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NICKEL COMPLEX-CATALYZED CODIMERIZATION OF ALLYL ESTERS WITH COMPOUNDS IN THE NORBORNENE SERIES

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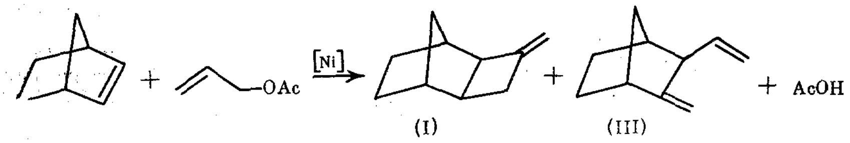
Among the transition metal complex-catalyzed reactions of simple olefins and dienes which command special attention are those processes that lead to strained polycyclic hydrocarbons. As an example, it was recently reported that 3-methylene-exotricyclo[4.2.1.-$0^{2,5}$]nonane (I), containing a methylenecylcobutane fragment, could be prepared in one step via the reaction of allyl acetate (AA) with norbornene (NB), catalyzed by the complex $[(i\text{-PrO})_3]_4Ni$ (II) [1].



(I) (III)

We have been studying this reaction recently, and have been unable to reproduce these results, however, probably because of the relatively low stability of the indicated complex and its extreme sensitivity to the nature of the solvent and the structure of the monomer precursors.

In order to develop effective new catalysts for the cyclodimerization of NB and AA to give exclusively (I), and also in order to extend the viability of this reaction to other allyl esters and NB derivatives, we have examined the reactivity of tri-, tetra-, penta-, and hexacyclic NB derivatives with a variety of allylic compounds containing both electron-donating and electron-accepting substituents. Low-valence Ni complexes, prepared *in situ* via the reduction of $Ni(acac)_2$ with Al and Mg derivatives in the presence of phosphines and phosphites, have been used as catalysts in these reactions.

Treatment of NB and AA in the presence of a catalytic system (CS) composed of $Ni(acac)_2$—$P(OR)_3$—$AlEt_3$ gave isomeric hydrocarbons, namely (I) and 2-methylene-exo-3-vinylbicyclo-[2.2.1]heptane (III), along with AcOH, just as was reported in the case of (II). The nature of the solvent exerts a significant influence on both the yields and product composition of this reaction (Table 1). For instance, the codimerization of AA and NB is most successful when the reaction is carried out in a medium composed of toluene and an aliphatic alcohol (methanol is an exception) at various component ratios. In a toluene—AcOH (1:2) medium, the direction of the reaction is shifted in favor of formation of the known NB dimer [2]; small amounts of AcOH, which is generated during the course of the reaction, do not seem to affect the activity and selectivity of the CS.

The reaction is also notably sensitive to the nature of the organophosphorus ligand. The most highly active catalysts were obtained using $(i\text{-PrO})_3P$, $(sec\text{-BuO})_3P$, and $(C_6H_{11}O)_3P$ as ligands (see Table 2). CS derived from these ligands showed activity in the 20-120°C temperature range.

The temperature also exerts a significant influence on the product composition of the reaction. At 20°C the predominant product is (I): when $Ni(acac)_2$—$(i\text{-PrO})_3P$—$AlEt_3$ is used

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TABLE 1. Effect of Solvent Nature on the Yield and Product Composition of the Reaction of Norbornene and Allyl Acetate [$Ni(acac)_2$—$(i\text{-}PrO)_3P$—$AlEt_3$ catalyst, 1:4:3, 25°C, 6 h, prepared in toluene]

Solvent	Toluene/solvent ratio (volume)	Total yield (I) + (III), %	Composition, %	
			(I)	(III)
Toluene	—	43	88	12
MeOH	1 : 2	14	100	0
EtOH	1 : 2	80	94	6
i-PrOH	1 : 2	82	94	6
The same	1 : 1	80	95	5
»	2 : 1	80	94	6
»	1 : 5	81	95	5
»	1 : 10	81	95	5
»	10 : 1	81	94	6
BuOH	1 : 2	81	95	5
sec-BuOH	1 : 2	80	92	8
t-BuOH	1 : 2	81	86	14
THF	1 : 2	58	77	23
AcOH *	1:2	Traces	Traces	—
AcOH †	1 : 0.7(+*i*-PrOH)	96	95.4	4.6

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*Norbornene dimer [2] is formed in 20% yield.

