , $(Ph_2PCH_2)_2$ and $(Et_2N)_3P$ are not active in the reaction concerned.

It must be noted that, in contrast to NB [1], NBD also enters into cyclocodimerization with allyl acetate in the presence of the three-component catalytic system $Ni(acac)_2-Bu_3P-Et_3Al$ which contains Bu_3P as the activator ligand. Under these conditions the selectivity for the isomer (II) can be increased considerably.

The use of the individual complexes Ni([(i-PrO)₃P]₃Ni - Et and [(i-Pro)₃P]₄Ni), first tested in [1, 2], as catalysts for the cyclocodimerization of NBD with allyl acetate enables exceptionally active catalytic systems for the synthesis of (I)-(III) to be obtained (Table 4). These complexes accomplish cyclocodimerization under milder conditions and over a shorter period but in their selectivity of action they are rather poorer than the three-component system Ni(acac)₂ - (i-PrO)₃P - Et₃Al. By remaining in the coordination sphere of the central atom of the catalyst excess Et₃Al or Al compounds formed during the preparation of the cyclocodimerization process.

We then studied the possibility of involving the substituted NBD (V)-(X) in the reaction.



TABLE 4. Dependence of the Yield and Composition of the Products from the Cyclocodimerization of NBD with Allyl Acetate on the Nickel Catalyst (NBD:allyl acetate = 1:1; NBD:catalyst = 25:1; solvent, toluene-i-PrOH (1:2), 20°C, NBD conversion 100%)

	Catalyst	Time h	Yield of	Isome tion,	ric co	omposi-
,		11me, 11	(1)—(111), %	(I)	(II)	(III)
	Ni (acac) ₂ : (<i>i</i> -PrO) ₃ P : Et ₃ Al (1:4:3) [(<i>i</i> -PrO) ₈ P] ₄ Ni [(<i>i</i> -PrO) ₈ P] ₈ Ni-Et	4 3 2	78 65 83	87 51 58	0 6 0	$\begin{array}{c} 13\\ 43\\ 42 \end{array}$

As was to be expected, the behavior of V, which does not have a substituent directly at the double bond is very similar to NBD in the reaction



The NBD derivatives (VI)-(X), which contain substituents in the 2 position do not form a cyclodimer with a tetracyclo $[4.3.0.0^2, 4.0^3, 7]$ nonane structure at all, irrespective of the reaction conditions, or the nature and structure of the components of the catalyst



As may be seen, the substituted NBD very much recall NB and its derivatives in the cyclocodimerization reaction with allyl acetate. According to [3] the introduction of a substituent into the 2 position of NBD leads to a symbatic shift in the ionization potentials of the $\pi\alpha a_1$ -, πb_1 -orbitals of the 1,4-diene system and has virtually no effect on the difference in the energies of these orbitals. Consequently, the difference in the behavior of the 2-substituted and unsubstituted NBD is most probably caused by steric hindrances and electronic factors.

With an increase in the reaction temperature above 30°C in the cyclocodimerization of substituted NBD with allyl acetate we observed the formation of a small amount of methylenevinyl isomers. However, the clearly exhibited tendency of these compounds to form resins under cyclocodimerization conditions did not permit a careful study of their structure.

The structure of the compounds obtained was verified on the basis of spectral data (Table 5); the ¹³C NMR spectra will be published in a separate paper.

EXPERIMENTAL

We used monomers of not less than 99% purity, prepared as in [5-7]. GLC was conducted on a Chrom-4 instrument with a 3×0.003 m column containing 10% PEG 6M on N=AW=HMDS Chromatone (0.125-0.160 mm), carrier gas helium (50 ml/min), evaporator temperature 300°C, temperature range 50-220°C. The IR spectra were recorded on a UR-20 instrument and the mass spectra on an MKh-1306 instrument. All the compounds were isolated by vacuum rectification on a column. The complexes [(i-PrO)₃P]₃Ni - Et and [(i-PrO)₃P]₄Ni were obtained as in [1, 4].

