

## Interaction of vinylpyridines with 1,3-dienes catalyzed by transition metal complexes

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The linear and cyclic cooligomerization of 2-vinyl-, 2-methyl-5-vinyl-, and 4-vinylpyridines with 1,3-dienes and trienes catalyzed by complexes of transition metals (Fe, Co, Ni, Mn, Cr, Pd, Ru, Rh, and Zr) was carried out to give unsaturated pyridines containing alkenyl and cycloalkenyl substituents.

**Key words:** Diels–Alder reaction; catalysis, transition metal complexes; co-telomerization; dienes; pyridine bases.

Vinylarenes (styrene, vinylthiophene, vinylpyrrole) are known to react with 1,3-dienes under the action of low-valence nickel complexes to give the corresponding 1,4*E*,9-decatrienes.<sup>1–4</sup> Prior to this work there were no literature data on the linear cooligomerization of vinylpyridines with 1,3-dienes.

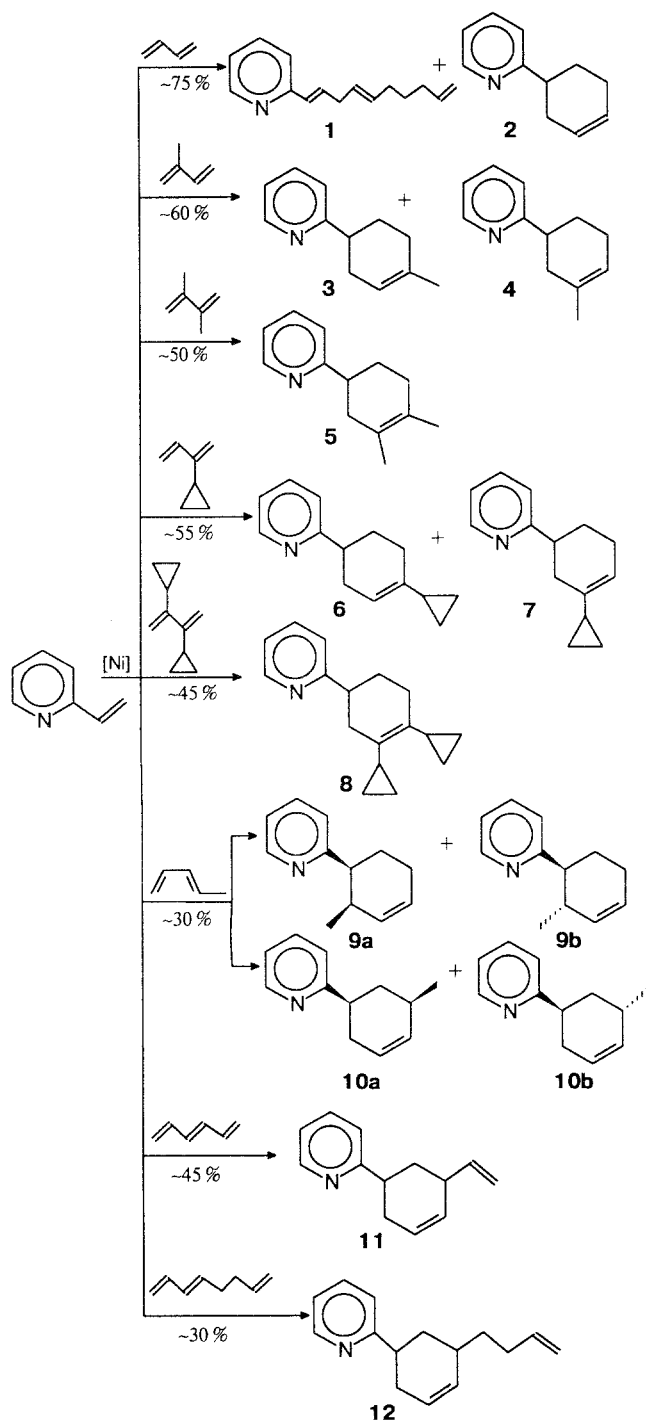
In order to study the reactivity of 2-, 3-, and 4-vinylpyridines towards 1,3-dienes and to find effective systems for catalyzing these reactions, the reactions of vinylpyridines with 1,3-butadiene, isoprene, 2,3-dimethylbutadiene, 2-cyclopropylbutadiene, 2,3-dicyclopropylbutadiene, piperylene, 1,3*E*,5-hexatriene, and

**Table 1.** The effect of the central atom in the catalyst on the yield and composition of the products of cooligomerization of 2-vinylpyridine with 1,3-butadiene [catalyst M(Acac)<sub>n</sub> : Zn : M'(Alk)<sub>m</sub> = (1÷3) : (3÷6) : (3÷10)]