†This is the amount of AcOH present at the end of the reaction.

TABLE 2. Effect of the Nature of the Organophosphorus Activator on the Yield and Product Composition of the Codimerization Reaction of Allyl Acetate and Norbornene [$Ni(acac)_2$—L—$AlEt_3$ catalyst, 1:4:3, toluene:i-PrOH, 1:2]

Activator L	T, °C	Time*, h	NB conversion, %	Yield (I) + (III), %	Composition, %	
					(I)	(III)
$(MeO)_3P$	20	10	0	0	—	—
$(MeO)_3P$	80	3.5	100	80.6	15	85
$(EtO)_3P$	20	10	0	0	—	—
$(EtO)_3P$	80	0.5	100	70	78	22
$(PrO)_3P$	20	10	0	0	—	—
$(PrO)_3P$	80	0.75	100	74	49	51
$(i\text{-}PrO)_3P$	20	10	100	82	99	1
$(i\text{-}PrO)_3P$	80	0.5	100	75	52	48
$(BuO)_3P$	20	10	0	0	—	—
$(BuO)_3P$	80	1	100	74	64	36
$(i\text{-}BuO)_3P$	20	10	0	0	—	—
$(i\text{-}BuO)_3P$	80	1	100	73	41	59
$(sec\text{-}BuO)_3P$	20	10	100	80	73	27
$(sec\text{-}BuO)_3P$	80	1	100	72	35	65
$(t\text{-}BuO)_3P$	20	10	0	0	—	—
$(t\text{-}BuO)_3P$	80	10	0	0	—	—
$(C_6H_{11}O)_3P$	20	4	100	76	68	32
$(C_6H_{11}O)_3P$ †	80	0.5	15	12	32	68
$(PhO)_3P$	20	10	0	0	—	—
$(PhO)_3P$ **	80	2	10	8	35	65
$(C_6H_{11}O)_3P$+	20	10	0	0	—	—
+$(EtO)_3P$	80	0.5	100	71	68	32
Ph_3P, Bu_3P, $[Ph_2P\text{–}CH_2]_2$, $[N(Et)_2]_3P$			0	0	0	0

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*At 20°C the reactions were carried out for 10 h, whereas at 80°C the reactions were run to complete NB conversion.

†The catalyst undergoes decomposition.

as the CS, a process selectivity of 99% with respect to (I) is achieved. At higher temperatures the differences noted for the series of phosphite ligands studied with respect to the reaction selectivity are no longer significant. This led us to conclude that at higher temperatures, under the conditions for cyclocodimerization in i-PrOH media, transesterification occurred, leading to the formation of $(i\text{-}PrO)_3P$, and that as a result, the catalytically active complex was always the same, regardless of the structure of the phosphite originally introduced into the reaction medium. A specially constructed series of experiments revealed, however, that for the reactions of alkyl- and aryl phosphites with i-PrOH

TABLE 3. Comparative Study of the Activity and Selectivity of Different Catalysts (reaction temperature 25°C)

Catalyst	Additive	Solvent	Time, h	NB Conversion, %	Yield of (I) + (III), %	Composition, %	
						(I)	(III)
$[(i\text{-PrO})_3P]_3NiEt$	None	Toluene	9	100	81	91	9,0
The same	»	i-PrOH	9	100	87	88	12
»	»	Toluene – i-PrOH, 1 : 2	9	100	80	79	21
»	$AlEt_3$, Ni : Al=1 : 1	Toluene	9	60	81	94	6
»	The same	Toluene – i-PrOH, 1 : 2	9	100	84	86	14
$[(i\text{-PrO})_3P]_4Ni$	same	Toluene	9	68	75	72	28
same	»	i-PrOH	9	81,8	80	76	24
»	»	Toluene – i-PrOH, 1 : 2	9	86	37	68	33
»	$AlEt_3$, Ni : Al=1 : 1	Toluene	10	68	75	72	28

up to 100°C, successive addition of AA, NB, AcOH, or the other indicated monomers to the CS did not lead to simultaneous transesterification of the phosphite ligands.

