6-(β-D-Ribofuranosyl)-2,2,9,9-tetrakis(trifluoromethyl)[1,3,5]oxadiazino[3,4-i]purine (II). Under the conditions of synthesis of (I), from 3.0 g adenosine and 10.2 g hexafluoroacetone in 15 ml DMFA we obtained 5.3 g (94%) (II), R_f 0.58, $[\alpha]_D^{20}$ −26.5° (C 1.0, MeOH), PMR spectrum (δ, ppm, CD_3OD): 8.47 br.s (1H, C^8H), 8.32 s (1H, C^5H), 6.03 d (1H, $C^{1'}H$, $J_{1',2'}$ = 5.24 Hz), 4.67 t (1H, $C^{2'}H$), 4.43 t (1H, $C^{3'}H$), 4.16 m (1H, $C^{4'}H$), 3.82 m (2H, $C^{5'}H$); ^{19}F NMR spectrum (δ, ppm, MeOH): −1.4 br.s, 2.1 br.s (1:1). Found: C 32.73; H 2.18; N 12.22; F 38.56%. $C_{16}H_{11}N_5O_5F_{12}$. Calculated: C 33.04; H 1.89; N 12.05; F 39.24%.

CONCLUSIONS

A new reaction of adenine and adenosine with hexafluoroacetone, affecting the amidine fragment of their molecules and leading to tricyclic 2,2,9,9-tetrakis(trifluoromethyl)[1,3,5]oxadiazine[3,4-i]purines, was conducted.

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INTRAMOLECULAR HYDROACYLATION REACTION CATALYZED BY $Co_2(\mu\text{-}N_2)(PPh_3)_6$ IN THE PRESENCE OF VARIOUS LIGANDS

M. G. Vinogradov, A. B. Tuzikov, and G. I. Nikishin

UDC 542.97:66.095.252:547.28

Rhodium [1, 2] and ruthenium compounds [3] have been used for the synthesis of ketones by the addition of aldehydes to olefins (hydroacylation reaction) catalyzed by metal complexes. We have recently shown that Co(0) phosphine complexes catalyze intramolecular hydroacylation in the case of the cyclization of 4-pentenal to cyclopentanone [4, 5]. Under the conditions found, the selectivity for the formation of cyclopentanone does not exceed 70% and the catalytic yield (CY) is 3 moles cyclopentanone per g-at Co. The proposed reaction mechanism (the phosphine ligands have been omitted in the scheme) entails either the participation of Co(0) and Co(I) species in the catalytic cycle (pathway a) or the participation of only Co(I) species (pathway b):

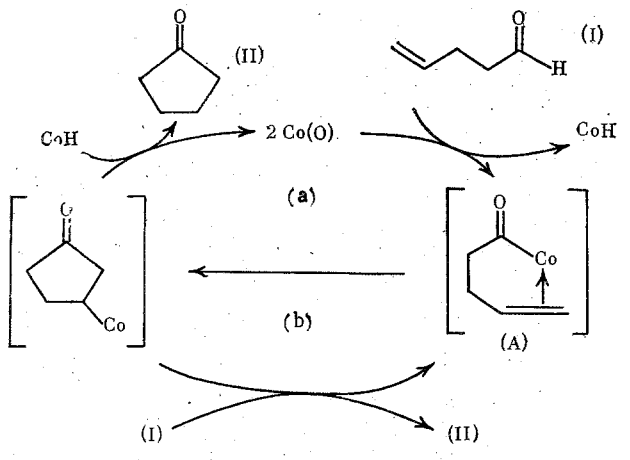

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TABLE 1. Effect of the Nature of the Ligand (L) on the Selectivity of the Cyclization of 4-Pentenal (I) to Cyclopentanone (II)[a]

