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Synthesis of some ketones via nano-nickel oxide catalyzed acylation of arylzinc reagents; strategy involving the use of mixed (methyl)(aryl)zincs

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Abstract: Nano-NiO catalyzed acylation of mixed (methyl)(aryl)zincs with aromatic acyl halides in THF at room temperature provides a new facile route for aryl–aroyl coupling. Among $NiCl_2.L_2$ and $NiCl_2.L$ (L = monodentate and bidentate phosphine ligand) catalysts, the lower catalyst loading of $NiCl_2$ (dppf) may seem attractive; however, nano-NiO, being the lowest cost catalyst, is more favorable for aroylation of (methyl)(aryl)zincs. This procedure also provides a supplement to Cu and Pd catalyzed acylation of diorganozincs.

Key words: Mixed diorganozincs, acylation, nickel catalyst, group selectivity

1. Introduction

Aromatic ketones have attracted much attention because of their various synthetic and biological applications. Ketones are prepared by using either direct coupling of acyl chlorides with organometallic compounds[1–3] or using Friedel–Crafts acylation.[4] Chemoselective conversion of ketones to functional groups[1,2,4] has advanced rapidly in recent years leading to synthesis of pharmaceutical and material science products. They are also important for forming chemoselective stable linkages with functionalized fragments in vitro and in vivo.[5–7]

In recent years, a large number of useful methodologies have been developed for the acylation of mostly Grignard,[8–15] organocopper,[16–18] and -zinc[19–21] compounds. Organolithium,[22] -bor,[23–25] -aluminium,[26] -tin,[27–29] -bismuth,[30,31] and -manganese[32] compounds have been also reported to furnish ketones with acyl halides.

In the acylation process, generally transition metal catalysis and/or organic catalysis is used. Grignard reagents, RMgX, have some disadvantages such as formation of *tert*-alcohols as side products. However, diorganozinc, R_2Zn, and monoorganozinc, RZnX, reagents, due to their high tolerance to many functional groups and high efficiency toward many electrophiles, are now widely used in organometallic synthesis. In the acylation of organozinc reagents, initially the use of Cu and Pd catalysis was reported.[12,33] However, the high cost of Pd catalysts[34,35] led to advances in the use of Co,[36,37] Fe,[36] and Ni[38,39] as catalysts in the acylation of RZnX[34,35,37,39] and R_2Zn[36,38] reagents.

Diorganozincs, R_2Zn, which have higher reactivity toward many electrophiles compared to monoorganozinc halides, RZnX, are not atom-economic due to their transfer of only one of the R groups. For this purpose, mixed diorganozincs, R^1R^2Zn, in which R^1 and R^2 groups react with different transfer yields have been developed.[40–54] Recently, R_RR_TZn reagents,[55,56] which have a transferable R_T group together with a resid-

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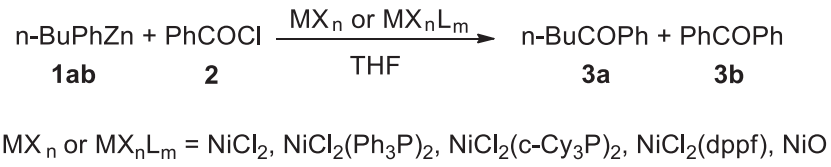
ual group, R_R group, have been successfully used in 1,2-addition,[55−58] 1,4-addition,[59−62] and C–C coupling reactions.[63−65]

Our research group has a long standing interest in research of synthetic use of mixed diorganozincs.[66−75] We have already investigated alkyl group transfer of (n-alkyl)(aryl)zincs reagents to aroyl chlorides and reported successful transition metal free coupling in THF in the presence of tri-n-butylphosphine.[66] We also found that group selectivity also depends on the donor solvent and in the CuI catalyzed acylation aryl group transfer takes place in THF:TMEDA (2:1). In this project, we planned to develop a new atom-economic protocol for aryl–aroyl coupling of (n-alkyl)(aryl)zincs using low cost and easily available nickel catalysis.

Herein, we report the use of nano-NiO catalysis in the convenient and efficient aryl selective aroylation of (n-alkyl)(aryl)zincs.

2. Results and discussion

Based on our previous experience with acylation of mixed diorganozincs,[66,68,70,71] first we decided to screen the suitability of nickel catalysts in the aryl–aroyl coupling of (n-alkyl)(aryl)zincs with benzoyl chloride. We chose reaction of (n-Bu)(Ph)Zn **1ab** with benzoyl chloride in THF as the model reaction (Scheme). As nickel catalysts, we analyzed extensively used $NiCl_2$ and $NiCl_2.L_2$ (L = ligand) to find the efficient catalytic conditions on the group selectivity of (n-Bu)(Ph)Zn **1ab** (Table 1). As ligands, we chose monodentate phosphine ligands, L = Ph_3P, (c-Hexyl)$_3$P and a bidentate phosphine ligand, L = dppf (1,2-bisdiphenylphosphino ferrocene), which we recently found as active ligands in the $NiCl_2.L_2$ catalyzed aryl–allyl coupling of (n-butyl)(aryl)zincs.[69] We also investigated the catalytic activity of nano-NiO in the acylation reaction. For this purpose, we chose nano-NiO (<50 nm) as the first example.