The low activity of CS derived from $(MeO)_3P$, $(EtO)_3P$, $(PrO)_3P$, $(BuO)_3P$, and $(PhO)_3P$ and especially phosphines is attributed to the fact that these ligands form relatively strong complexes with Ni, which hinders approach to the central atom of the catalyst and activation of NB and AA. For the complexes prepared from the indicated ligands, the concentration of NiL_4 is in the range given by $K_{diss} = 10^{-9}$–10^{-10}, whereas in the case of (II) the concentration of NiL_4 is given by $2.7 \cdot 10^{-5}$ [3]. According to [4], catalyst activity in such reactions as isomerization processes can be correlated directly with K_{diss}.

The following experimental data also serve to confirm this conclusion. The codimerization reaction of AA with NB at 20°C in the presence of $(i\text{-PrO})_3P$, $(sec\text{-BuO})_3P$, and $(C_6H_{11}O)_3P$ can be terminated by the addition of phosphites such as $(EtO)_3P$, which are inactive at this temperature, to the reaction mixture; at higher temperatures, 80°C, the reaction can be renewed, and the ratio of the two codimers (I) and (III) is close to the value obtained when the less active phosphite is used in pure form (Table 2).

The feasibility of forming complexes of the composition NiL_4 by the reduction of $Ni(acac)_2$ with $AlEt_3$ in the presence of phosphites has been demonstrated in a previous paper [3]. Thus, reduction of $Ni(acac)_2$ with triethylaluminum in the presence of $(i\text{-PrO})_3P$ gives complex (II) in 30% yield. The large differences in process selectivity for the codimerization of NB and AA in the presence of complex (II) in pure form, versus in the presence of the CS employed herein, have stimulated us to attempt to isolate the catalytically active form of the complex in this reaction. Thus, in contrast to [3], we were able to isolate from the reaction mixture obtained by treatment of $Ni(acac)_2$ with triethylaluminum in the presence of $(i\text{-PrO})_3P$ (Ni:P:Al = 1:4:3) at –10–(–15°C) a complex with 80% yield, having a molecular weight of 715–720 (cryoscopic; the molecular weight calculated for (II) is 891); this complex has not previously been described. Thermal decomposition of the complex gave ethane, ethylene, H_2, as well as traces of butenes and hexenes; workup of this complex with 10% H_2SO_4 gave an amount of ethane corresponding to the presence of one ethyl group in the complex (accuracy ±10%). Polarography of a solution of this complex in MeCN indicated that the Ni atom was present in the complex in the +1 oxidation state [5, 6]. Based on these pieces of data, we have assigned this newly isolated complex the structure (IV):

$$\begin{tikzcd} & {[(i\text{-PrO})_3P]_3NiEt} \arrow[dl, "H_2SO_4"'] \arrow[dr, "\Delta"] & \\ C_2H_6 & (IV) & C_2H_6 + C_2H_4 + H_2 + C_4H_8 + C_6H_{12} \end{tikzcd}$$

The catalytic activity of complex (IV), prepared in a known manner, in alcohol–toluene as solvent was very similar to the activity of the $Ni(acac)_2$–$(i\text{-PrO})_3P$–$AlEt_3$, 1:4:3 (see Table 3) catalytic system. It is interesting that the activity of complex (IV) decreased upon the addition of $AlEt_3$. It was also found that the activity of the system could be restored if alcohol was added to the reaction system composed of (IV)–$AlEt_3$ (cf. Table 3). These experiments lead us to assume with confidence that excess organoaluminum reducing

TABLE 4. Effect of $Ni(acac)_2:(i\text{-}PrO)_3P$:NB Mole Ratio on the Yield and Product Composition of the Codimerization Reaction of Norbornene and Allyl Acetate (25°C, 6 h, toluene–i-PrOH, 1:2, $Ni(acac)_2$–$(i\text{-}PrO)_3P$–$AlEt_3$ catalyst, NB conversion 100%)

$Ni(acac)2:(i\text{-}PrO)_3P$ Mole Ratio	Addition of NB to reduction (Ni:NB, moles)	Yield of (I) + (III), %	Composition, %	
			(I)	(III)
0–3	0	Catalyst decomposes		
1	0–3	same		
1	4	80	90	10
2	4	82	94	6
3	4	82	95	5
4	0	82	94	6
4	4	82	94	6
5	0	80	92	8
6	0	79	90	10
10	0	78	84	16

