Zinc Acetate as a Catalyst for the Hydroacylation Reaction of Azodicarboxylates with Aldehydes

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Abstract: $Zn(OAc)_2 \cdot 2H_2O$ is found to be an effective catalyst for the hydroacylation reaction of azodicarboxylates with aldehydes. A wide range of aldehydes, including aliphatic, aromatic and heterocyclic compounds, was considered. Most of the hydroacylation reactions afforded the hydroacylation products in good to excellent yields. The overall system is simple, economical and has practical advantages for construction of carbon-nitrogen bonds.

Keywords: Aldehydes, azo compounds, C-N bond formation, hydroacylation, zinc catalyst.

INTRODUCTION

Carbon-nitrogen bond-forming reactions have great importance in organic chemistry, since an overwhelming number of biologically active compounds, natural as well as nonnatural, are amino compounds or derivatives thereof [1]. Dialkyl azodicarboxylates, with a central azo functionality flanked by two carboalkoxy groups, are excellent electrophiles. They are commercially available. So, over the last few decades, a very efficient reaction, which involves the use of azodicarboxylates as electrophiles, has been successfully used for such carbon-nitrogen bond formation [2]. Hydroacylation reaction with direct functionalization of the aldehydic C-H to form a variety of hydrazine imides is a highly efficient synthetic methodology to form a carbon-nitrogen bond. The hydroacylation reaction with aldehydes has been studied under several conditions [3, 4]. However, the reaction results in relatively low yields and requires long times when aromatic aldehydes are used as the substrates. In addition, very costly precious metals are used. Therefore, there is the quest for newer and more efficient methods to develop simple and efficient reaction conditions, while increaseing the scope of the substrates without the use of expensive metal catalyst.

Zinc stands out as a convenient alternative to costly precious metals, because zinc salts are often cheap and environmentally benign. Zinc-based catalyts can be applied in many reactions. Mimoun *et al*. reported an excellent achievement of economical reduction method with zinc catalysts [5]. The zinc-catalyzed reduction of ketones was followed by Carpentier [6], de Parrodi [7], Mikami [8], and Riant [9]. Recently, zinc acetate proved to be an efficient catalyst for hydrosilylation of ketones and aldehydes in the combination with $(EtO)_2MeSiH$ [10]. Chakraborty *et al*. have demonstrated that $Zn(OAc)_2 \cdot 2H_2O$ is a potent catalyst towards the ring-opening polymerization of cyclic esters and lactide [11].

Zinc catalysts have proved to be active and versatile in many types of reactions. To the best of our knowledge, there has been no general study on the hydroacylation reaction between aldehydes and azodicarboxylates catalyzed by zinc catalysts. We wish to report here that zinc-catalyzed hydroacylation between azodicarboxylates and aldehydes provides the hydrazine under mild and ligand-free conditions.

RESULTS AND DISCUSSION

Initially, the hydroacylation reaction between diisopropyl azodicarboxylate with benzaldehyde was selected as a model reaction for optimizing the reaction conditions. Firstly, we studied the effect of various solvents for the hydroacylation reaction (Table **1**). The reaction proceeded smoothly in conventional organic solvents. The isolated yields were significantly influenced by the solvent employed. Among the solvents tested, MeCN was proven to be the best compared to the others (Table **1**, entry 1). EtOAc, Methanol, CH_2Cl_2, DMF and 1,4-Dioxane could also provide relatively good yields of the desired products (Table **1**, entries 2, 5, 6 and 7). Other solvents, EtOH and THF gave lower yields (Table **1**, entries 3 and 8).

The effect of catalyst loading on the hydroacylation reaction is shown in Table **1**. Poor yields were also obtained without the use of a catalyst (Table **1**, entries 9). The amount of the zinc acetate dihydrate catalyst employed in the reaction is important. When the catalyst loading was less than 15 mol%, the yield of the corresponding product was relatively lower (Table **1**, entries 10 and 11). A yield of 80% was obtained when 20 mol% Zn was applied (Table **1**, entry 1), and the yield did not apparently improve further when the Zn loading was more than 25 mol%. Only different reaction rates were observed for the reaction (Table **1**, entry 12). The effect of the ratio of benzaldehyde to diisopropyl azodicarboxylate was investigated. Lower ratio of benzaldehyde to diisopropyl azodicarboxylate led to a reduction of reaction yield (Table **1**, entry 13 and 14).

