A Direct Amination of Isoprene by Aniline – Catalyzed by Palladium Complexes

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Abstract. The reaction of isoprene with aniline, catalyzed by Pd $(acac)_2-(RO)_3P$ -CF₃COOH, (1:4:4) (R = Me, Et, acac = $(CH_3CO)_2CH$ -) in MeCN solution, results in high (up to 89 mol.%) selectivity of N-(3-methyl-2-buten-1-yl) aniline. The presence of telomeric products in the reaction mixture is observed at a P/Pd ratio of 1:2 and 1:1. The use of (1,1,1-trifluoro, 4-perfluorocyclo-

hexyl -2,4-butanedionato) palladium as the catalyst gives rise to 92 mol% mol.selectivity of telomers by the favored tail-to-head and head to head coupling.

Keywords: Palladium; Telomerization; Catalysts.

Introduction

A one-pot for the synthesis of allylamines is the direct amination of 1,3-dienes, catalyzed by transition metal complexes of the nickel triad (Schema 1). These reactions obviously have a lack, due to their low selectivity. Therefore, revealing the true intermediate metallocomplexes, responsible for formation of each product, is a major task for the decision of a selectivity problem. Untill now, no mechanism has explained all the features of this reaction. The C_{10} -Pd complexes, prepared by the reaction of isoprene, are formed as a mixture of two isomers [Pd (PR₃) (η^1 , η^3 -Me₂C₈ H₁₀)], having the methyl groups in the 2,6- or 2,7-position [1]. In other words, from the four possible directions of addition of the two isoprene molecules, only tail-to-tail and tail-tohead coupling products are observed. In the case of the palladium system, no evidence was found for the formation of the head to head isomer, as in the case of nickel. The stoichiometric reactions of the complex [Pd (PR₃) η^1 , η^3 - C_8H_{12})] with acidic nucleophiles, such as alcohols, acetic acid, and with a variety of active methylene compounds have been described. Reactions of this kind are impossible in the case of secondary amines [2]. Notwithstanding isoprene reacts with dialkylamines in MeCN or MeOH solution in the presence of a catalytic system consisting of $Pd(acac)_2$ or $Pd(OAc)_2$ and trialkylphosphite or phosphines as a phosphoric ligand; this gives rise to the formation of telomers at all four possible coupling positions of the isoprene units [3-6]. The addition of an acid as a co-catalyst, even one as weak as CO_2 , gave rise to a substantial increase in activity of the catalyst. Besides using acids with various pK_a, it is possible to control the distribution of isomeric

A.N. Nesmeyanov Institute of Organo-Element Compounds Russian Academy of Sciences Vavilov Str. 28 119991 Moscow / Russia fax.: 7(095)135-5085 e-mail: petrushkina@rambler.ru telomers [4, 6]. The assumption that in the presence of uncoordinating acids, the cationic palladium complexes responsible for formation of telomers with a head-to-head skeleton are formed, was confirmed by the use of wellknown cationic palladium complexes as catalysts [7]. In the presence of coordinating acids, the change in composition and the ratio of catalytic system, $PdX_2 - R_3P-HX$ (HX – the acid), allows for the formation of telomers with a natural 2,6-dimethyloctane skeleton, including α -geranyldialkylamines [6, 8]. IR and UV spectra of products of the reaction with $Pd(acac)_2 - BF_3 \cdot OEt_2 - C_4H_6$ were investigated [9] and the structure of cationic hydridpalladium complex, $[(C_4H_6)_nPdH]BF_4$, is proposed. This complex was active in the telomerization of 1,3 – butadiene with dialkylamines. Selective formation of the head-to-head isomer was also achieved [10] in the absence of an acid as the co-catalyst or



Fig. 1 The effect of the phosphorus/palladium ratio on the product distribution in the palladium catalyzed reaction of isoprene and aniline. Reaction conditions: $0.375 \text{ mmol Pd}(acac)_2$, $0 - 1.5 \text{ mmol}(RO)_3P$; 1.5 or 3.75 mmol TFA; 9 ml CH₃CN; 150 mmol isoprene; 75 mmol aniline; 100 °C; 32 h.