Run	Catalyst*	Total yield (%)	Composition of the reaction products (%)**					
			1	2	VCH	OT	COD	CDDT
1	Ni(Acac) <sub>2</sub>	75	55	10	10	3	1	10
2	Fe(Acac) <sub>2</sub>	40	20	10	50	—	5	5
3	Pd(Acac) <sub>2</sub>	70	25	5	10	40	10	—
4	Co(Acac) <sub>2</sub>	56	33	20	27	1	3	5
5	Cr(Acac) <sub>3</sub>	48	—	15	41	—	16	11
6	Mn(Acac) <sub>2</sub>	35	—	15	31	—	28	—
7	Rh(Acac) <sub>3</sub>	40	3	17	30	—	30	4
8	Ru(Acac) <sub>3</sub>	37	5	9	30	—	30	3
9	Zr(Acac) <sub>4</sub>	58	10	20	31	—	34	—
10	Cp <sub>2</sub> ZrCl <sub>2</sub>	70	—	75	10	—	12	—
11	RhCl <sub>3</sub>	45	—	30	25	5	28	2
12	RuCl <sub>3</sub>	40	—	27	20	8	13	10
13	Ni(Acac) <sub>2</sub> /MgEt <sub>2</sub>	37	40	10	12	7	8	12
14	Ni(Acac) <sub>2</sub> /MgPr <sub>2</sub>	39	38	12	14	10	12	14
15	Ni(Acac) <sub>2</sub> /PBu <sub>3</sub>	70	49	13	8	—	2	18
16	Ni(Acac) <sub>2</sub> /PPR <sub>3</sub>	69	50	10	12	4	4	10
17	Ni(Acac) <sub>2</sub> /P(C <sub>5</sub> H <sub>11</sub> ) <sub>3</sub>	68	46	12	9	4	8	9
18	Ni(Acac) <sub>2</sub> /P(CH <sub>2</sub> Ph) <sub>3</sub>	70	48	15	11	3	7	9
19	Ni(Acac) <sub>2</sub> /AlBu <sub>3</sub>	71	49	11	12	—	4	17
20	Ni(Acac) <sub>2</sub> /HALBu <sub>2</sub>	64	51	10	10	—	8	15
21	Ni(Acac) <sub>2</sub> /AlBu <sub>2</sub> Cl	52	44	14	13	—	6	18
22	Ni(Acac) <sub>2</sub> /AlEt <sub>2</sub> Cl	50	43	13	14	—	9	11
23	Ni(Acac) <sub>2</sub> /AlEtCl <sub>2</sub>	42	42	11	16	3	12	6
24	Ni(Acac) <sub>2</sub> /AlCl <sub>3</sub>	35	38	13	18	3	16	4

\*PPh<sub>3</sub> was used as the ligand in runs 1–9, 11–14, 19–24; in runs 1–9, 5–18 metal complexes were reduced with Et<sub>3</sub>Al. \*\*The yields of the higher oligomers obtained in the reaction (up to 100 % lacking) are not indicated.

Scheme 1



1,3*E*,7-octatriene catalyzed by metallocomplex compounds of Fe, Co, Ni, Mn, Cr, Zr, Pd, Ru, and Rh have been studied.

One-, two-, and three-component systems comprising compounds of the above metals, arylphosphines, trialkylalanes, alkylhaloalanes, and dialkyl derivatives of magnesium were tested as catalysts. As a consequence, it was found that the optimum conditions for the cooligo-

merization of the above monomers are: aromatic solvents (benzene, toluene), 100–150 °C, 3–6 h. The most effective catalysts of cooligomerization of vinylpyridines with 1,3-dienes are obtained starting from nickel complexes, whereas  $\text{Cp}_2\text{ZrCl}_2$  was shown to favor the formation of  $(4\pi + 2\pi)$  adducts.

Thus, the interaction of 2-vinylpyridine with butadiene (in the molar ratio 2.5 : 6) catalyzed by  $\text{Ni}(\text{Acac})_2\text{-PPh}_3\text{-AlEt}_3$  under the chosen conditions ( $\text{C}_6\text{H}_6$ , 110 °C, 6 h) gives 2-(1*E*,4*E*,9-decatrienyl)pyridine (**1**), 2-(3-cyclohexenyl)pyridine (**2**), and a mixture of homo-oligomers of butadiene: 4-vinylcyclohexene (VCH), 1,3*E*,6-octatriene (OT), and 1*Z*,5*Z*-cyclooctadiene (COD) in the ratio 55 : 10 : 14, as well as *trans,trans,trans*-cyclododeca-1,5,9-triene (CDDT) in ~75 % integral yield (Table 1).

Changing the concentration and the ratio of the catalyst components or the starting monomers does not lead to an increase in selectivity with respect to **1**. Increasing the butadiene concentration in the reactant mixture results in a significant increase in the fraction of butadiene homo-oligomers. Taking this into account, further experiments involving other pyridines and 1,3-dienes were carried out using the  $\text{Ni}(\text{Acac})_2\text{-PPh}_3\text{-AlEt}_3$  catalyst.