TABLE 5. Effect of the Nature of the Reducing Agent on the Yield and Composition of the Codimers (I) and (III) ($Ni(acac)_2$–$(i\text{-}PrO)_3P$–reductant catalyst, 1:4:3, NB: AA = 1:1 20°C, 10 h)

Reductant	NB conversion, %	Yield (I) + (III), %	Composition, %	
			(I)	(III)
$AlEt_3$	100	82	99	1
$Al(i\text{-}Bu)_3$	100	78	85	15
$AlEt_2Cl$	100	20	88	12
$LiAlH_4$	100	74	85	15
$MgBu_2$	60	78	94	6
$NaBH_4$	100	48	96	4
t-BuOK		No reaction		
i-PrONa		same		

agent deactivates the catalyst as a consequence of complex formation with the latter. The main reason for the favorable effect of alcohol on the reaction is probably its role in decomposing excess $AlEt_3$ and disrupting the type of complex formation noted above. The low efficacy of methanol as solvent in this reaction system can be explained in terms of the low solubility of complex (IV) in methanol. These results also lead us to conclude that $[(i\text{-}PrO)_3P]_3NiEt$, compound (IV), is one of the intermediate complex forms which is necessary for the reaction of NB and AA.

The positive results obtained using pure complex (II) as the catalyst, as well as the data obtained in the study of the effect of the $Ni(acac)_2:(i\text{-}PrO)_3P$ molar ratio on the yield and composition of the products of the cross reaction of NB with AA (Table 4), indicate that complex (IV) is not the catalytically active site for this reaction. It is probable that, under the conditions of the cyclocodimerization reaction, complex (IV) undergoes a series of successive conversions leading to the formation of less stable catalytically active complexes containing Ni–H and Ni–Ni bonds, which are necessary for the formation of codimer products.

Studies of the $Ni(acac)_2:(i\text{-}PrO)_3P$ ratio and the effect of NB used as an additive in the catalyst composition on the cyclocodimerization reaction have also permitted us to confirm that the coordinating ability of NB is similar to that of alkyl phosphites. At a $Ni(acac)_2$: alkyl phosphite ratio of 1:3, the low valent Ni complexes begin to decompose; this can be avoided by the addition of 4 moles of NB to the catalytic system prior to reduction. The catalyst prepared in this manner, however, has a shorter lifetime and is rapidly deactivated as a consequence of the formation of colloidal nickel. Other olefins, even though they may be strained (3,3-dimethylcyclopropene and cyclopentene), do not stabilize the complex, which is consistent with data [7] indicating that the Ni–NB bond is much stronger than the bond formed between nickel ions and cyclopentene.

TABLE 6. Effect of Structure of the Allylic Component on the Yield and Product Composition of the Reaction with Norbornene (Ni(acac)$_2$—(i-PrO)$_3$P—AlEt$_3$ Catalyst, 1:4:3, 25°C, benzene—i-PrOH, 1:2, NB conversion 100%)

Allyl Compound	Time, h	Yield of (I) + (III), %	Composition, %	
			(I)	(III)
Allyl formate	1.5*	43	100	0
Allyl acetate	6	82	94	6
Allyl propionate	6	84	81	19
Allyl benzoate	5.5	59	79	21

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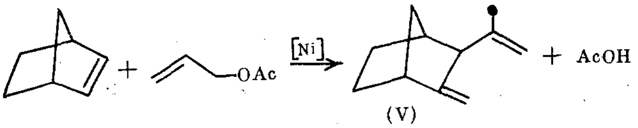
*Catalyst decomposes after 1.5 h, at a NB conversion of 26%.

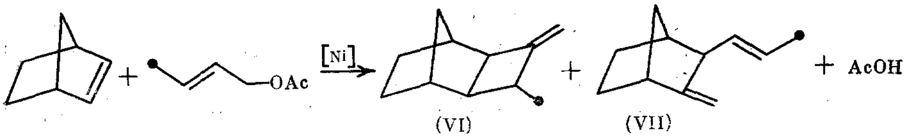
AlEt$_3$, Al(i-Bu)$_3$, MgBu$_2$, and LiAlH$_4$ were found to be the most effective reducing agents for the Ni(acac)$_2$—P(OR)$_3$ catalyst in the reaction of AA with NB (Table 5).

