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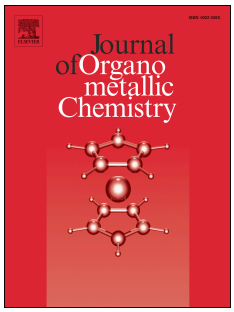

Nitroaldol reaction catalyzed by arylhydrazone di- and triorganotin(IV) complexes

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Nitroaldol reaction catalyzed by arylhydrazone di- and triorganotin(IV) complexes

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Organometallic and catalytic chemists from Portugal, Azerbaijan and Russia dedicate this work to **Professor Irina Petrovna Beletskaya**.

Abstract

Two known organotin(IV) complexes, $[Sn(C_6H_5)_3HL^1]$ (**1**, H_2L^1 = 2-(2-(2,4-dioxopentan-3-ylidene)hydrazinyl)benzoic acid) and $[Sn(C_2H_5)_2(1\kappa O,2\kappa O\text{-}H_3L^2)(1\kappa O^2\text{-}H_3L^2)(\mu_3\text{-}O)]_2$ (**2**, H_4L^2 = 2-(2-(2,4,6-trioxotetrahydropyrimidin-5(2H)-ylidene)hydrazinyl)benzoic acid) were synthesized. Both compounds **1** and **2** act as homogenous catalysts for the diastereoselective nitroaldol (Henry) reaction of aliphatic and aromatic aldehydes with nitroethane in different solvents such as dichloromethane, acetonitrile or methanol. Complex **2** was found to be the more efficient catalyst for the Henry reaction in methanol, producing β-nitroalcohols with good yields (65−89 %) and diastereoselectivities (*syn/anti* 72:28−77:23).

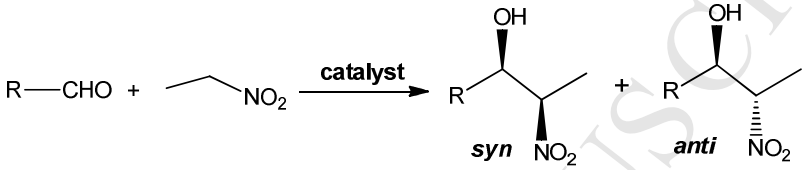
Keywords: Di- and triorganotin(IV) complexes; C−C coupling of aldehydes with nitroethane; β-nitroalcohols.

1. Introduction

Due to the Lewis acid character of organotin compounds, they are an important class of acid catalysts, which are milder than Brønsted acids, but their utilization has been significantly increased [1−6]. For instance, organotin compounds are applied as homogeneous catalysts in a series of industrial reactions, in which esters are produced *via* (trans)esterification, *e.g.*, in the synthesis of fatty acid alkyl esters [3], polyesters [4,5] and lactones [6]. As far as we know, only one organotin compound, $(n\text{-}Bu)_3SnH$, has been applied in nitroaldol (Henry) reaction [7a].

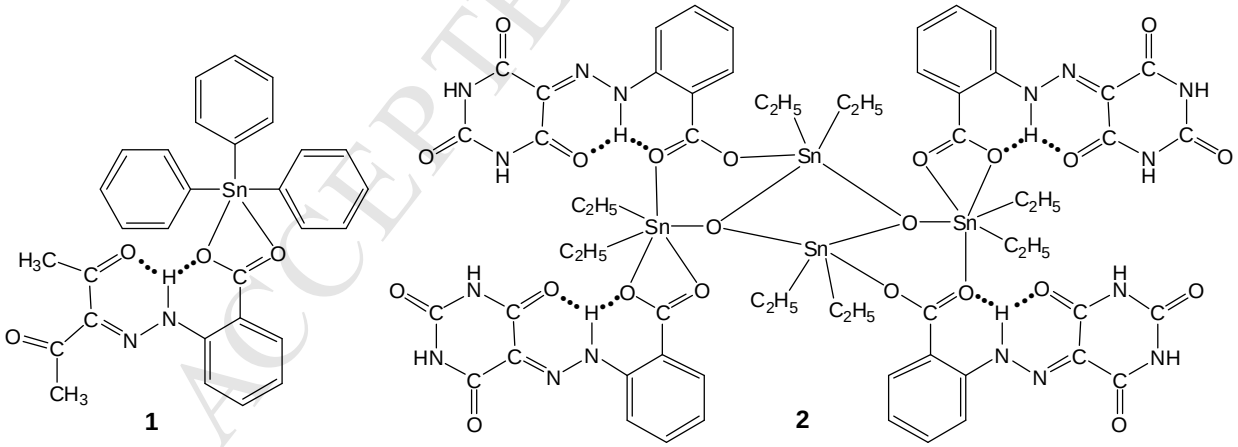
The nitroaldol (Henry) is a Lewis acid/base-catalyzed C−C coupling of an aldehyde and nitroalkane, to produce corresponding β-nitroalkanol (Scheme 1) [7]. The resulting products, β-nitroalkanols, are important and versatile intermediates in the synthesis of 2-amino alcohols, nitroalkenes and α-nitroketones [7−12]. For the synthesis of β-nitroalkanols, alkali metal hydroxides, alkoxides or amines [13,14], as well as heterobimetallic complexes with lanthanide