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Scheme 1

a cationic complex as a catalyst. The reaction of isoprene with aromatic amines in the presence of the catalysts, $PdX_2 - R_3P$, results in only tail-to-head and tail-to-tail telomers [11, 12]. The attempt to prepare head-to-head and head-to-tail telomers by this method were very successful in the case of mono- and dialkylamines; that is, by the use of catalytic system, $PdX_2 - R_3P$ -HX (HX – acid); it failed in the case of anilines. It was found that the formation, mainly, of hydroamination products (adducts) [12, 13] and the formation of telomers did not exceed 5-6 %.

Results and Discussion

The possibility of managing the ratio of l:l-adducts to 2:ltelomers for the reaction of isoprene and Et_2NH has been shown earlier [4]. A change in catalyst composition and reaction conditions proved successful. Therefore, we studied influence the catalyst composition of $Pd(acac)_2-(RO)_3P$ -TFA (TFA – trifluoroacetic acid) on distribution of products of isoprene (I) reaction with aniline (II) in MeCN solution (Scheme 1). The results are given in Table 1.

Table 1 Composition of products of isoprene reaction with PhNH₂ in the presence of the catalyst, Pd(acac)₂-(RO)₃-CF₃CO₂H in MeCN solution at 100 °C (0.375 mmol Pd(acac)₂, 0 -1.5 mmol (RO)₃P; 0.375-15 mmol TFA; 9 ml CH₃CN; 150 mmol isoprene; 75 mmol aniline)

Catalyst		τ (h)	Isoprene conversion, %		selectivity,										
Molar ratio of catalyst components	R			dimers	adducts	telomers	(III)	(V)	mol % (VI)	(VII)	(VIII)	(IX)	(X)	(XI)	unidentifiable
1:4:4	Me	32	76	1	99	-	84	8	1	5					
	Et	32	62	-	100	-	89	5	2	4					
1:4:10	Me	32	39	33	66	-	57	3	_	7					
	Et	32	83	8	91	-	59	14	7	12					
	Et	87	85	8	92	-	47	21	9	15					
1:4:20	Me	32	70	43	57	-	36	10	3	10					
	Et	32	49	4	96	-	42	15	8	31					
1:4:40	Et	32	67	51	49	-	15	8	12	14					
1:2:4	Me ^{a)}	168	59	9	9	82	3.5	1	0.5	4	7	18	35	_	22
	Et ^{a)}	168	73	$7(2^{b})$	28	65	16	6	1	5	6	15	26	_	18
	Et	32	98	$6(0,1^{b})$	71	23	38	14	4	15	2	6	11	1	3
1:2:10	Et	32	85		100	_	51	14	9	26					
1:1:1	Et	31	82	_	31	69	11	10	2	8	7	18	34	3	9
	Et	82	95	_	77	23	17	24	7	29	2	5	12	1	5
1:1:4	Me	37	56	12	62	26	23	16	1	22	2	7	12.5	0.5	4
	Et	85	80	9	54	37	10	8	5	31	3	10	17	1	6
1:1:10	Et	32	96	5	84	11	47	15	1	21	1	3	5	1	1
1:0:10	Et	32	37	_	100	_	50	20	10	21					
1:2:4 ^{c)}	Et	7	19	-	8	92	1	2	1	4	27	2	44	9	10

^{a)} Reaction was carried out at 20 °C

^{b)} Hydrogenized dimers of isoprene M⁺=138

c) Reaction carried out in the presence of complex (XV) instead Pd(acac)₂



In the case of the diene (I) reaction with amine (II) (Fig.1), we observed a picture completely distinct from that of diene (I) reaction with Et₂NH. At the TFA/Pd ratio of 10, a maximal selectivity to the formation of adducts was observed with a at P/Pd ratio of 0 and 2; at the TFA/Pd ratio of 4, maximal selectivity of adduct formation was found at P/Pd ratios of 1 and 4; the selectivity was minimal at P/Pd = 2, in the case of both phosphites. The law of symmetry was observed for the selectivity of telomers formation; that is, the maximal selectivity of telomers was observed at P/Pd = 2 (65 %).