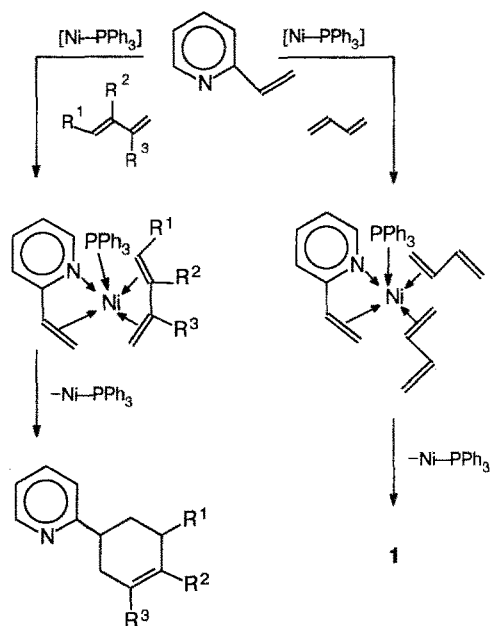
The interaction of 2-vinylpyridine with isoprene, 2,3-dimethylbutadiene, 2-cyclopropylbutadiene, 2,3-dicyclopropylbutadiene, *trans*-piperylene, 1,3*E*(*Z*),5-hexatriene, and 1,3*E*,7-octatriene under the conditions described above afforded only the  $(4\pi + 2\pi)$  adducts **3–12** in high yields (Scheme 1) in all the experiments regardless of the ratio of the starting monomers.

In the case of isoprene, 2-(4-methyl-3-cyclohexenyl)pyridine (**3**), and 2-(3-methyl-3-cyclohexenyl)pyridine (**4**) were formed in the ratio 1 : 1 in 60 % integral yield. The experiments with the other 1,3-dienes listed above resulted exclusively in  $(4\pi + 2\pi)$  adducts **5–12** in 30–55 % yields. In this case even traces of linear cooligomers could not be found.

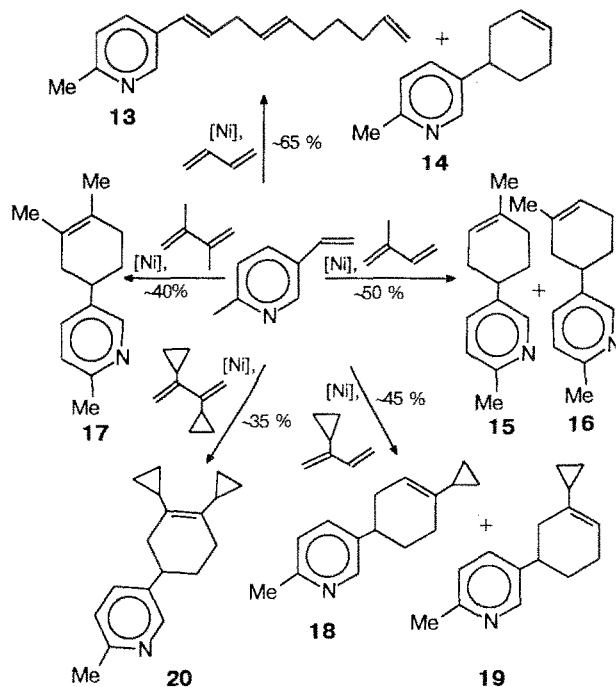
In order to obtain **12** in a satisfactory yield, the cyclo-cooligomerization has to be carried out for 6 h at 140 °C. On passing from butadiene to 1- and 2-substituted 1,3-dienes and trienes the yield of  $(4\pi + 2\pi)$  adducts decreases from 75 % to 30 %.

The following mechanism of the interaction of 1,3-dienes with 2-vinylpyridine in the presence of low-valence nickel complexes can be proposed. In the experiments with the rather bulky molecules of 1- or 2-substituted dienes or trienes, the catalytically active Ni-complexes (which include one molecule of vinylpyridine and one molecule of diene in the coordination sphere of the central atom of the catalyst) are probably formed, which results in the 1:1 adducts. In the case of butadiene it seems likely that complexes containing two molecules of diene and one molecule of vinylpyridine are formed. The transformation of these complexes in the coordination sphere of the metal gives the corresponding linear cooligomer **1** (Scheme 2).

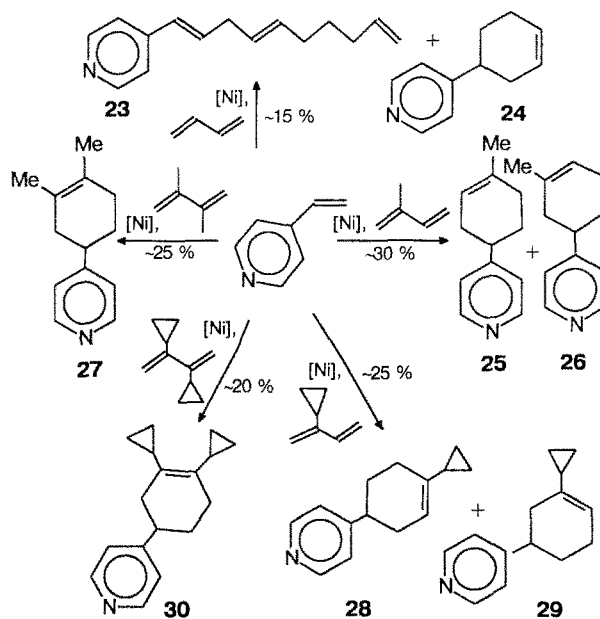
Scheme 2



Scheme 3



Scheme 4



The same results were also obtained for the other vinylpyridines. Thus, cooligomerization of 2-methyl-5-vinylpyridine with butadiene afforded 2-methyl-5-(1*E*,4*E*,9-decatrienyl)pyridine (**13**) and 2-methyl-5-(3-cyclohexenyl)pyridine (**14**) in the ratio 65 : 35 and in ~65 % total yield. The interaction of 2,3-dimethylbutadiene, 2-cyclopropyl-, and 2,3-dicyclopropylbutadiene with isoprene resulted only in the Diels-Alder adducts **15–20**\* in ~35–50 % yields (Scheme 3).