A series of other allyl compounds in addition to AA were examined and found to be active in codimerization reactions with NB; these included allyl formate and allyl esters of propionic and benzoic acids. Allyl alcohol, allyl halides, as well as simple allyl ethers and thioethers did not undergo reaction with NB under the conditions described herein. The cyclocodimerization reaction of allyl formate with NB allowed us to prepare the cyclic dimer (I) with 100% selectivity, although the total yield of codimers in this reaction was considerably lower than in the case of AA. The catalyst decomposition which is observed in the experiments involving allyl formate can be explained in terms of the formation of HCOOH during the course of the reaction (Table 6).

Treatment of methallyl acetate with NB under the conditions described above leads to only one of the possible isomers, namely 2-methylene-3-exoisopropenylbicyclo[2.2.1]heptane (V), in 75% yield.



Crotyl acetate is less reactive and reacts with NB only at 80°C to give a mixture of two isomeric compounds, 3-methyl-4-methylenetricyclo[4.2.1.0^{2,5}]-nonane (VI) and 2-methylene-exo-3-(propen-1-yl)bicyclo[2.2.1]heptane (VII) (total yield 60%).



Compounds (V)-(VII) were identified by comparison with authentic samples [8, 9].

We have further examined the codimerization of AA with NB derivatives of different structure. As can be seen from the data in Table 7, the codimerization of AA with a variety of compounds is a selective reaction which affects only an unsubstituted norbornene double bond. Thus, more complex structural derivatives of the parent strained olefin, which contain 5,6-exo-substituents, do not greatly change the reaction time or the yield and composition of codimer products. In contrast, 5,6-endo-substituted compounds can hinder the reaction significantly, depending on the size of the substituent, and can in fact completely suppress the reaction in some cases. The codimerization process is also completely blocked by the presence of substituents attached directly to the norbornene double bond (cf. Table 7).

The structures of the codimer products were analyzed by ^{13}C-NMR spectroscopy. A separate paper will consider this approach. The PMR spectra of the new compounds prepared herein are quite complex and thus provide little analytical information.

TABLE 7. Dependence of Total Yield and Product Composition on the Structure of the Norbornene Compound, and Physical Chemical Properties of Codimer Products

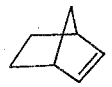
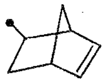
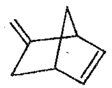
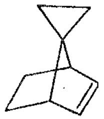
Olefin	T., °C	Time, h	Total yield of codimers, %	Composition, %	Structure of codimer products	bp, °C (p, mm Hg)	n_D^{20}	IR spectrum (ν, cm^{-1})	m/e
	20	10	82	(I) 99 (III) 1	3-Methylene-exo-tricyclo-[4.2.1.0^{2,5}]nonane (I)*				
	80	0.5	75	(I) 52 (III) 48	2-Methylene-exo-3-vinylbicyclo-[2.2.1]heptane (III)*				
	20	10	78	(VIII) 6 (IX) 94	2-Methylene-5(6)-methyl-exo-3-vinyl-bicyclo[2.2.1]heptane (VIII)	76–78(20)	1.4683	890, 915, 995, 1670, 3080	148
	80	0.5	69	(VIII) 46 (IX) 54	3-Methylene-7(8)-methyl-exo-tricyclo-[4.2.1.0^{2,5}]nonane (IX)	65–66(17)	1.4900	880, 1670, 3070	148
	20	10	78	(X) 6 (XI) 94	2,5(6)-Dimethylene-exo-3-vinylbi-cyclo[2.2.1]heptane (X)	65–66(20)	1.4780	890, 915, 990, 1680, 3075	146
	80	0.5	68	(X) 58 (XI) 42	3,7(8)-Dimethylene-exo-tricyclo-[4.2.1.0^{2,5}]nonane (XI)	77–78(20)	1.5011	880, 1670, 1650, 3075	146
	20	10	91	(XII) 58 (XIII) 42	Spiro{2-methylene-exo-vinylbicyclo-[2.2.1]heptane-7,1'-cyclopropane} (XII)	54–55(15)	1.4951	890, 915, 995, 1670, 1015, 3080	160
	80	0.3	86	(XII) 81 (XIII) 19	Spiro{3-methylene-exo-tricyclo-[4.2.1.0^{2,5}]nonane-9,1'-cyclopropane} (XIII)	62–63(5)	1.5068	880, 1020, 1670, 3080	160
	20	10	62	(XIV) 30 (XV) 70	2(4)-Methyl-6-methylene-exo-7-vinyl-endo-tricyclo[3.2.1.0^{2,4}]octane (XIV)	93(27)	1.4980	890, 910, 990, 1020, 3075	160
	80	0.3	54	(XIV) 54 (XV) 46	7(9)-Methyl-3-methylene-exo-endo-tetracyclo[4.3.1.0^{2,5}.0^{7,9}]decane (XV)	99–101(27)	1.5074	890, 1670, 1020, 3082	160