Under our optimized reaction conditions, the scope of this hydroacylation reaction was explored. A variety of aldehydes were examined for the hydroacylation reactions. As shown in Table **2**, most of the hydroacylation reactions afforded the hydroacylation products in good to excellent yields. Aromatic aldehydes were good substrates for this reaction and afforded the hydroacylation products in good

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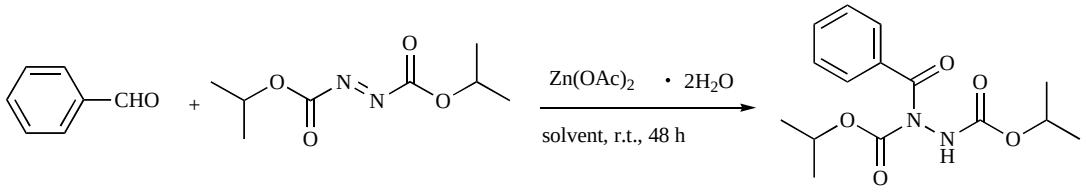
Table 1. Optimization Reaction of Benzaldehyde with Diisopropyl Azodicarboxylate[a]



Entry	Solvent	Zn (mol%)	Yield (%)[b]
1	MeCN	20	80
2	EtOAc	20	54
3	MeOH	20	51
4	EtOH	20	38
5	CH_2Cl_2	20	52
6	DMF	20	56
7	1,4-Dioxane	20	61
8	THF	20	42
9	MeCN	0	<5
10	MeCN	10	47
11	MeCN	15	50
12	MeCN	25	80
13	MeCN	20	30[c]
14	MeCN	20	54[d]
15	MeCN	20	80[e]

[a]Reaction conditions: diisopropyl azodicarboxylate (0.5 mmol), benzaldehyde (1 mmol), catalyst, solvent (3 mL), r.t., 48 h. [b]Isolated by silica gel column chromatography and based on diisopropyl azodicarboxylate. [c]the ratio of benzaldehyde to diisopropyl azodicarboxylate was 1.2:1. [d]the ratio of benzaldehyde to diisopropyl azodicarboxylate was 1.5:1. [e]the ratio of benzaldehyde to diisopropyl azodicarboxylate was 2.5:1.

yields. The hydroacylation reactions with benzaldehyde obtained the desired products **1** in high yields (Table **2**, entry 1). The electronic nature of the substituents, either electron-withdrawing or electron-donating groups on the aromatic aldehydes was affording hydroacylation products **2**-**5** in high yields (Table **2**, entries 2-5). To broaden the scope of the reaction, heterocyclic compounds aldehydes were used in the reaction and also gave the desired products in good yields (50-64 %, Table **2**, entries 6-8). The aldehydes with unsaturation also provided the desired products in good yields (Table **2**, entry 9). The aliphatic saturated aldehydes, with either linear or branched substituents when used in the reaction with diisopropyl azodicarboxylate, afforded the desired products in good to excellent yields (86-97%, Table **2**, etries 10-13).

CONCLUSION

In conclusion, $Zn(OAc)_2 \cdot 2H_2O$ is found to be an effective catalyst for the hydroacylation reaction of azodicarboxylates with aldehydes. The corresponding target products were obtained in good to excellent yields, and an array of functional groups was tolerated under the mild conditions with respect to aldehydes. The protocol used inexpensive zinc acetate dihydrate as the catalyst, no additional ligand and additive were required, so the overall system is simple, economicals and has practical advantages for construction of carbon-nitrogen bonds.

EXPERIMENTAL

All chemicals were obtained from commercial sources and used as received. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker NMR spectrophotometer (400 MHz) in $CDCl_3$ solution at room temperature. Mass spectra were obtained using Finnigan LCQ Advantage MAX spectrometer.