We were not able to perform the reaction between 2-methyl-5-vinylpyridine and a mixture of 1,3*E*(*Z*)-5-hexatrienes and 1,3*E*,7-octatriene. Under the chosen conditions the latter are transformed to higher oligomers, which have not yet been identified.

The formation of both the linear (**23**) and cyclic (**24**) cooligomers in the ratio 80 : 20 was observed in the experiments with 4-vinylpyridine and butadiene. However, only the six-membered cyclodimers (**25–30**) were isolated in the reactions with isoprene, 2,3-dimethylbutadiene, 2-cyclopropyl-, and 2,3-dicyclopropylbutadiene (Scheme 4). In order to obtain compounds **23–30** in satisfactory yields, the respective reactions had to be carried out at 150 °C; still, the yields of the desired substituted pyridines under these conditions were not more than 30 %. We also failed to perform the

cooligomerization of a mixture of 1,3*E*(*Z*),5-hexatrienes and 1,3*E*,7-octatriene with 4-vinylpyridine.

Our results indicate that the vinylpyridines studied can be arranged in the following series according to their

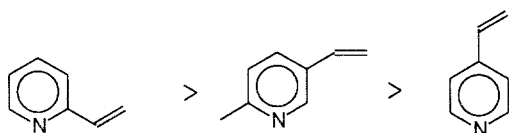
\*The interaction of 2-methyl-5-vinylpyridine with *trans*-piperylene in the presence of  $\text{Cp}_2\text{ZrCl}_2$  yielded the adducts **21a,b**, the structures of which are similar to those of **9a,b** and **10a,b**, respectively.

**Table 2.** The integral yield and the ratio of Diels–Alder adducts obtained in the presence of  $\text{Cp}_2\text{ZrCl}_2$  catalyst ( $\text{Cp}_2\text{ZrCl}_2$ –vinylpyridine–diene, 0.34 : 3 : 3.5)

1,3-Diene	2-Vinylpyridine		2-Methyl-5-vinylpyridine		4-Vinylpyridine	
	Yield (%)	The ratio of regioisomers	Yield (%)	The ratio of regioisomers	Yield (%)	The ratio of regioisomers
Butadiene	95	100	80	100	90	100
Isoprene	90	45 : 55	75	40 : 60	90	40 : 60
2,3-Dimethylbutadiene	85	100	70	100	85	100
2-Cyclopropylbutadiene	85	50 : 50	75	45 : 55	90	40 : 60
2,3-Dicyclopropylbutadiene	80	100	70	100	90	100
<i>trans</i> -Piperylene	90	5 : 40 : 5 : 50	75	5 : 45 : 5 : 45	90	10 : 20 : 10 : 60

Note. The reactions were carried out in benzene at 150 °C for 4 h.

reactivity in cooligomerization with 1,3-dienes and trienes catalyzed by low-valence nickel complexes:



The investigation of the effect of the nature of the catalyst on the direction and structural selectivity of cooligomerization of vinylpyridines with 1,3-dienes revealed that many catalytic systems tested by us favored the formation of both linear and cyclic co-telomers. Nickel complexes had the largest selectivity for the linear telomers **1**, **13**, **23**, whereas the employment of  $\text{Cp}_2\text{ZrCl}_2$  resulted only in the formation of the six-membered [1+1] adducts in all experiments regardless of the catalyst concentration, the ratio of the starting monomers, or the reaction conditions. In this case the ratio of regio-isomers obtained from the corresponding vinylpyridines and 1- and 2-substituted dienes remained practically constant, being on the average about 50 : 50 (Table 2).

The yields of the  $(4\pi+2\pi)$  cycloadducts **2–12**, **14–22**, and **24–32\*** were found to reach their maxima in the reactions catalyzed by  $\text{Cp}_2\text{ZrCl}_2$  at 120–150 °C. In this case the reactivity of 4-vinylpyridine was approaching that of 2-vinylpyridine. Thus, 4-vinylpyridine was more active as a dienophile than 2-methyl-5-vinylpyridine.

The structures of the compounds obtained were proven by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy, mass-spectrometry, and elemental analysis. Thus, six low-field signals at  $\delta$  114.48 (t), 126.62 (d), 131.66 (d), 132.69 (d), 138.54 (d) and four strong-field signals at  $\delta$  28.66 (t), 31.97 (t), 33.21 (t), 35.98 (t) in the  $^{13}\text{C}$  NMR spectrum of **13** indicated the presence of a decatriene

fragment. The triplet and doublet signals at  $\delta$  114.48 and 138.54, respectively, indicated unambiguously the presence of a terminal double bond in the molecule of **13**. The location of the double bonds in the decatriene were also confirmed by  $^1\text{H}$  NMR spectra. Thus, the spectrum of pyridine **13** contained a multiplet signal at  $\delta$  2.92 with integral intensity corresponding to two protons; this signal can be attributed to the methylene group located between the two double bonds. The methylene protons  $-\text{CH}_2-\text{CH}_2-\text{CH}_2-$  resonated as a multiplet signal centered at  $\delta$  1.9; its integral intensity corresponded to four protons (the downfield shift of the  $sp^3$ -hybridized proton signals to  $\delta$  1.9 indicated the presence of double bonds adjacent to the methylene groups). Another multiplet signal with a center at  $\delta$  1.49 and integral intensity corresponding to two protons was attributed to the methylene group in the  $\beta$ -position with regard to double bonds.