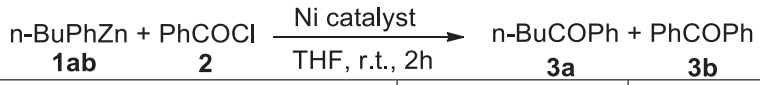


Scheme. Group selective coupling of (n-butyl)(phenyl)zinc **1ab** with benzoyl chloride **2a** in the presence of nickel catalysts.

In the optimized catalyst concentrations, $NiCl_2$ performed poorly (Table 1, entry 2). Addition of LiCl resulted in a better yield of 49% with a n-Bu transfer:Ph transfer ratio of 16:84 (Table 1, entry 3). $NiCl_2$ with Ph_3P and (c-Hexyl)$_3$P ligands gave coupling with 44% and 57% yields, respectively, and with low Ph selectivity (Table 1, entries 4 and 5). However, gratifyingly, using $NiCl_2$(dppf) as a catalyst in the catalyst loading of 1-0.5 mol % increased the yield to 68%–77% and seemed promising for Ph selectivity resulting in a n-Bu transfer:Ph transfer ratio of 12:88 (Table 1, entries 6 and 7). Coupling in the presence of nano-NiO was also quite successful (Table 1, entries 8–10). Optimized 10 mol % catalyst afforded 71% coupling and n-Bu transfer:Ph transfer ratio of 8:92 (Table 1, entry 9). Addition of LiCl had no effect (Table 1, entry 10). In this work, we did not investigate the effect of particle size of nano-NiO on coupling yield.

It seems that $NiCl_2$(dppf) and nano-NiO are the best nickel catalysts for Ph selective coupling of (n-Bu)(Ph)Zn **1ab** with benzoyl chloride **2**. Before deciding between $NiCl_2$(dppf) or nano NiO as the most active catalyst in the benzoyl coupling of (n-butyl)(phenyl)zinc **1ab**, we compared the atom economic utility of **1ab**

Table 1. Screening nickel catalysts in the coupling reaction of (n-butyl)(phenyl)zinc **1ab** with benzoyl chloride **2**. Optimization of the reaction parameters. [a]



Entry	Nickel catalyst/additive	Total yield, % [b,c]	Group selectivity [d] **3a**:**3b**
1	-	20	50:50
2	$NiCl_2$ (20 mol %)	22	27:73
3	$NiCl_2$ (20 mol %) / LiCl (1 equiv.)	49	16:84
4	$NiCl_2(Ph_3P)_2$ (5 mol %)	44	36:64
5	$NiCl_2[(c\text{-}Hexyl)_3P]_2$ (5 mol %)	57	39:61
6	$NiCl_2$(dppf) (1 mol %)	68	12:88
7	$NiCl_2$(dppf) (0.5 mol %)	77	12:88
8	Nano NiO (20 mol %)[e]	66	7:93
9	Nano NiO (10 mol %)[e]	71	8:92
10	Nano NiO (10 mol %)[e] / LiCl (1 equiv.)	72	14:86

[a] The reactions were carried out using 1 mmol of benzoyl chloride **2** and 2 mmol of (n-butyl)(phenyl)zinc **1ab**. Mol % amount of catalysts were indicated.

[b] The sum of GC yields of n-Bu coupling product **3a** and Ph coupling product **3b**.

[c] All the data are the average of at least two experiments.

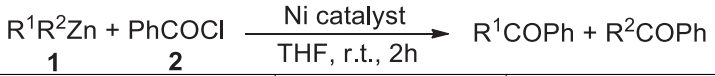
[d] The ratio of GC yields of **3a** and **3b**.