No.	Ligand L	T., °C	Conversion of (I), %	CY[b]	Selectivity of formation from (I), %					
					(II)	(III)	(IV)	(Va, b)	(VI)	(VII)
1	$Ph_2P(CH_2)_3PPh_2$	20	17	1,5	88	c[c]	–	–	–	–
		70	100	8,3	83	c	c	–	–	c
2	$Ph_2P(CH_2)_2PPh_2$	20	13	1,05	81	c	–	–	c	–
		70	100	7,7	77	c	–	–	7	4
3	Same[d]	70	54	3,3	61	c	c	–	16	7
4	PBu_3	20	19	1,5	79	13	–	–	c	–
		70	100	6,7	67	5	–	–	13	c
5	P(cyclohexyl)$_3$	20	45	4,0	89	2	c	–	–	c
		70	82	4,1	50	7	6	24	–	12
6	P(*i*-Pr)$_3$	20	31	2,2	71	6	c	5	–	c
		70	93	2,5	27	7	11	42	c	5
7	Tris(p-dimethylaminophenyl)-phosphine	20	23	1,4	61	7	c	26	–	–
		70	77	1,6	21	10	12	41	5	4
8	PPh_3	20	9	0,7	78	c	c	17	c	c
		70	90	1,25	14	9	9	57	6	4
9	$Ph_2PCH_2PPh_2$	20	12	0,7	58	13	8	13	–	–
		70	72	1,2	17	5	11	56	3	3
10	P(OBu)$_3$	20	37	0,05	1	4	–	c	–	–
		70	80	0,9	11	4	6	28	c	c
11	$Me_2N(CH_2)_2NMe_2$	20	71	0,8	11	5	–	74	–	c
		70	100	0,75	8	5	3	68	3	5
12	α,α'-Dipyridyl	20	63	–	–	3	13	67	–	–
		70	87	–	–	3	24	59	–	–

[a] Catalytic system: $Co_2(\mu\text{-}N_2)(PPh_3)_6$ + L (2 moles mono- or 1 mole bidentate ligand per g-at Co), [Co] = 0.05 g-at/liter, $[(I)]_0/[Co]$ = 10, benzene, 1 h.
[b] Catalytic yield of cyclopentanone (II), mole/g-at Co.
[c] Traces.
[d] 2 moles $Ph_2P(CH_2)_2PPh_2$ per g-at Co.

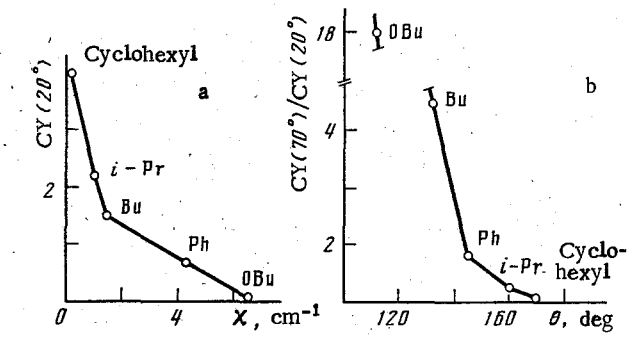
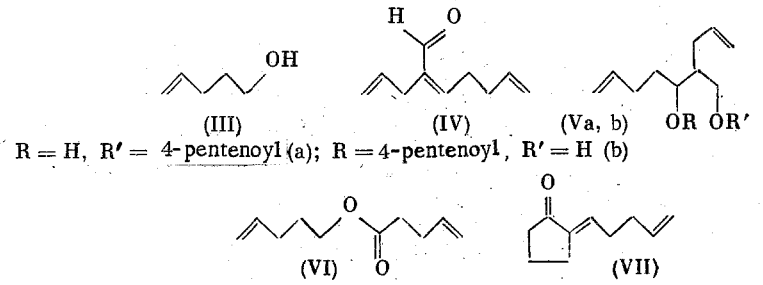


Fig. 1. Dependence of the CY of cyclopentanone at 20°C on the σ-donor capacity of the ligands and the dependence of CY(70°C)/CY(20°C) on the conic angle θ (b). The reaction conditions are indicated in a note to Table 1.

In the present work, we studied the cyclization of 4-pentenal catalyzed by $Co_2(\mu\text{-}N_2)(PPh_3)_6$ [5] in the presence of various ligands in order to clarify their effect on the activity of the catalytic system and the reaction selectivity.