We considered the possible use of other methods for the enhancement of telomer selectivity. The study of diene (I) telomerization with monoalkyl amines and the comparison of these results with those of the isoprene telomerization with dialkylamines allows us to make assumptions about the participation of coordination complexes of Pd(acac)₂ with phosphoric ligands and amines, like XII and XIII in the formation of catalytic active centres [14] (Scheme 2).

This assumption was confirmed later by [15], which was devoted to the study of IR and ¹H NMR spectra of reaction products of mixture $Pd(acac)_2 - BF_3 \cdot OEt_2$ with Et_2NH . The structure of the cationic complex containing two amine ligands was proposed. It catalyzed the telomerization of butadiene and Et₂NH with the same efficiency, as the catalytic system $Pd(acac)_2$ -BF₃ · OEt₂. Thus, the complex shown in Scheme 2, is the precursor of an active complex containing amine ligands together with butadiene with the formula [L_m-Pd-H]⁺ BF₄, which is formed in situ. Certainly, we supposed that in the case of a reaction of isoprene with aniline, the appropriate coordination palladium complexes explain the unusual results for this reaction. However, as was shown earlier [16] bis-amine complexes are not formed from Pd(acac)₂ and anilines; in this case, amide complexes like XIV are mainly formed (Scheme 3).

The complexes containing amide ligands are able to catalyze butadiene telomerization with Et₂NH as was shown

in 1978 [16]. Apparently, anilide-palladium complexes can catalyze telomerization in the case of anilines too, as in the absence of an acid co-catalyst, telomers of isoprene and aniline are formed with tail to tail skeleton. In the presence of acid, apparently, the protonation of amide-palladium complexes (XIV) can not give rise to bis- anilines complexes which can catalyze the telomerization. The bis-aniline complexes can be formed from more acidic $bis(\beta$ -diketonato) palladium, for example, such as Pd(hFac)₂ [17]. As similar bis-amine palladium complexes in the case of Et₂NH have proved to be active catalysts for telomerization and result in the formation of similar bis-aniline complexes in situ, we used (1,1,1-trifluoro, 4-perfluorocyclohexyl -2,4-butanedionato) palladium¹⁾ (XV) as a catalyst for telomerization and found the expected result. The main products of reaction were telomers with tail-to-head and head-to-head skeletons. Complex (XV) was prepared by method described in [18].

Experimental Part

Infrared spectra were recorded on a Carl Zeis "Specord M-82" spectrometer using KBr pellets. ¹H NMR spectra were recorded on Bruker WP-200SY and Bruker AMX-400 instruments at 200 MHz and 400 MHz, respectively (CDCl₃, internal standard - TMS). The GC-MS analysis carried out on the Analitical VG 7070E instrument at 70 eV and a temperature of 150 °C for the ionic source. The MS analysis carried out on the Finnigan Polaris Q instrument at 70 eV and a temperature of 150 °C for ionic source C. The GC analyses were carried out on a Finnigan 9001 instrument using a 30 m DB 5.625 capillary quartz column (temperature program from 50 up to 200 °C, with a rate of 8°/ min and from 200 up to 310 °C with a rate of 120°/min); C₂₁H₄₄ was the GC standard. Isomeric composition of products (VIII-XI) was determined by comparison of retention rate [12]. The monomers were used with 99 % purity. Isoprene, solvents, ligands and TFA were purified and stored under argon. Aniline was distilled over KOH pellets and kept under argon. Palladium acetylacetonate was prepared according to the literature. All reactions were carried out under argon.