[e] Aldrich (<50 nm).

in the presence of these catalysts (Table 2). For this purpose, we found the background yields of **1ab**, i.e. acylation yields of homo diorganozinc reagents, n-Bu_2Zn, $\mathbf{1a}_2$ and Ph_2Zn, $\mathbf{1b}_2$. We also evaluated a methyl group as residual group instead of a n-butyl group in the (n-alkyl)(phenyl)zinc **1** in order to find a higher yield and phenyl selectivity of acylation. The background yields for uncatalyzed benzoylation of mixed diorganozincs **1ab** were 90% for n-Bu_2Zn $\mathbf{1a}_2$ (Table 2, entry 1) and 66% for Ph_2Zn $\mathbf{1b}_2$ (Table 2, entry 2). We also found the acylation yields of Ph_2Zn $\mathbf{1b}_2$ in the presence of $NiCl_2$(dppf) and nano NiO (Table 2, entries 3 and 4). As seen, the acylation of Ph group in (n-Bu)(Ph)Zn **1ab** takes place with about the same yield as in the acylation of Ph_2Zn $\mathbf{1b}_2$ with catalysis of $NiCl_2$(dppf) (Table 2, entries 5 and 3) and also with catalysis of nano-NiO (Table 2, entries 6 and 4). These results confirmed the atom-economic character of (n-Bu)(Ph)Zn **1ab** in the nickel catalyzed acylation with **2**.

In addition, the data revealed that for aryl–aroyl coupling of either (n-Bu)(Ph)Zn **1ab** or (Me)(Ph)Zn **1bc** could be used in $NiCl_2$(dppf) or NiO catalyzed reactions. With catalysis of 0.5 mol % $NiCl_2$(dppf), acylation of (n-Bu)(Ph)Zn **1ab** results in 77% yield and 88% transfer of Ph group, whereas acylation of (Me)(Ph)Zn **1bc** gives 86% yield with complete Ph transfer (Table 2, entries 5 and 7). Nano-NiO catalyzed acylation of (n-Bu)(Ph)Zn **1ab** leads to 71% yield and 92% Ph transfer, while acylation of (Me)(Ph)Zn **1bc** leads to 84% yield and with complete Ph transfer (Table 2, entries 6 and 8). Among these catalysts, the lower catalyst loading of $NiCl_2$(dppf) may seem attractive; however, nano-NiO, being the lowest cost catalyst, seemed more favorable for aroylation of (methyl)(aryl)zincs. In addition, our detailed literature survey did not show use of nano-NiO in the reactions of organozinc reagents so far.

Table 2. Coupling of n-Bu$_2$Zn **1a**$_2$, Ph$_2$Zn **1b**$_2$, and (Me)(Ph)Zn **1bc** with benzoyl chloride **2** in THF in the presence of NiCl$_2$(dppf) and nano-NiO catalysts.[a]



Entry	R^1, R^2, catalyst	Total yield, %[b,c]	Group selectivity[d] R^{1}COPh:R^{2}COPh
1	n-Bu, n-Bu	90	-
2	Ph, Ph	66	-
3	Ph, Ph, NiCl$_2$(dppf) (0.5 mol %)	82	-
4	Ph, Ph, nano-NiO (10 mol %)[f]	67	-
5	n-Bu, Ph, NiCl$_2$(dppf) (0.5 mol %)[e]	77	12:88
6	n-Bu, Ph, nano-NiO (10 mol %)[e,f]	71	8:92
7	Me, Ph, NiCl$_2$(dppf) (0.5 mol %)	86	0:100
8	Me, Ph, nano-NiO (10 mol %)[f]	84	0:100

[a] The reactions were carried out using 1 mmol of benzoyl chloride **2** and 2 mmol of **1a**$_2$, **1b**$_2$, or **1bc**. Mol % amount of catalyst was indicated.

[b] The sum of GC yields of R^{1}COPh and R^{2}COPh.

[c] All the data are the average of at least two experiments.

[d] The ratio of GC yields of R^{1}COPh and R^{2}COPh.

[e] Taken from Table 1.

[f] Aldrich (<50 nm).

We next applied the optimal conditions for nano-NiO (<50 nm) catalyzed phenyl–benzoyl coupling using (Me)(Ph)Zn **1bc** to further evaluate the scope of this reaction for synthetic transfer of aryl groups of (methyl)(aryl)zincs to aroyl chlorides. The results are summarized in Table 3. The data are averages of at least two independent experiments. The products were characterized using ^{1}H NMR analysis. We were pleased to find that acylation of a variety of (methyl)(substituted phenyl)zincs (Table 3, entries 1–5) succeeded with high yields. Good yields were also obtained in the reaction for the transfer of the phenyl group (Table 3, entry 6) and 4-tolyl group (Table 3, entry 7) to 4-toluoyl chloride. However, despite all efforts, a low yield was obtained in the acylation of (methyl)(3-cyanophenyl)zinc with benzoyl chloride (Table 3, entry 8). The expected ketones were not observed in the acylation of (methyl)(4-bromophenyl)zinc (Table 3, entry 9) and (methyl)(4-methoxycarbonylphenyl)zinc (Table 3, entry 10) and polymerization was obtained possibly due to reactive substituents.