A ligand exchange reaction proceeds upon the treatment of $Co_2(\mu\text{-}N_2)(PPh_3)_6$ by phosphine, phosphite, or amine. The entering group L may displace the dinitrogen ligand (N_2 is released) or the triphenylphosphine ligands. The complexes obtained from $Co_2(\mu\text{-}N_2)(PPh_3)_6$ by ligand exchange with various ligands L in benzene were used without separation from solution as catalysts for the cyclization of 4-pentenal to cyclopentanone (Table 1). The following by-products are obtained: 4-penten-1-ol (III), 2-(2-propenyl)-2,6-heptadienal (IV), a mixture of mono(4-pentenoates) of 2-(2-propenyl)-6-heptene-1,3-diol [(Va)/(Vb) ≈ 1:1], 4-pentenyl 4-pentenoate (VI), and 2-(4-pentenylidene)cyclopentanone (VII)



Products (III)-(VII) are formed from 4-pentenal, probably with the participation of cobalt hydrides [5]: the reduction of 4-pentenal by cobalt hydride complexes leads to (III) and a cobalt alcoholate which, in turn, catalyzes the formation of (IV)-(VI) from 4-pentenal as well as the reaction of cyclopentanone with 4-pentenal leading to (VII).

The data in Table 1 indicate that the nature of the ligand has a significant effect on the 4-pentenal conversion, reaction selectivity, and CY of cyclopentanone. The conversion and CY markedly increase with an increase in the temperature from 20 to 70°C. At 20°C, the cyclization reaction virtually stops after 1 h with a relatively small conversion of (I), which then slowly increases on account of the formation of side products (III)-(VII). An increase in the temperature increases the catalyst activity. We have found that the optimal temperature is 70°C.

For monodentate ligands at 20°C, i.e., under mild conditions, the catalytic yield increases with increasing σ-donor capacity of the ligand (Fig. 1) given by the electronic parameter ν defined by the equation $\nu\ (cm^{-1}) = 2056.1 + \sum_{i=1}^{3} \chi_i$, where χ is the contribution of the P atom to the value of ν for each ligand (the σ-donor capacity of the ligand increases with decreasing χ and thus, decreasing ν) [6]. An increase in the σ-donor capacity of the ligands apparently facilitates the oxidative addition of 4-pentenal to Co(0) and Co(I) complexes, thereby increasing the rate of the reaction as a whole [7].

The introduction of chelating diphosphines such as 1,2-bis(diphenylphosphino)ethane (DPPE) or 1,2-bis(diphenylphosphino)propane leads to a sharp increase in catalyst selectivity and enhancement of the CY. Bis(diphenylphosphino)methane, which apparently is incapable of forming stable chelates, virtually does not differ in its effect on the reaction indices from PPh_3. If more than 1 mole diphosphine is taken per g-at Co (see Table 1, example 3), the catalyst activity and selectivity are reduced. This reduction is likely related to blockage of the coordination sites in the cobalt complex required for the hydroacylation reaction.

The nature of ligand L also affects the nature of the side reactions. This effect may be related to change in the basicity of the alcoholates and cobalt enolates formed upon their reaction with (I) and responsible for these reactions. Upon the introduction of diamine ligands (N,N,N',N'-tetramethylethylenediamine and α,α'-dipyridyl) into the Co(o) complex, the major reaction products are 1,3-diol monoesters (Va) and (Vb).

The nature of the solvent has a strong effect on the reaction selectivity and CY (Table 2). The best results were obtained in acetonitrile, but it is more convenient to use 1:1 acetonitrile–benzene in light of the low solubility of the starting complexes in MeCN. The reaction catalyzed by the $Co_2(\mu\text{-}N_2(PPh_3)_6$ + DPPE system in this case proceeds over 1 h at 70°C with almost 100% selectivity, and the cyclopentanone catalytic yield is 20.