BINOL (BINOL = 2,2'-dihydroxy-1,1'-binaphthyl) systems [15], Mg–Al hydrotalcite [16,17], guanidines [18], benzyltrimethylammonium hydroxide [19], a rhodium complex in the presence of a silyl ketene acetal [20], amberlyst A-21 [13], cinchona alkaloid [21], proazaphosphatranes [22], Cu-bis(oxazoline) [23] or Co-salen (salen = *N*,*N'*-bis(salicylidine)ethylenediamine) complexes [24,25] Zn(II) dinuclear complexes [26,27] or a mixture of $Zn(OTf)_2$ (OTf = triflate) and (+)-*N*-methylephedrine [28], Cu(II)-arylhydrazones [29], Zn(II)-1,3,5-triazapentadienato [30], etc. were applied as homogeneous catalysts in Henry reaction between aldehydes and nitroalkanes. However, there is no application of organotin complexes in this transformation. Thus, the search for efficient and cheap homogenous protocol for the C−C coupling of aldehydes with nitroalkanes is still highly desirable.



Scheme 1. The nitroaldol (Henry) reaction.

Hence, on the basis of the above considerations, we focused this work on the following aims: i) to prepare known di- and triorganotin(IV) complexes, $[Sn(C_6H_5)_3HL^1]$ (**1**, H_2L^1 = 2-(2-(2,4-dioxopentan-3-ylidene)hydrazinyl)benzoic acid) and $[Sn(C_2H_5)_2(1\kappa O,2\kappa O\text{-}H_3L^2)(1\kappa O^2\text{-}H_3L^2)(\mu_3\text{-}O)]_2$ (**2**, H_4L^2 = 2-(2-(2,4,6-trioxotetrahydropyrimidin-5(2H)-ylidene)hydrazinyl)benzoic acid) (Scheme 2) [31]; ii) to test the catalytic activity of the prepared di- and triorganotin(IV) complexes in nitroaldol reaction.



Scheme 2. Schematic representations of complexes **1** and **2** [31].

2. Experimental

2.1. Materials and instrumentation

All the chemicals were obtained from commercial sources (Aldrich) and used as received. H_2L^1, H_4L^2, **1** and **2** were synthesized according to the reported procedure [31]. The ^1H NMR spectra were recorded at room temperature on a Bruker Avance II + 400 (UltraShield™ Magnet) spectrometer

operating at 400 MHz for proton. The chemical shift is reported in ppm using tetramethylsilane as the internal reference.

2.2. Catalytic activity studies

To a 10 mL vial were added the catalyst (1.0−6.0 mol%) and 2 mL solvent (CH_2Cl_2, MeCN or MeOH) and the solution was stirred for 2 min at room temperature. Then, the aldehyde (1 mmol) and nitroethane (4 mmol) were added and the resulting transparent homogeneous solution was stirred at room temperature for the appropriate time. The solvent was removed under reduced pressure and the resulting mixture was directly purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 6:1) to afford the Henry reaction product (isolated yield) [32]. The analytical data of the obtained β-nitroalcohols are in good agreement with literature [33,34]. The *syn*/*anti* diastereoselectivity of the β-nitroalcohols was determined by ^{1}H NMR spectroscopy (in $CDCl_3$) based on the vicinal coupling constants of the products between the α-N−C−*H* and the α-O−C−*H* [17,32−35].