TABLE 7 (Continued)

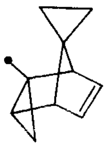
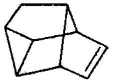
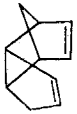
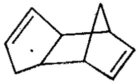
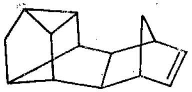
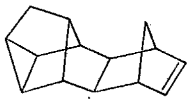
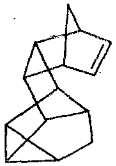
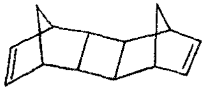
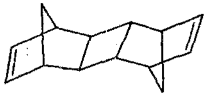
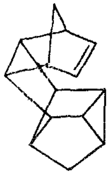
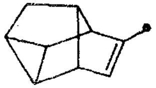
Olefin	T., °C	Time, h	Total yield of codimers, %	Composition, %	Structure of codimer products	bp, °C (p, mm Hg)	n_D^{20}	IR spectrum (ν, cm^{-1})	m/e
	20	10	60	(XVI) 47 (XVII) 53	Spiro{2(4)-methyl-6-methylene-exo-7-vinyl-endotricyclo$[3.2.1.0^{2,4}]$octane-8,1'-cyclopropane} (XVI)	86–87 (8)	1.5084	890, 910, 995, 1020, 1670, 3080	186
	80	0,2	50	(XVI) 58 (XVII) 42	Spiro{7(9)-methyl-3-methylene-exo-endo-tetracyclo$[4.3.1.0^{2,5}.0^{7,9}]$-decane-10,1'-cyclopropane} (XVII)	96–98 (8)	1,5127	880, 1020, 1650, 3070	186
	20	10	88	(XVIII) 16 (XIX) 84	8-Methylene-exo-9-vinyltetracyclo-$[4.3.0.0^{2,4}.0^{3,7}]$nonane (XVIII)	80 (10)	1.5021	790, 810, 890, 915, 990, 1670, 1020, 3075	158
	80	0.5	79	(XVIII) 68 (XIX) 32	3-Methylene-exo-pentacyclo-$[5.4.0.0^{2,5}.0^{6,10}.0^{9,11}]$undecane (XIX)	89 (10)	1,5147	790, 810, 880, 1670, 3075	158
	20	30	61	(XX) 100	9-Methylene-endo-exo-tricyclo-$[5.4.1.0^{2,6}.0^{8,11}]$dodec-3(4)-ane (XX)	97 (8)	1.5342	695, 885, 1670, 3980	172
	20	12	65	(XXI) 100	9-Methylene-exo-exo-tricyclo-$[5.4.1.0^{2,6}.0^{8,11}]$dodec-3(4)-ene (XXI)	52–55 (0,08–0,1)	1,5255	705, 878, 1670, 3050, 3070	172
	20	12	60	(XXII) 100	13-Methylene-endo-exo-exo-heptacyclo-$[9.4.1.0^{2,10}.0^{3,8}.0^{4,6}.0^{5,9}.0^{12,15}]$-hexadecane (XXII)	94–95 (0,05–0.08)	1.5508	795, 815, 880, 1670, 3070	224
	20	12	57	(XXIII) 100	13-Methylene-exo-exo-exo-heptacyclo$[9.4.1.0^{2,10}.0^{3,8}.0^{4,6}.0^{5,9}.0^{12,15}]$hexadecane (XXIII)	80–84 (0.03–0,05)	1.5476	800, 820, 886, 1670, 3020, 3070	224

TABLE 7 (Continued)