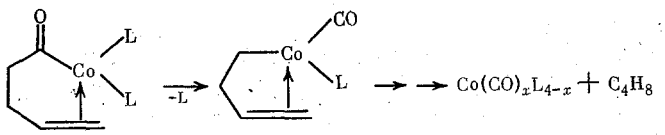
Upon running this reaction in acetone, the product of the condensation of acetone with 4-pentenal, viz., 3,7-octadien-2-one (VIII), is formed as a side product, while ethyl 4-pentenoate (IX) is formed in ethanol in addition to (III) and (VII).

In examining the effect of the ligands and solvent on the reaction indices for intramolecular hydroacylation, we should also take account of the important role of decarbonylation in the intermediate complex (A), which leads to cobalt carbonylphosphine complexes [5, 8]:

TABLE 2. Effect of the Nature of the Solvent and Selectivity of the Cyclization of 4-Pentenal (I) to Cyclopentanene (II)[a]

Solvent	Conversion of (I), %	CY[b]	Formation selectivity from (I), %	
			(II)	side products
MeCN	100	10	~100	–
1:1 MeCN–benzene	100	20[c]	~100	–
10:1 Benzene–PhCN	100	8,5	85	8(VII)
Acetone	100	8,4	84	10(VIII)
DMF	100	8,0	80	12(VII)
Benzene	100	7,7	77	7(VI), 4(VII),
Dimethoxyethane	94	5,9	63	5(VI), 8(VII)
THF	89	5,6	63	6(VI), 7(VII)
Ethanol	100	5,4	54	12(III), 15(VII), 5(IX)
Pyridine	97	3,7	38	25(Va,b), 12(IV), 13(VII)

[a]Catalytic system: $Co_2(\mu\text{-}N_2)(PPh_3)_6$ + DPPE (1 mole per g-at Co), [Co] = 0.05 g-at/liter, $[(I)]_0/[(Co)] = 10$, 70°C, 1 h.
[b]Catalytic yield of cyclopentanone (II), mole/g-at Co.
[c]$[(I)]_0/[Co] = 20$.



(A)

It is apparently this reaction which is specifically responsible for catalyst deactivation. Indeed, the carbonylphosphine complexes obtained from $Co_2(CO)_8$ by ligand exchange with PPh_3, PBu_3, and DPPE [9] are inactive in the cyclization of 4-pentenal in benzene or acetonitrile at temperatures up to 90°C.

The decarbonylation reaction rate should depend on the facility of the replacement of the phosphine ligand at the cobalt atom. The ease of replacement and position of equilibrium in ligand exchange reactions depend on the ligand bulk, which has been characterized by the conic angle θ [10]. In the case of bulky ligands such as P(cyclohexyl)$_3$ or P(i-Pr)$_3$ (the conic angle has a large value), the phosphine is apparently readily eliminated from the cobalt coordination sphere by less bulky groups (CO in this case). As a result, the decarbonylation reaction proceeds rapidly even at room temperature, the catalyst is deactivated, and an increase in reaction time or temperature up to 70°C does not lead to a significant increase in CY (see Table 1). On the other hand, phosphines with small bulk such as PBu_3 and, especially, chelating diphosphines such as DPPE are eliminated from the coordination sphere with greater difficulty. Thus, they retard the decarbonylation reaction and increase the lifetime of the catalytically active sites. An increase in temperature up to 70°C using such ligands gives a marked effect (see Table 1 and Fig. 1b). The suppression of the decarbonylation reaction upon the introduction of chelating diphosphines was shown in the case of the rhodium acyl complex, $Rh(COPh)[Ph_2P(CH_2)_3PPh_2]Cl_2$, in which the decarbonylation reaction, in contrast to its triphenylphosphine analog, is not observed at temperatures up to 190°C [11].

Hence, we may explain the significant increase in reaction selectivity and cyclopentanone CY when using acetonitrile as the solvent. MeCN is a good coordinating solvent and has relatively small bulk. The decarbonylation products of 4-pentenal are virtually not observed upon carrying out the reaction in acetonitrile or in acetonitrile–benzene.