3. Results and discussion

Firstly, we examined the catalytic performance of **1** and **2**, as well as Ph_3SnCl, $(Et_2Sn)O$, H_2L^1 and H_4L^2 in a model nitroaldol reaction between benzaldehyde and nitroethane in different solvents (dichloromethane, acetonitrile and methanol) at room temperature (Table 1). The use of protic solvents usually provides better results than aprotic ones [36−38], what is also observed in our case (Table 1). Catalyst **2** behaves as the most active (73%) and diastereoselective (*syn* : *anti* = 74:26) catalyst among Ph_3SnCl, $(Et_2Sn)O$, H_2L^1, H_4L^2, **1** and **2** in the methanol medium as well as under catalyst- and solvent-free conditions (entry 28, Table 1). In methanol, the catalytic activity of complex **2** is higher than that of **1** (entries 25 and 28, Table 1), what can eventually be associated to the acidic protons of the pyrimidine moiety of the former complex, where the NH group(s) can play a H-bond donor role in the activation of the C=O group of benzaldehyde. Thus, methanol was chosen as the sole solvent for further studies. Control (blank) experiments were carried out in the absence of any metal catalyst or in the presence of Ph_3SnCl, $(Et_2Sn)O$, H_2L^1 and H_4L^2. In the former case (entries 2−4) no nitroaldol coupling product was detected, whereas, with Ph_3SnCl, $(Et_2Sn)O$, H_2L^1 or H_4L^2 low product yield (7, 6, 2 or 7 %, respectively) was obtained (entries 11−22) in methanol. To establish the optimized conditions, the variations of reaction time (0.5−24 h), catalyst amount (1−6 mol %) and temperature (20−75^{o}C) were applied (Table 2). The increase of reaction time from 0.5 h to 24 h led to higher conversion (entries 1−6, Table 2), however the 6 h appears to be the optimal reaction time. The variation (1−6 mol %) of the catalyst amount (entries 7−12) resulted in a significance effect on the yield. Thus, 5 mol % loading is optimal for the given reaction conditions and thus this amount was used for the further studies. By increasing the

temperature from 20°C to 75°C the yield of the corresponding β-nitroalkanol was little more but with lower diasteroselectivity (entries 11, 13−15, Table 2). Hence, room temperature was taken as optimized temperature for this reaction giving good yield (78%) of corresponding β-nitroalkanol with *syn* : *anti* = 74:26 (entry 11, Table 2).

Table 1. Catalyst screening and optimization.[a]

Entry	Catalyst	Solvent	Yield, %[c]	Selectivity, *syn/anti*[d]
1[b]	Blank	No solvent	–	–
2	Blank	CH_2Cl_2	–	–
3		MeCN	–	–
4		MeOH	–	–
11	Ph_3SnCl	CH_2Cl_2	3	55:45
12		MeCN	4	56:44
13		MeOH	7	58:42
14	$(Et_2Sn)O$	CH_2Cl_2	2	56:44
15		MeCN	4	53:47
16		MeOH	6	50:50
17	H_2L^1	CH_2Cl_2	–	–
18		MeCN	–	–
19		MeOH	2	51:49
20	H_4L^2	CH_2Cl_2	–	–
21		MeCN	–	–
22		MeOH	7	53:47
23	**1**	CH_2Cl_2	32	61:39
24		MeCN	46	66:34
25		MeOH	59	70:30
26	**2**	CH_2Cl_2	39	68:32
27		MeCN	57	70:30
28		MeOH	73	74:26

[a] Reaction conditions: catalyst precursor: Ph_3SnCl, $(Et_2Sn)O$, **1** and **2** (4.0 mol%), dichloromethane, acetonitrile or methanol (2 mL), nitroethane (4 mmol) and benzaldehyde (1 mmol), reaction time: 24h, reaction temperature: 20 °C. [b] Solvent-free conditions, using nitroethane as solvent (2 mL), [c] Isolated yields after column chromatography. [d] Determined by ^{1}H NMR.

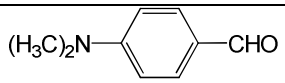
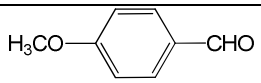
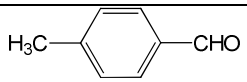
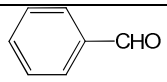
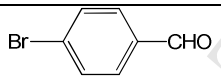
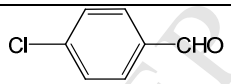
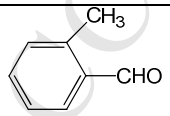
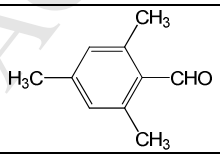
Table 2. Optimization of the Henry reaction condition catalyzed by **2**.[a]

Entry	Time, h	Amount of catalyst, mol%	Temp., °C	Yield, %[b]	Selectivity, *syn/anti*[c]
1	0.5	4.0	20	33	74:26
2	1	4.0	20	49	74:26
3	4	4.0	20	67	75:25
4	6	4.0	20	73	75:25
5	8	4.0	20	73	74:26
6	24	4.0	20	73	74:26
7	6	1.0	20	29	75:25
8	6	2.0	20	50	75:25
9	6	3.0	20	65	74:26
10	6	4.0	20	73	74:26
11	6	5.0	20	78	74:26
12	6	6.0	20	78	75:25
13	6	5.0	35	80	73:27
14	6	5.0	55	82	72:28
15	6	5.0	75	83	70:30
16[d]	6	5.0	20	36	70:30

[a] Reaction conditions: 1.0−6.0 mol% of catalyst precursor (typically 5.0 mol%), MeOH (2 mL), nitroethane (4 mmol) and aldehyde (1 mmol). [b] Isolated yields after column chromatography. [c] Determined by ^{1}H NMR. [d] Solvent-free conditions, using nitroethane as solvent (2 mL).