Olefin	T., °C	Time, h	Total yield of codimers, %	Composition, %	Structure of codimer products	bp, °C (p, mm Hg)	n_D^{20}	IR spectrum (ν, cm^{-1})	m/e
	20	30	62	(XXIV) 100	13-Methylene-exo-endo-exo-heptacyclo-[9.4.1.0^{2,10}.0^{3,8}.0^{4,6}.0^{5,9}.0^{12,15}]-hexadecane (XXIV)	90–93 (0,02–0,03)	1,5529	805, 815, 880, 1670, 3070	224
	20	24	59	(XXV) 100	12-Methylene-endo-trans-exo-exo-hexacyclo[8.4.1.1^{4,7}.0^{2,9}.0^{3,8}.0^{11,14}]-hexadec-5-ene (XXV)	70–75 (0.03–0.05)	1,5447	730, 880, 1570, 1640, 1670, 3080	224
	20	12 †	54	(XXVI) 100	12-Methylene-exo-trans-exo-exo-heptacyclo[8.4.1.1^{4,7}.0^{2,9}.0^{3,8}.0^{11,14}]-hexadec-5-ene (XXVI)	78–82 (0,03–0,05 mp 44–45		710, 885, 1665, 3070	224
	20	24	50	(XXVII) 100	6(7),14-Dimethylene--exo--exo-trans-exo-exo-heptacyclo[10.4.1.1^{4,9}.0^{2,11}.0^{3,10}.0^{5,8}.0^{13,16}]octadecane (XXVII)	mp 167,5–168.5		890, 1670, 3070	264
					Does not react				
					Same				

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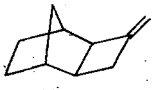
*Physicochemical constant of the compounds (I) and (III) agreeing with literature given in [1].
†Conversion 90%.

In conclusion, systematic investigation of the cyclocodimerization of NB and its derivatives with allyl esters has shown that the reaction is quite general and can be applied effectively as a method for the selective introduction of a methylenecyclobutane fragment to mono- and diolefins containing a reactive norbornene double bond.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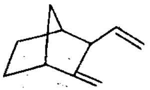
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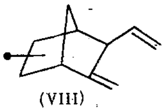
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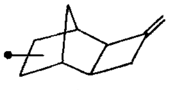
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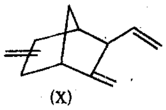
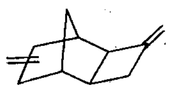

(X)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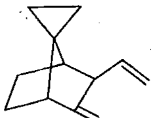
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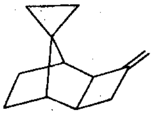
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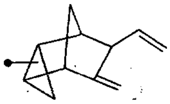
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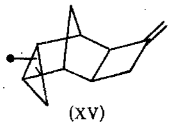
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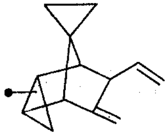
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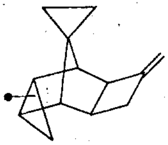
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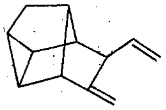
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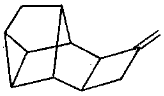
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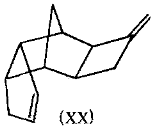
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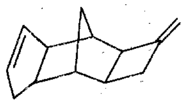
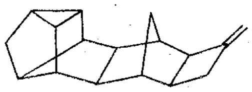

(XXI)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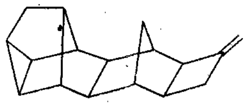
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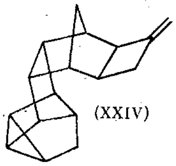
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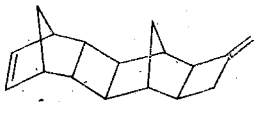
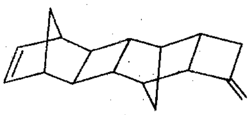

(XXV)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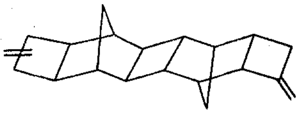
(XXVII)

The structure of the intermediate catalytically active Ni^+ complex, which is necessary for the formation of methylenecyclobutane hydrocarbons from allyl esters and norbornene derivatives, has also been elucidated.