EXPERIMENTAL

The PMR spectra were taken on a Bruker WM-250 spectrometer. The IR spectra were taken on a Specord 75-IR spectrometer. The gas–liquid chromatographic analysis was carried out on an LKhM-8MD(5) chromatograph, using 3 m × 3 mm steel columns packed with 5% PEG-20M, 5% XE-60, and 5% SE-30 on Chromaton N-AW-DMCS, a flame ionization detector, nitrogen as the carrier gas, and temperature programming. The reaction products were identified chromatographically using standard compounds. All the reactions with Co(0) complexes were carried out in argon atmosphere.

A sample of 4-pentenal was obtained according to our previous procedure [5]. Bis(diphenylphosphino)methane, 1,2-bis(diphenylphosphino)propane, PBu_3, $P(cyclohexyl)_3$, $P(i\text{-}Pr)_3$, tris(p-dimethylaminophenyl)phosphine, $P(OBu)_3$, N,N,N',N'-tetramethylethylenediamine, and α,α'-dipyridyl were obtained as purified commercial samples. The sample of PPh_3 was purified as described in our previous work [5].

The solvents were purified and dried by standard methods and flushed with argon prior to use.

Co(μ-N_2)(PPh_3)$_6$. A sample of 13.09 g (20 mmoles) $CoCl_2(PPh_3)_2$ obtained as described in our previous work [5] and 6.56 g (25 mmoles) was stirred for 15 min in 50 ml THF at 0°C in a nitrogen stream. Then, 40 ml 1 M sodium naphthalide in THF was added dropwise at this temperature with rapid stirring in a nitrogen stream. Dark-red crystals formed after some time. Then, 200 ml cooled ether was added and stirred. The solution was separated from the precipitate by decantation. The precipitate was washed with three 150 ml portions of cooled ether, placed on a filter, and dried in vacuum. In order to remove NaCl, the crystals were washed several times with water, 3% aq. HCl, and again with water and dried in vacuum. The dry crystals were again washed with ether and dried in vacuum at 0.05 mm to give 10.5 g (61%) dark cherry-red crystals. Upon heating to 120°C 0.5 g complex gave from 6.12 to 6.71 ml N_2 (calculated 6.51 ml). Found: C 74.88; H 5.28; P + Co 17.78%. Calculated for $C_{108}H_{90}N_2P_6Co_2$: C 75.44; H 5.28; P + Co 17.66%. The properties of this compound correspond to those described by Aresta et al. [12].

Catalytic Cyclization of 4-Pentenal (I). A sample of 2.5 mg (0.125 mmole) $Co_2(\mu\text{-}N_2)(PPh_3)_6$, 0.5 mmole of the monodentate ligand L, or 0.25 mmole of the bidentate ligand were placed in a glass ampul and 4 ml solvent was added. After stirring for 15 min at 20°C, 2.5 mmoles 4-pentenal and undecane as an internal standard in 1 ml solvent were added. The ampul was sealed and maintained at the given temperature for 1 h. The products were analyzed by gas–liquid chromatography. The results obtained are given in Tables 1 and 2.

Compounds (III)-(Va, b) were identified as in our previous work [5], and (VI) and (VII) were identified using authentic samples obtained by convergent synthesis.

4-Pentenyl 4-pentenoate (VI) was synthesized from 4-pentenal by the action of $Al(O\text{-}i\text{-}Pr)_3$ in CCl_4 [13], bp 90-91°C (15 mm). PMR spectrum (δ, ppm): 1.66 m ($CH_2\underline{CH_2}CH_2$), 2.06 m (=CCH_2), 2.32 m ($COCH_2\underline{CH_2}$), 4.02 t (CH_2O, J = 6.5 Hz), 4.88-5.04 m ($2HC_2$=), 5.64-5.84 m (2CH=). IR spectrum (ν, cm^{-1}): 1643 (C=C), 1737 (C=O), 3080 (=C–H).