The singlet signals in the  $^{13}\text{C}$  NMR spectrum at  $\delta$  156.53 and 131.66 and the doublet signals at  $\delta$  147.21 and 122.83, as well as the doublet signals in the  $^1\text{H}$  NMR spectrum at  $\delta$  8.42 ( $^3J = 2.1$  Hz), 7.05 ( $^3J = 3.9$  Hz), and 7.55 (dd) indicated the presence of substituents at the C(2) and C(5) atoms of the aromatic pyridine ring.

The structures of decatrienylpyridines **1** and **23** were confirmed in a similar way.

Thus, we were the first to investigate the cooligomerization of 2-, 3-, and 4-vinylpyridines with 1,2-dienes and trienes catalyzed by transition metal complexes. It has been shown that the linear cooligomerization of vinylpyridines with butadiene, which makes it possible to obtain 1*E*,4*E*,9-decatrienes in one step, can take place. The comparative reactivity of vinylpyridines has been studied and effective complex catalysts based on Ni and Zr compounds have been proposed.

## Experimental

The vinylpyridines and 1,3-dienes used in this work were 99 % pure. GLC analyses were carried out on a Khrom-5 chromatograph (flame ionization detector, column 1.2 m long with 15 % Apieson on Zeolite-545, helium as the carrier gas).  $^1\text{H}$  NMR spectra were recorded with Tesla BS-476 and Bruker

\* The interaction of 4-vinylpyridine with *trans*-piperylene in the presence of  $\text{Cp}_2\text{ZrCl}_2$  yielded the adducts **31a,b** and **32a,b**, the structures of which are similar to **9a,b** and **10a,b**, respectively.