Reaction of isoprene with aniline in MeCN solution

Pd (acac)₂ or complex (XV) (0.375 mmol), (EtO)₃P or (MeO)₃P (0.375, 0.75, or 1.5 mmol), MeCN (9 ml), isoprene (150 mmol), aniline (75 mmol) and finally CF₃CO₂H (0.375, 0.75, 1.5, 3.75, 7.5 or

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15 mmol) was placed in a glass tube in argon. The sealed tube was heated to or maintained at 20 $^{\circ}$ C (see the Table). The products distilated in vacuo with t.b. 40-170 $^{\circ}$ C (2 mmHg) was analyzed by GC and GC-MS methods. ¹H NMR spectra of isomers (III, V, VII, VIII, XI) have been published in [12].

Adduct (VI): ¹H NMR (CDCl₃), $\delta =: 1.16$ and 1.21 (s, 6H, 2CH₃); 4.69-5.00 (m, 2H, CH₂=); 5.17-5.43 (m 1H, CH =); 6.61 (m 3H, Ph); 7.14 (m 2H, Ph). MS (70 eV, 150 °C): m/z = 161 (M⁺, 67 %), 146 (M⁺ - CH₃, 92 %), 120 (M⁺ - C₃H₅, 96 %), 118 (M⁺ - C₃H₇, 16 %), 93 (M⁺ - C₅H₈, 40 %), 77 (M⁺ - C₆H₅, 25 %).

Telomer (IX): ¹**H**, **NMR** (CDCl₃), $\delta = 0.97$ (d, 3H, ^{6A}CH₃, J = 6.54 Hz); 1.35-1.49 (m, 4H, ⁴CH₂, ⁵CH₂); 2.01-2.14 (m, 3H, ⁶CH); 1.66 (s, 3H, ^{2A}CH₃); 3.89 (t, 2H, ³CH, J = 6.03 Hz); 4.84-5.92 (m, 1H, ⁷CH, J_{trans} = 18.06, J_{cis} = 9.66, J_{gem} = 1.5 Hz); 4.92 and 4.95 (s and s, 2H, ¹CH₂); 5.62-5.72 (m, 2H, ⁸CH₂, J_{trans} = 18.06, J_{cis} = 9.66, J₇₋₆ = 7.48 Hz); 6.58-6.77 (m, 3H, C₆H₃); 7.13-7.23 (m, 2H, C₆H₅).). **MS** (70 eV, 150 °C): m/z = 229 (M⁺ 12 %), 172 (M⁺ - C₄H₂, 8%), 146 (M⁺ - C₆H₁₁, 10%), 93 (M⁺ - C₁₀H₁₆, 100%).

(1,1,1-trifluoro, 4-perfluorocyclohexyl -2,4butanedionato) palladium (XV)

Mercury(II) oxide (6.5 g, 30 mmol) was dissolved in a solution (60 cm³) of perchloric acid (1 mol dm⁻³). The solution of mercury(II) perchlorate thus prepared was added with stirring to a solution (20 cm³) of Na₂[PdCl₄] (0.5 mol dm⁻³) kept at 0 °C. A solution of the Na(CF₃COCH₂COC₆F₁₁) salt which was prepared by dissolving of CF₃COCH₂COC₆F₁₁ (17 cm³, 50 mmol) in a solution (20 cm³) of sodium hydroxide (2 mol dm⁻³), was added dropwise. The precipitate was filtered, washed several times with water, and dried on vacuo. The brown powder was treated with hexane, and the insoluble material was filtered off. The solvent was evaporated away under reduced pressure to leave yellow needles (9.44 g) in a 89 % yield. Recrystallization from benzene gave yellow needles. Analytical Data: C₂₀H₂F₂₈O₄Pd: C 26.02 (calc. 25.43); F 55.84 (56.32) %.

IR (KBr, pellet): v 1531vs, 1596vs, 1617m, 1661m and 808m cm⁻¹ are assigned to the v(C=O) + v(C=C) and chelate ring π (CH) vibrations, v(C-F) 1125-1207vs, 1243vs, br, 1317 vs,br cm⁻¹. The region below 700 cm⁻¹ shows

composited bands as 462 and 484 cm⁻¹ and are tentatively assigned to the cis isomer. **MS** (70 eV, 150 °C): m/z = 944 (M⁺, 11 %), 663 (M⁺ - C₆F₁₁, 5 %),

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