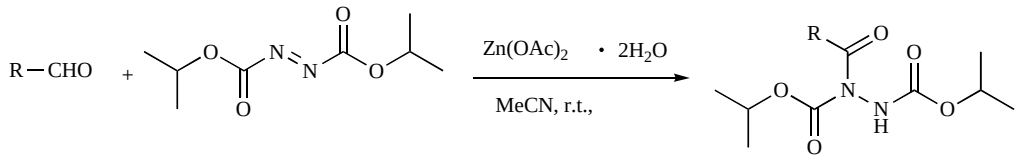
General Procedure for the Hydroacylation Reaction of Aldehydes and Azodicarboxylates Catalyzed by Zinc acetate dihydrate

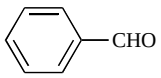
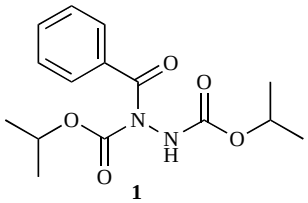
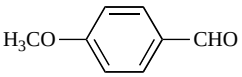
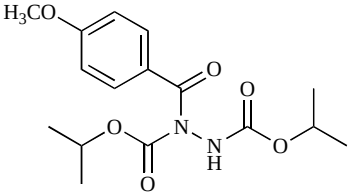
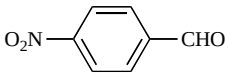
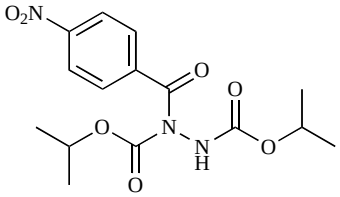
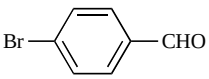
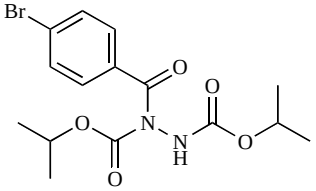
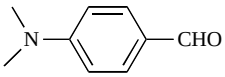
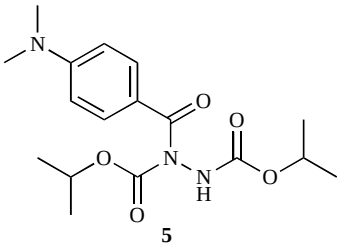
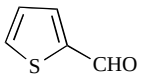
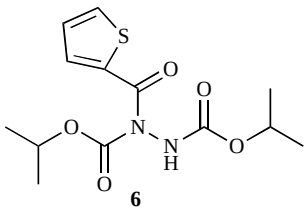
Aldehyde (1 mmol), azodicarboxylate (0.5 mmol) and Zinc acetate dihydrate (0.1 mmol) were mixed in acetonitrile (5 mL). The mixture was stirred at room temperature. When the reaction was complete, the solution was evaporated and the residue purified by column chromatography on silica gel using hexane:ethyl acetate (5:1) as the eluent to afford the product diisopropyl 1-acylhydrazine-1,2-dicarboxylate.

Hydroacylation Product **1**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.68-7.26 (m, 5H), 6.86 (s, 1H), 5.01-4.87 (m, 2H), 1.29 (d, J = 6 Hz, 6H), 0.99 (d, J = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.2, 155.3, 152.9, 135.2, 133.5, 131.8, 130.1, 128.4, 128.1, 72.4, 70.6, 22.9, 21.9, 21.6, 21.3; MS (ESI) calcd for $C_{15}H_{20}N_2O_5$ M^- 307.13, found: 307.17.

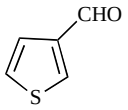
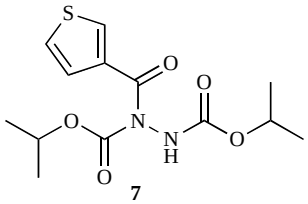
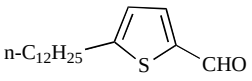
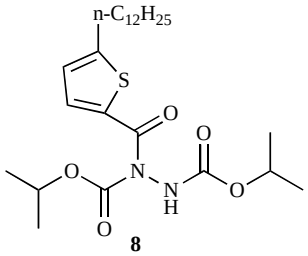
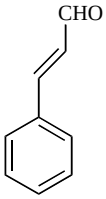
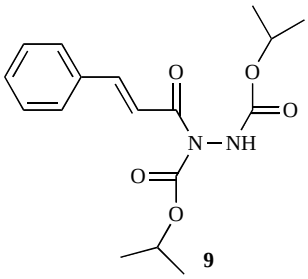
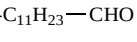
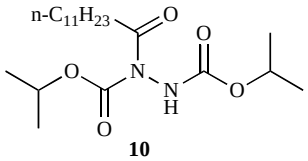
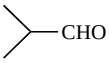
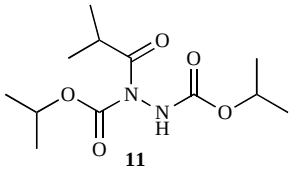
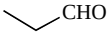
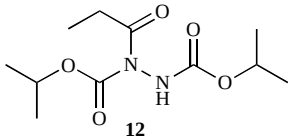
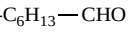
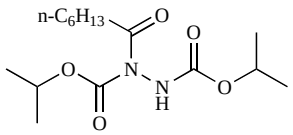
Hydroacylation Product **2**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.72 (s, 2H), 6.95-6.90 (m, 3H), 5.03-4.97 (m, 1H), 4.95-