**Table 3.** Characteristics of the products obtained

Compound	B.p./°C (p/Torr)	$n_D^{20}$	Found Calculated (%)			Molecular formula	$\delta$		[M] <sup>+</sup>
			H	N	C		<sup>1</sup> H NMR	<sup>13</sup> C NMR	
<b>1</b>	133—136(3)	1.5378	<u>83.77</u> 84.01	<u>7.13</u> 7.31	<u>6.08</u> 6.17	C <sub>15</sub> H <sub>18</sub> N	1.48 (m, 2 H, CH <sub>2</sub> ); 2.05 (m, 4 H, CH <sub>2</sub> ); 2.92 (t, 2 H, CH <sub>2</sub> ); 4.9—5.1 (m, 2 H, CH); 5.4—5.6 (m, 2 H, CH); 5.7—5.9 (m, 1 H, CH); 6.5—6.73 (td, 2 H, CH); 7.18—8.5 (m, 4 H, CH (Py))	28.61 (t); 31.97 (t); 33.21 (t); 35.66 (t); 114.49 (t); 120.9 (d); 121.49 (d); 127.33 (d); 130.35 (d); 131.9 (d); 133.98 (d); 136.16 (d); 138.59 (d); 149.34 (d); 156.03 (s)	213
<b>6,7</b>	132—134(5)	1.5412	<u>83.24</u> 83.19	<u>9.36</u> 9.39	<u>6.28</u> 6.31	C <sub>14</sub> H <sub>17</sub> N	0.4—0.6 (m, 4 H, CH <sub>2</sub> ); 1.3—1.4 (m, 2 H, CH <sub>2</sub> ); 1.6 (m, 1 H, CH); 1.7—2.4 (m, 4 H, CH <sub>2</sub> ); 2.8—3.0 (m, 1 H, CH); 5.5 (m, 1 H, CH); 7.05—8.5 (m, 4 H, CH (Py))	3.55 (t); 4.23 (t); 16.68 (d); 26.58 (t); 28.43 (t); 31.09 (t); 41.9 (d); 118.32 (d); 120.5 (d); 120.6 (d); 135.7 (d); 137.47 (s); 148.62 (d); 165.3(s)	199
<b>8</b>	143—144(1)	1.5368	<u>84.86</u> 84.77	<u>7.86</u> 7.88	<u>5.59</u> 5.63	C <sub>17</sub> H <sub>21</sub> N	0.4 (m, 4 H, CH <sub>2</sub> ); 0.5 (m, 4 H, CH <sub>2</sub> ); 0.8 (m, 2 H, CH <sub>2</sub> ); 1.6 (m, 2 H, CH); 1.8—2.0 (m, 4 H, CH <sub>2</sub> ); 2.6 (m, 1 H, CH); 7.0—8.5 (m, 4 H, CH (Py))	4.0 (t); 4.0 (t); 4.1 (t); 4.1 (t); 13.2 (d); 13.3 (d); 26.1 (t); 28.6 (t); 32.4 (t); 42.4 (t); 120.8 (d); 120.9 (d); 130.2 (s); 130.6 (s); 136.0 (d); 149.0 (d); 165.8 (s)	239
<b>9a, 9b</b>	95—97(1)	1.5354	<u>83.86</u> 83.70	<u>8.32</u> 8.10	<u>7.95</u> 7.94	C <sub>12</sub> H <sub>15</sub> N	0.62 (d, 3 H, CH <sub>3</sub> ); 1.6 (m, 2 H, CH <sub>2</sub> ); 2.3 (m, 2 H, CH <sub>2</sub> , H.CH); 3.0 (m, 1 H, CH); 5.7 (m, 2 H, CH); 7.05—8.5 (d, 4 H, CH (Py)); 0.85 (d, 3 H, CH <sub>3</sub> )	18.4 (q); 25.9 (t); 29.6 (t); 35.4 (d); 45.3 (d); 121.1 (d); 122.2(d); 125.9 (d); 133.2 (d); 136.1(d); 149.2 (d); 164.4 (s)	173
<b>10a, 10b</b>	95—97(1)	1.5343	<u>83.86</u> 83.70	<u>8.32</u> 8.10	<u>7.95</u> 7.94	C <sub>12</sub> H <sub>15</sub> N	1.15 (d, 3 H, CH <sub>3</sub> ); 1.1 (d, 3H, CH <sub>3</sub> )	20.0(q); 26.0 (t); 30.1 (t); 34.1 (d); 50.7 (d); 120.8 (d); 121.8 (d); 125.8 (d); 133.2 (d); 135.8 (d); 149.2 (d); 165.4 (s)	173
<b>11</b>	116—118(1)	1.5446	<u>82.64</u> 82.74	<u>8.58</u> 8.33	<u>5.94</u> 5.89	C <sub>13</sub> H <sub>15</sub> N	1.5—2.0 (m, 4 H, CH <sub>2</sub> ); 3.1—3.3 (m, 2 H, CH); 4.7—4.9 (m, 2 H, CH <sub>2</sub> ); 5.2—5.9 (m, 3 H, CH); 7.05—8.53 (m, 4 H, CH (Py));	21.89 (t); 26.33 (t); 44.27 (d); 45.57 (t); 116.49 (d); 121.2 (d); 122.02 (d); 127.92 (d); 129.33 (d); 135.99 (d); 138.16 (d); 149.05 (d); 163.90 (s)	185
<b>12</b>	130—132(1)	1.5346	<u>82.38</u> 82.01	<u>8.86</u> 8.88	<u>4.61</u> 4.56	C <sub>15</sub> H <sub>19</sub> N	1.2—2.1 (m, 8 H, CH <sub>2</sub> , H.CH); 2.7 (m, 1 H, CH); 4.7—5.0 (m, 2 H, =CH <sub>2</sub> ); 5.6—5.9 (m, 3 H, CH); 7.08—8.55 (m, 4 H, CH (Py))	25.47 (t); 29.7 (t); 30.39 (t); 33.4 (t); 39.4 (d); 48.11 (d); 114.16 (t); 121.15 (d); 122.18 (d); 128.68 (d); 130.52 (d); 136.26 (d); 138.38 (d); 149.16 (d); 165.30 (s)	213
<b>13</b>	138—139(1)	1.5398	<u>84.81</u> 84.42	<u>9.15</u> 9.04	<u>6.01</u> 5.81	C <sub>16</sub> H <sub>21</sub> N	1.48 (m, 2 H, CH <sub>2</sub> ); 2.15 (m, 4 H, CH <sub>2</sub> ); 2.51 (s, 3 H, CH <sub>3</sub> ); 2.9 (m, 2 H, CH <sub>2</sub> ); 4.9—5.05 (m, 2 H, =CH <sub>2</sub> ); 5.5 (m, 3 H, CH); 6.21 (dt)—6.32 (d) (2 H, CH); 7.07—8.42 (m, 3 H, CH (Py))	24.0 (q); 28.66 (t); 31.97 (t); 33.21 (t); 35.98 (t); 114.48 ; 122.83 (d); 126.62 (d); 127.49 (d); 130.41 (d); 131.66 (d); 132.69 (d); 138.54 (d); 147.21 (d); 156.53 (s)	227
<b>18, 19</b>	137—138(3)	1.5346	<u>80.91</u> 80.73	<u>10.43</u> 9.92	<u>5.97</u> 6.12	C <sub>15</sub> H <sub>19</sub> N	0.4 (m, 2 H, CH <sub>2</sub> ); 0.5 (m, 2 H, CH <sub>2</sub> ); 1.3 (m, 2 H, CH <sub>2</sub> ); 1.7 (m, 1 H, CH); 1.9—2.2 (m, 4 H, CH <sub>2</sub> ); 2.5 (s, 3 H, CH <sub>3</sub> ); 2.7 (m, 1 H, CH); 5.5 (m, 1 H, CH); 7.1—8.3 (m, 3 H, CH (Py))	4.0 (t); 4.7 (t); 17.0 (d); 23.9 (t); 23.9 (q); 26.9 (t); 33.1 (t); 33.4 (d); 118.7 (d); 122.9 (d); 134.6 (d); 138.4 (d); 139.1 (s); 148.1 (d); 155.9 (s)	213
<b>20</b>	152—154(1)	1.5362	<u>84.73</u> 84.64	<u>7.33</u> 7.28	<u>5.99</u> 5.86	C <sub>18</sub> H <sub>23</sub> N	0.4 (m, 4 H, CH <sub>2</sub> ); 0.5 (m, 4 H, CH <sub>2</sub> ); 0.9 (m, 2 H, CH <sub>2</sub> ); 1.64 (2 H, CH); 1.85 (4 H, CH <sub>2</sub> ); 2.46 (s, 3 H, CH <sub>3</sub> ); 2.67 (m, 1 H, CH); 7.01—8.4 (m, 3 H, CH (Py))	4.0 (t); 4.03 (t); 4.1 (t); 4.12 (t); 13.19 (d); 13.42 (d); 24.1 (q); 26.6 (t); 28.6 (t); 33.4 (t); 40.4 (d); 123.6 (d); 130.6 (s); 131.2 (s); 134.83 (d); 139.81 (s); 148.6 (d); 155.62 (s)	253