EXPERIMENTAL

The purity of the monomers used in this study was ⩾ 99%. IR spectra were recorded on a UR-20 spectrophotometer. GLC analyses were carried out on a Tsvet-102 chromatograph (3 m × 3 mm column with 15% PEG 6-M on N-AW-HMDS chromatone); helium carrier gas (50 ml/min), injector temperature 300°C, column temperature 50-200°C. All isomers were separated from one another by fractionation on a column. Complex (II) $[(i\text{-}PrO)_3P]_4Ni$ was prepared according to a previous method [10].

General Method for the Preparation of the Catalytic System and for the Reactions. A solution of 0.2 g (0.78 mmole) of $Ni(acac)_2$ in 2 ml of dry toluene was treated with 3.12 mmole of the corresponding phosphite, cooled to −5-(−10°C) and then stirred vigorously under Ar as 0.27 g (2.36 mmole) of $AlEt_3$ was added dropwise. The color of the solution changed from green to light green. After 5 min 4 ml of dry i-PrOH was added at −10°C, followed by 20 mmole of allyl acetate and olefin. The resulting mixture was placed in a thermostatted reactor under an Ar stream. After completion of the reaction the mixture was cooled to 20°C, diluted with pentane, and stirred while 5-6 ml of NH_4OH was added to destroy the catalyst. The organic layer was separated, washed with water, and dried over $MgSO_4$. The solvent was evaporated and the residue distilled under vacuum. The properties of the new compounds are reported in Table 7.

Synthesis of $[(i\text{-}PrO)_3P]_3NiEt$ (IV). A solution of 1.0 g (3.89 mmole) of $Ni(acac)_2$ in 5 ml dry toluene was treated with 3.2 g (15.56 mmole) of $(i\text{-}PrO)_3P$ and cooled to −10-(−15°C). The mixture was stirred vigorously under a stream of Ar and 1.3 g (11.67 mmole) of $AlEt_3$ was added slowly and carefully; the mixture was stirred an additional 10 min at −15°C and then carefully treated dropwise with 10 ml dry i-PrOH and 2 ml MeCN. White crystals formed; they were removed by filtration, washed with cold dry MeCN (4 × 10 ml), and dried in vacuo at ∿ 20°C. Yield of (IV), 2.3 g (83%), mp 51.5°C (dec). Molecular weight 715-720 (cryoscopic), calculated, 712.

CONCLUSIONS

1. The basic principles governing the cyclocodimerization of norbornene with allyl compounds have been elucidated for their reaction in the presence of a three-component catalyst system, $Ni(acac)_2$–$P(OR)_3$–AlR'_3 (or MgR''_2); a highly selective method has also been developed for the introduction of a methylenecyclobutane fragment to a norbornene hydrocarbon derivative.

2. A new Ni complex has been prepared; it appears to be the catalyst which is active for the cyclocodimerization of norbornene with allylic compounds.

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OXIDATION OF UNSATURATED LINEAR AND CYCLIC HYDROCARBONS BY MOLECULAR OXYGEN CATALYZED BY COMPLEXES OF TRANSITION METALS

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and U. M. Dzhemilev

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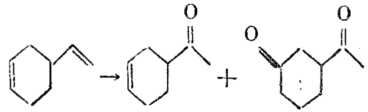
In the continuation of investigations on the oxidation of higher polyunsaturated compounds, and also with the object of developing effective and selective methods of the functionalization of olefins, we studied the oxidation of linear and cyclic hydrocarbons by molecular O_2 catalyzed by the $PdCl_2$-CuCl system [1]; the hydrocarbons contain one or several double bonds with varying geometry.

Derivatives of cyclohexene, norbornene, norbornadiene (NBD), quadricyclane, 1E,5Z-cyclodecadiene, methylenetricyclane, bismethylenetricyclane, methyldeltacyclene, and 1,5E,9-decatriene were selected as the objects of investigation. The 1:10 system of $PdCl_2$-CuCl as the solution in THF was utilized as the catalyst; this permitted the adequate ease of separation of the reaction products from the catalyst, and the isolation of the highest yields of the carbonyl compounds.

The oxidation of 4-vinyl-1-cyclohexene (I) with oxygen at 60°C leads to the formation of 4-acetyl-1-cyclohexene (II) and 3-acetylcyclohexanone (III) in the ratio of 96:4 and a total yield of 90%.



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