Table 2. Hydroacylation Reaction of Aldehydes with Azobicarboxylates[a]



Entry	Aldehyde	Time (h)	Product	Yield (%)[b]
1		48	 **1**	80
2		32	 **2**	83
3		96	 **3**	62
4		52	 **4**	67
5		96	 **5**	54
6		70	 **6**	64

(Table 2). Contd…..

Entry	Aldehyde	Time (h)	Product	Yield (%)[b]
7		18	 **7**	63
8		46	 **8**	50
9		48	 **9**	70
10		18	 **10**	93
11		22	 **11**	97
12		12	 **12**	86
13		16	 **13**	88

[a] Reaction conditions: diisopropyl azodicarboxylate (0.5 mmol), aldehyde (1 mmol), Zinc acetate dihydrate (0.1 mmol), MeCN (5 mL), r.t. [b] Isolated by silica gel column chromatography and based on diisopropyl azodicarboxylate.

4.89 (m, 1H), 3.88 (s, 3H), 1.29 (d, J = 5.2 Hz, 6H), 1.13 (d, J = 4.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.6, 162.9, 155.4, 153.2, 132.2, 131.0, 126.9, 113.6, 113.4, 55.4, 21.9, 21.4; MS (ESI) calcd for $C_{16}H_{22}N_2O_6$ M^- 337.14, found: 337.04.

Hydroacylation Product **3**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.29 (d, J = 8.4 Hz, 2H), 7.82 (d, J = 6.8 Hz, 2H), 5.05- 4.91 (m, 2H), 1.27, (d, J = 6 Hz, 6H), 1.15, (d, J = 5.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.4, 155.2, 152.3, 149.2, 141.2, 130.5, 128.6, 124.3, 123.4, 73.2, 71.0, 21.9, 21.7,

21.4; MS (ESI) calcd for $C_{15}H_{19}N_3O_7$ M^- 352.12, found: 352.16.

Hydroacylation Product **4**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.58 (d, J = 11.2 Hz, 4H), 7.04 (s, 1H), 5.03-4.97 (m, 1H), 4.94-4.88, (m, 1H), 1.27 (d, J = 13.2 Hz, 6H), 1.12 (d, J = 5.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.4, 155.2, 152.7, 133.9, 131.8, 131.6, 131.4, 129.7, 126.7, 72.7, 70.8, 21.9, 21.4; MS (ESI) calcd for $C_{15}H_{19}BrN_2O_5$ M^- 385.04, found: 385.22.

Hydroacylation Product **5**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.76-7.70 (m, 2H), 6.90 (d, J = 7.2 Hz, 1H), 6.61 (t, J = 6.2 Hz, 1H), 6.38 (s, 1H), 5.05-4.92 (m, 2H), 3.09 (s, 6H), 1.26 (d, J = 6.4 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.4, 153.7, 153.4, 112.1, 111.4, 110.9, 110.3, 72.2, 71.7, 40.0, 21.9, 21.7, 21.5; MS (ESI) calcd for $C_{17}H_{25}N_3O_5$ M^- 350.17, found: 350.17.

Hydroacylation Product **6**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.90 (t, J = 1.2 Hz, 1H), 7.61 (d, J = 4.8 Hz, 1H), 7.27 (d, J = 2.4 Hz, 1H), 7.09 (d, J = 4.8 Hz, 1H), 6.95 (s, 1H), 5.08-5.01 (m, 2H), 1.30 (d, J = 5.2 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.7, 155.5, 152.7, 135.6, 134.7, 133.7, 127.2, 72.6, 70.8, 21.9, 21.6, 21.5; MS (ESI) calcd for $C_{13}H_{18}N_2O_5S$ M^- 313.09, found: 313.13.