Table 3 (continued).

Compound	B.p./°C (p/Torr)	$n_D^{20}$	Found— Calculated (%)			Molecular formula	$\delta$ <sup>1</sup> H NMR	<sup>13</sup> C NMR	[M] <sup>+</sup>
			H	N	C				
21a,b, 22a,b	101—102(1)	1.5345	82.77 82.89	7.68 7.41	6.77 7.07	C <sub>13</sub> H <sub>15</sub> N	0.85 (d, 3 H, CH <sub>3</sub> ); 1.5 (m, 2 H, CH <sub>2</sub> ); 2.3 (m, 2 H, CH <sub>2</sub> , H.CH); 2.5 (s, 3 H, CH <sub>3</sub> ); 2.7 (m, 1 H, CH); 5.7 (m, 2 H, CH); 7.1—8.3 (m, 3 H, CH (Py)); 0.6 (d, 3 H, CH <sub>3</sub> ); 0.95 (d, 3 H, CH <sub>3</sub> )	19.9 (q); 23.9 (q); 25.8 (t); 30.6 (t); 36.7 (d); 45.8 (d); 123.0 (d); 126.2 (d); 133.1 (d); 135.0 (d); 138.5 (s); 148.8 (d); 156.1 (s)	187
23	135—137(2)	1.5386	84.80 84.03	7.19 7.09	6.27 6.19	C <sub>13</sub> H <sub>20</sub> N	1.46 (m, 2 H, CH <sub>2</sub> ); 2.02 (m, 4 H, CH <sub>2</sub> ); 2.66 (m, 2 H, CH <sub>2</sub> ); 4.5—5.1 (m, 2 H, CH); 5.3—5.4 (m, 2 H, CH); 5.6—5.8 (m, 2 H, CH); 5.8—5.9 (m, 2 H, CH); 7.03—8.5 (m, 4 H, CH (Py))	28.82 (t); 31.9 (t); 33.17 (t); 35.39; 114.41 (t); 123.79 (d); 127.23 (d); 130.37 (d); 132.15 (d); 133.8 (d); 137.76 (d); 147.51 (d); 147.51 (d); 153.0 (s)	213
28, 29	114—116(1)	1.5311	82.84 82.89	8.96 9.08	6.68 6.61	C <sub>13</sub> H <sub>17</sub> N	0.42 (m, 2 H, CH <sub>2</sub> ); 0.53 (m, 2 H, CH <sub>2</sub> ); 1.7 (m, 1 H, CH); 1.3 (m, 2 H, CH <sub>2</sub> ); 1.85—2.3 (m, 4 H, CH <sub>2</sub> , H.CH); 5.5 (m, 1 H, CH); 7.13—8.5 (m, 4 H, CH (Py))	4.11 (t); 4.75 (t); 17.09 (d); 26.86 (t); 29.24 (t); 32.45 (t); 39.73 (d); 118.4 (d); 122.5 (d); 122.5 (d); 138.62 (s); 149.74 (d); 149.74 (d); 156.07 (s); 4.02 (t); 4.7 (t); 17.09 (d); 25.25 (t); 29.08 (t); 34.06 (t); 39.87 (t); 119.45 (d); 122.5 (d); 122.5 (d); 137.8 (s); 149.74 (d); 149.74 (d); 156.07 (s)	199
30	146—148(1)	1.5359	84.38 84.43	7.46 7.48	5.67 5.72	C <sub>17</sub> H <sub>21</sub> N	0.4 (m, 4 H, CH <sub>2</sub> ); 0.55 (m, 4 H, CH <sub>2</sub> ); 0.8 (m, 3 H, CH <sub>2</sub> ); 1.55 (m, 2 H, CH); 1.75 (m, 4 H, CH <sub>2</sub> ); 2.55 (m, 1 H, CH); 7.1—8.4 (m, 4 H, CH (Py))	4.12 (t); 4.21 (t); 4.21 (t); 4.31 (t); 13.36 (d); 13.36 (d); 25.89 (t); 28.93 (t); 33.48 (t); 39.84 (t); 122.45 (d); 122.45 (d); 130.01 (s); 131.17 (s); 149.83 (d); 149.83 (d); 155.98 (s)	239
31a,b, 32a,b	104—107(1)	1.5363	82.57 82.30	8.18 8.00	7.45 7.46	C <sub>12</sub> H <sub>15</sub> N	0.61 (d, 3 H, CH <sub>3</sub> ); 0.78 (d, 3 H, CH <sub>3</sub> ); 0.9 (3 H, CH <sub>3</sub> );	19.8 (q); 25.5 (t); 30.0 (t); 36.1 (t); 42.6 (d); 123.0 (d); 123.0 (d); 126.1 (d); 132.6 (d); 149.7 (d); 149.7 (d); 155.1 (s)	173