2-(4-Pentenylidene)cyclopentanone (VII) was obtained by the condensation of 4-pentenal with cyclopentanone catalyzed by NaOH in ethanol, bp 55-57°C (0.2 mm). PMR spectrum (δ, ppm): 1.88 m (ring CH_2), 2.18 m (2 CH_2C=), 2.27 t (CH_2CO), 2.53 m (ring =CCH_2), 4.90-5.03 m (=CH_2), 5.66-5.83 m (CH=), 6.1-6.5 m (CH=CC=O). IR spectrum (ν, cm^{-1}): 1650 (C=C), 1720 (C=O), 3080 (=C–H).

CONCLUSIONS

1. The efficiency of the catalytic system containing Co(0) and various ligands (phosphines, diphosphines, phosphites, and diamines) in the intramolecular hydroacylation reaction is greatest when using chelating diphosphines 1,2-bis(diphenylphosphino)ethane and 1,2-bis(diphenylphosphino)propane (ligand:Co = 1:1).

2. For monodentate phosphorus-containing ligands, the activity and selectivity of the catalytic system increase with increasing donor capacity and decreasing bulk of the ligands.

3. In the presence of the $Co_2(\mu\text{-}N_2)(PPh_3)_6$ + 1,2-bis(diphenylphosphino)ethane catalytic system, 4-pentenal cyclizes to cyclopentanone in acetonitrile at 70°C with about 100% selectivity at complete conversion (20 moles per g-at Co).

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CYCLOPENTADIENYL DERIVATIVES OF MAGNESIUM AND SODIUM IN CROSS-COMBINATION REACTION WITH ALLYL COMPOUNDS CATALYZED BY Pd COMPLEXES

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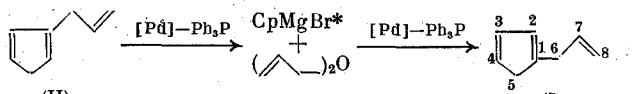
In a continuation of our study on cross-combination of organomagnesium reagents with O-, N-, and S-containing allyl compounds [1], we studied the reaction of cyclopentadienylmagnesium bromide, bis(cyclopentadienyl)magnesium, and also cyclopentadienylsodium with allyl ethers and esters, allyl sulfides, quaternized allylamines, and allyl sulfones, catalyzed by transition-metal complexes, to develop effective methods for preparing difficultly available allylcyclopentadienes. According to [2-4], the noncatalyzed cross-combination of cyclopentadienylmagnesium chloride and cyclopentadienylsodium with allyl halides leads to the formation of a mixture of isomeric allylcyclopentadienes in yields not higher than 40%.

Salts of Cu, Ti, Zr, Fe, Co, Ni, Cr, and Pd were tested as catalysts in these reactions; $Pd(acac)_2$ and $PdCl_2$, activated by Ph_3P, have the highest catalytic activity. We used a model reaction of cross-combination of diallyl ether with cyclopentadienylmagnesium bromide to study the influence of the nature of the solvent and reaction conditions on the yield of the combination products. The maximal yields of allylcyclopentadienes were obtained in THF and Et_2O at 40°C at a reaction duration of 2 h. A mixture of 1- and 2-allylcyclopentadienes (I) and (II) is thus formed in a ratio of ~85:15 in a quantitative yield. This reaction does not proceed in the absence of palladium catalyst



(II) (I)

*CpMgBr = 

The ratio and yield of (I) and (II) vary noticeably, depending on the nature of the ligand in the catalyst. For example, the overall yield of (I) and (II) decreases from 96 to 55% in the series of PPh_3, $(C_6H_{11}O)_3P$, $(C_6H_{13})_3As$, and $(PhO)_3P{=}O$ ligand–activators, and the content of (II) in these experiments increases to 60% (Table 1). The structure of the allyl compounds thus practically does not influence the composition of allylcyclopentadienes (Table 2).

Under the conditions studied, because of the equivalency of the carbon atoms of the cyclopentadienyl anion, probably 5-allylcyclopentadiene is first formed containing a mobile H atom at C^5. The subsequent migration of H and the shift of the double bonds in the cyclopentadienyl ring leads to a mixture of (I) and (II):

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