Hydroacylation Product **7**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.97 (s, 1H), 7.37 (s, 1H), 7.29-7.27 (m, 1H), 5.01-5.95 (m, 2H), 1.26 (d, J = 6.4 Hz, 6H), 1.19 (d, J = 5.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.3, 155.3, 152.9, 136.0, 131.7, 127.6, 125.4, 72.4, 70.7, 21.9, 21.7, 21.4; MS (ESI) calcd for $C_{13}H_{18}N_2O_5S$ M^- 313.09, found: 312.99.

Hydroacylation Product **8**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.71 (t, J = 6.4 Hz, 1H), 7.55-7.52 (m, 1H), 6.82 (s, 1H), 5.08-4.98 (m, 2H), 2.84 (t, J = 7.6 Hz, 2H), 1.71-1.65 (m, 2H), 1.32-1.13 (m, 26H), 0.99-0.86 (m, 7H), ^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.5, 155.9, 135.2, 130.9, 128.8, 125.5, 72.3, 72.0, 31.9, 31.3, 30.5, 29.6, 29.5, 29.3, 29.2, 29.0, 27.7, 22.6, 21.9, 21.7, 19.1, 14.1; MS (ESI) calcd for $C_{25}H_{42}N_2O_5S$ M^- 481.27, found: 481.37.

Hydroacylation Product **9**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.10 (d, J = 7.2 Hz, 1H), 7.81-7.29 (m, 7H), 5.09-4.99 (m, 2H), 1.31 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.5, 152.9, 145.8, 131.8, 130.9, 129.2, 128.9, 128.8, 128.6, 118.8, 72.3, 71.8, 21.8, 21.7, 21.2; MS (ESI) calcd for $C_{17}H_{22}N_2O_5$ $(M+Na)^+$ 357.14, found: 357.10.

Hydroacylation Product **10**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.67 (s, 1H), 5.05-4.94 (m, 2H), 2.89 (s, 2H), 1.65 (d, J = 6.8 Hz, 2H), 1.32-1.25 (m, 21H), 0.88 (t, J = 6.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 174.0, 155.1, 152.6, 72.1, 70.4, 31.9, 29.6, 29.4, 29.3, 29.2, 29.1, 29.0, 24.7, 24.6, 22.6, 21.8, 21.7, 14.1; MS (ESI) calcd for $C_{20}H_{38}N_2O_5$ $(M+Na)^+$ 409.27, found: 409.18.

Hydroacylation Product **11**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.79 (s, 1H), 5.07-4.94 (m, 2H), 3.66-3.60 (m, 1H), 1.32 (d, J = 6 Hz, 6H), 1.20 (d, J = 6.8 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 178.3, 155.2, 152.5, 72.1, 70.3, 33.7, 21.8, 21.6, 19.3, 18.8; MS (ESI) calcd for $C_{12}H_{22}N_2O_5$ M^- 273.15, found: 273.25.

Hydroacylation Product **12**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.73, (s, 1H), 5.07-4.93 (m, 2H), 2.92 (d, J = 6 Hz, 2H), 1.33-1.28 (m, 12H), 1.18-1.13 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 174.7, 155.1, 152.6, 72.1, 70.3, 30.5, 21.8, 21.7, 8.9; MS (ESI) calcd for $C_{11}H_{20}N_2O_5$ M^- 259.13, found: 259.15.

Hydroacylation Product **13**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.61 (s, 1H), 5.05-4.95 (m, 2H), 2.89 (s, 2H), 1.67-1.64 (m, 4H), 1.32-1.30 (m, 20H), 0.87 (b, J = 6.4 Hz, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.5 155.1, 152.5, 71.1, 69.9, 36.8, 31.7, 31.3, 28.6, 24.5, 22.5, 22.3, 22.1, 21.6, 21.2, 13.8; MS (ESI) calcd for $C_{15}H_{28}N_2O_5$ M^- 315.19, found: 315.17.

CONFLICT OF INTEREST

Declared none.

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