The substrate scope was then investigated. A variety of aliphatic and aromatic aldehydes were tested under the optimized conditions using **2** as the catalyst (Table 3). As shown in Table 3, β-nitroalcohols are obtained in moderate to good yields ranging from 65% to 89%. Aldehydes containing either electron-donating or electron-withdrawing substituents at *para*- position of the aromatic ring of aryl aldehydes gave moderate yields (69−85%) with similar diasteroelectivities (entries 1−7, Table 3). In general, the electron-withdrawing substituents on the phenyl ring of the aryl aldehydes favour the reaction, whereas electron-donating ones decrease the yield of β-nitroalcohols. When the reaction was performed with 2-methylbenzaldehyde and 2,4,6-trimethylbenzaldehyde, the corresponding 2-nitroalcohols were obtained in 67% and 65% yields with similar diasteroelectivities, which shows that the position of substituents were hampered the reaction (compare the entries 3, 8 and 9 in Table 3). Furthermore, aliphatic aldehydes were smoothly converted to β-nitroalcohols in good yields and diasteroelectivity (up to *syn/anti* = 77:23) (entries 10−14, Table 3).

Table 3. Henry reaction of nitroethane with various aldehydes catalyzed by **2**.[a]

Entry	Substrate	Yield, %[b]	Selectivity, *syn/anti*[c]
1		69	73:27
2		73	73:27
3		74	74:26
4		78	74:26
5		79	74:26
6		80	75:25
7		85	75:25
8		67	73:27
9		65	72:28
10	CH_3CH_2CHO	89	77:23
11	$CH_3(CH_2)_2CHO$	88	77:23
12	$CH_3(CH_2)_3CHO$	88	77:23
13	$CH_3(CH_2)_4CHO$	87	76:24
14	$CH_3(CH_2)_5CHO$	85	76:24

[a] Reaction conditions: 5.0 mol% of catalyst **2**, MeOH (2 mL), nitroethane (4 mmol) and aldehyde (1 mmol), reaction time: 6 h. [b] Isolated yields after column chromatography. [c] Determined by ^{1}H NMR.

The activity of **2** is much higher than those reported for other metal catalysts: the scorpionate complex [NiCl{$SO_3C(pzPh)_3$}] (pz = pyrazolyl; 31.5% yield for benzadehyde) [39], lanthanide/sodium amide systems (48−85%) [15], pyrrolidine-based organocatalyst (67%) [40], copper(II) complexes (70–77%) with amidoterephthalate [41], 2-((*E*)-(((1*S*)-quinolin-4-yl(5-vinylquinuclidin-2-yl)methyl)imino) methyl)phenol (72) [42], (*S*)-2-((2-(hydroxydiphenylmethyl) pyrrolidin-1-yl)methyl)-6-(trifluoromethyl) phenol (81) [43], etc.

The reaction mechanism should be similar to the reported examples with related catalytic system [29]: ligand-assisted (with free C=O group, as a H-bond acceptor) deprotonation of the methylene group of nitroethane (to give a nitronate species), and then an activation of benzaldehyde by cooperation of metal center and free NH moieties of **2** towards an electrophilic attack occurs. Finally, the attack on the nitronate leads to the respective C−C coupling to give a β-nitroalkanol product.

4. Conclusions

Two previously reported di- and triorganotin(IV) complexes bearing arylhydrazones of active methylene compounds [31] have been prepared and applied as catalysts in the C−C coupling of aldehydes with nitroethane (Henry reaction). Due to the acidic proton(s) of the pyrimidine moiety, the catalytic activity of complex **2** (diorganotin) is higher than that of **1** (triorganotin) in methanol at room temperature, providing β-nitroalkanols in high yields (65−89%) in 6 h. To our knowledge current study is the first report on the application of Sn(IV)-arylhydrazone complexes in Henry reaction, and thus it opens such a possibility and shows that complexes of that type can operate effectively in the presence of protic solvent methanol. Further modifications of the arylhydrazone ligands deserve to be explored to reach a higher diasteroselectivity and yield.

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Highlights

► Arylhydrazone diorganotin(IV) complex acts as an effective catalyst in the nitroaldol reaction
► The β-nitroalcohols were obtained in good to high yield
► The activity depends on the amounts of catalyst and nature of solvents