<u>Method of Preparing the Catalytic System and Conducting the Reaction</u>. 0.5 g (1.95 mmole) of Ni(acac)₂ was dissolved under argon in 5 ml of dry toluene and 7.78 mmole of the corresponding phosphite added. The solution was cooled to -5° C or to -15 to -20° C and 0.67 g (5.84 mmole) of Et₃Al added dropwise with stirring. After 5-10 min 10 ml of dry

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TAB.	Cyc	Ë	ł

z/w	132 132	132	172	158	158	158	162	176	204	248	166
IR spectrum v, cm ⁻¹	730, 1575, 895, 1675, 3075 730, 1575, 895–855, 1660, 910,	990, 1638, 3080, 810, 1010, 975 880, 1665, 3080, 810, 1010, 975	885, 1670, 3075	735, 1545, 880, 1675, 3078, 995, 1020	735, 1545, 890, 1678, 915, 988,	1015, 30(6), 3075, 790, 800, 820, 1015, 3060, 985	730, 1564, 880, 1680, 3070, 1080-1020, 3400-3200	885, 1675, 3075, 1115–1095, 698, 1630	885, 1668 , 3075, 1245–1235, 1740, 698, 1628	890, 1670, 3075, 1540, 1620, 1230, 1265, 1720	885, 1670, 3080, 680, 1580, 740
n_D^{20}	1,502/ 1,4808	1,5100	1,5330	1,5125	1,5060	1,5180	1,5205	1,5006	1,5018	1,5148	1,5100
bp, °C (p, mm Hg)	65 (25) 56 (25)	70(25)	56,0- E0 E /0 E)	70(10)	64(10)	78(10)	89-91 (0,5)	95-97 (10)	84-85 (1.0)	113-116 (0.2)	71(9)
Codimer, content in mixture, %	(I), 76 (II), 1	(111), 23	(IV)	(XI), 58	(XII), 12	(XIII), 30	(XIV), 100	(XV), 100	(XVI), 100	(XVII), 100	(XVIII), 100
Yield of codimers, %	78		54		77		50	8	95	96	76
Diene conversion (%)	100		100		100		17	100	58	100	100
Time, h	3.5	`	15		ų			∞	x	15	7
Diene	NBD		NBD		(V)		(IV)	(111)	(IIII)	(IX)	(X)
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*Cyclocodimerization carried out at 25° C. †Two moles of allyl acetate in relation to NBD used in the experiment. ‡Catalyst decomposed after 8 h.

isopropyl alcohol was added slowly with intense mixing. This led to the deposition of fine white crystals. Then 48.6 mmole of the corresponding diene and allyl acetate was added and the resulting mixture transferred under argon to a thermostatted reactor having a magnetic stirrer. At the end of the reaction the mixture was diluted with 15-20 ml of pentane and 5-10 ml of aqueous ammonia added to decompose the catalyst. The organic layer was washed with water and dried over MgSO₄. The solvent was evaporated off and the residue distilled under vacuum. The physical chemical constants and spectral characteristics of the products are presented in Table 5.

CONCLUSIONS

The cyclocooligomerization of allyl acetate with norbornadiene and its derivatives to compounds which are not readily accessible in the series tricyclo[$4.2.1.0^2$, ⁵]nonane, tetracyclo[$4.3.0.0^2$, ³.0², ⁴]nonane and tetracyclo[$4.4.1.0^2$, ⁵.0⁷, ¹⁰]undecane has been achieved with yields of 60-95%, involving the participation of low-valency nickel complexes.

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CYCLODIMERIZATION OF 3, 3-DIMETHYLCYCLOPROPENE IN THE PRESENCE

OF ZIEGLER-NATTA NICKEL SYSTEMS

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Cyclopropene hydrocarbons are known to undergo cyclodimerization into a tricyclo- $[3.1.0.0^2, *]$ hexane system in the presence of some transition metal complexes [1-3] and also under the effect of zeolites [4] or Lewis acid etherates [5].

The possibility of cyclodimerization of 3,3-dimethylcyclopropene (DMCP) in the presence of catalysts of the Ziegler type: nickel compounds combined with aluminum-containing Lewis acids, transitional systems for dimerization of aliphatic olefins, was studied for the first time in the present article. The role of the individual components of these systems in the dimerization of DMCP was determined. The composition of these catalytic systems suggests the dimultaneous existence of different active sites of transformation of cyclopropenes (ionic, ion-coordination, coordination) in the reaction medium.

DMCP is cyclodimerized in the presence of some Ni(0) complexes with labile bonds of the ligands which are easily displaced by the substrate [2, 3]. We found that stable and trially inactive Ni complexes can also be catalysts of this reaction when they are used combination with alkylaluminum halides or Al_2O_3 . In the presence of the well-known Re catalyst, DMCP does not undergo significant transformations in ether solution at room temperature. However, when an equimolar amount of $Et_3Al_2Cl_3$ is added to $Ni(CO)_2(PPh_3)_2$ (Ct-1), fast and relatively selective transformation of DMCP into 3,3,6,6-tetramethyltricyclo-

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