AM-300 spectrometers in CDCl<sub>3</sub>, <sup>13</sup>C NMR spectra were recorded with Jeol 90Q and Bruker AM-300 spectrometers in CDCl<sub>3</sub>. Mass-spectra were obtained using an MX-1306 instrument (the energy of ionizing electrons 70 eV, the temperature in the ionizing camera 200 °C).

**Cooligomerization of 2-vinyl-, 2-methyl-5-vinyl-, and 4-vinylpyridines with 1,3-dienes and trienes in the presence of the Ni(Acac)<sub>2</sub>—PPh<sub>3</sub>—AlEt<sub>3</sub> catalytic system.** AlEt<sub>3</sub> (1.2 mmol) was added under argon flow to a solution of Ni(Acac)<sub>2</sub> (0.4 mmol) and PPh<sub>3</sub> (1.2 mmol) in 1 mL of toluene, and the mixture was stirred for 10 min. The solution of the catalyst was then placed under argon flow into a steel autoclave ( $V = 17 \text{ cm}^3$ ), which contained vinylpyridine (25 mmol), butadiene (60 mmol), or a substituted 1,3-diene or triene (35 mmol). The autoclave was heated for 6 h at 110—140 °C with continuous stirring, and then cooled. The reaction mass was extracted with ether (3×50 mL), the extract was passed through aluminum oxide, the solvent was distilled off, and the residue was distilled *in vacuo*. The characteristics of the decatrienyl- and cyclohexenylpyridines are shown in Table 3.

**Cyclodimerization of 2-vinyl, 2-methyl-5-vinyl, and 4-vinylpyridines with 1,3-dienes in the presence of Cp<sub>2</sub>ZrCl<sub>2</sub> as the catalyst.** 1,3-Diene (35 mmol), vinylpyridine (30 mmol), Cp<sub>2</sub>ZrCl<sub>2</sub> (0.34 mmol), and 2 mL toluene were introduced into a steel autoclave ( $V = 17 \text{ cm}^3$ ) which was heated for 4 h at 150 °C and then cooled. The reaction mass was distilled in a vacuum. The integral yield and the ratio of reaction products are given in Table 2; the spectral characteristics are presented in Table 3.

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## Reaction of furfurylidene acetone with Grignard reagents

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The interaction of furfurylidene acetone with methylmagnesium iodide and ethylmagnesium halides has been studied. In the first case 2-methyl-4-(2-furyl)-3-buten-2-ol is formed as the product of 1,2-addition (yield 73 %). In the second case 4-(2-furyl)-2-hexanone (42 %) is the result of 1,4-addition, whereas 3-methyl-5-(2-furyl)-3-heptanol (45 %) is formed by consecutive 1,2- and 1,4-addition. In all cases the products of 1,3-addition were found.

**Key words:** furfurylidene acetone; 2-methyl-4-(2-furyl)-3-buten-2-ol; 3-methyl-5-(2-furyl)-3-heptanol; 4-(2-furyl)-2-hexanone.

Earlier we showed<sup>1</sup> that the substitution of a halogen atom in a «mixed» organomagnesium compound in the course of reactions with 2-alkoxytetrahydrofuranes leads to the formation of various compounds. It is also known that the main product of the reaction of furfurylidene acetone (FA) (1) with ethylmagnesium bromide is 4-(2-furyl)-2-hexanone, which is formed as the result of 1,4-addition.<sup>2</sup> However, in the latter work<sup>2</sup> we could not obtain conclusive evidence of the structure of the ketone obtained (*i.e.*, the point of attachment of the Grignard reagent as a cryptobase to the FA molecule). The effect of the radical R in RMgX on the direction of RMgX addition to the above  $\alpha,\beta$ -unsaturated ketone was also not investigated.

The addition of methylmagnesium iodide to 6-(2-furyl)-3,5-hexadiene-2-one, which is the vinyl analog of

FA, only occurs at the keto group.<sup>3</sup> In this connection we studied the reaction of FA with Grignard reagents, giving special attention to the regioselectivity of this process.

We discovered that the reaction of FA with a tenfold excess of ethylmagnesium bromide gives 4-(2-furyl)-2-hexanone (2) and 3-methyl-5-(2-furyl)-3-heptanol (3) as the main products and 4-(2-furyl)-3-ethyl-2-butanone (4) and 3-methyl-5-(2-furyl)-4-penten-3-ol (5) as the by-products (Scheme 1).

It should be noted that the decomposition of the reaction mixture was carried out by adding water. The reverse order of adding water decreases the yield of carbinol 3 to a mere 12 %. In this case the subsequent addition of the Grignard agent molecule to the  $\alpha,\beta$ -unsaturated ketone takes place. First the product of