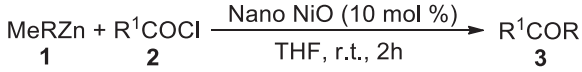
3. Conclusions

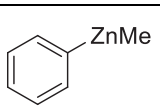
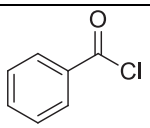
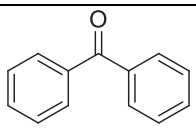
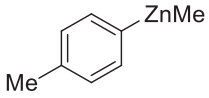
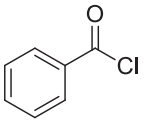
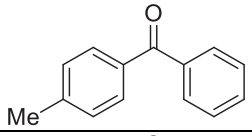
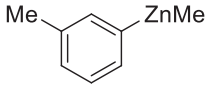
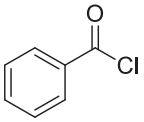
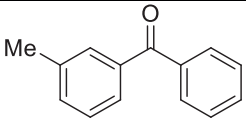
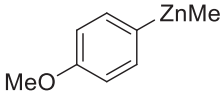
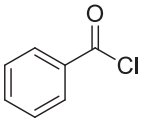
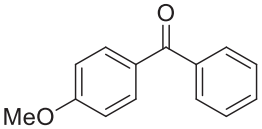
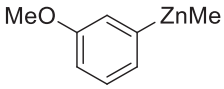
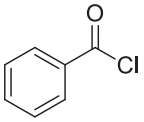
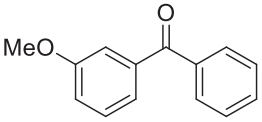
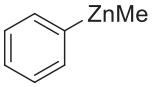
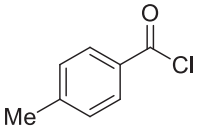
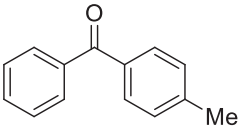
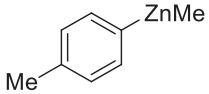
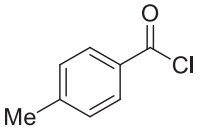
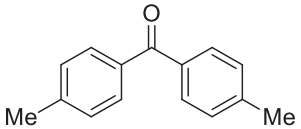
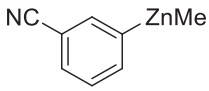
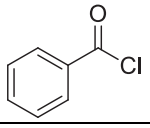
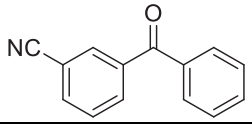
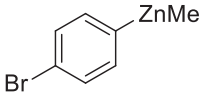
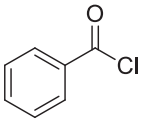
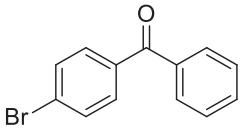
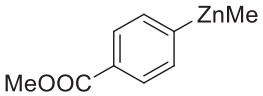
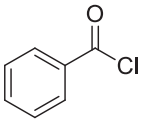
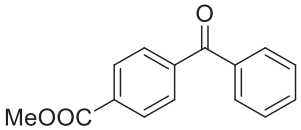
In conclusion, we have demonstrated that

(i) Room temperature acylation of mixed (methyl)(aryl)zincs with aroyl halides in the presence of inexpensive nano-NiO catalysis provides an atom-economic and facile new route for aryl–aroyl coupling of diorganozincs. This procedure is a supplement to Cu and Ni catalyzed acylation of Grignard reagents[10–15] and organozinc reagents.[19–21,33–39]

(ii) Nano-NiO seems to be a good catalyst for acylation of organozinc reagents. However, further studies are underway to investigate the effect of particle size on the catalysts' efficiency and on the mechanism of the nano-NiO catalyzed acylation.

Table 3. Nano-NiO catalyzed aryl–aroyl coupling of (methyl)(aryl)zincs **1** with aroyl chlorides **2**.[a]



Entry	MeRZn[b]	R^1COCl	Product	Yield, %[c]
1				91
2				79
3				81
4				64
5				76
6				75
7				84
8				14
9				-
10				-

[a] The reactions were run with 2:1 molar ratio of **1**:**2**. General reactions conditions: (Me)(Ar)Zn reagent (10 mmol) in THF, aroyl chloride (5 mmol), nano-NiO (Aldrich, <50 nm, 0.5 mmol) were reacted at room temperature for 2 h (see Experimental section).

[b] (Me)(Ar)Zn reagent was prepared in situ by reacting arylzinc chloride with MeMgCl in THF (see Experimental section).

[c] Isolated yields.

4. Experimental section

All reactions were carried out under nitrogen in well-dried glassware.[76] All chemicals used were of reagent grade or purified according to the literature procedures. GC analyses were carried out using a Thermo Finnigan gas chromatograph equipped with a ZB-5 capillary column packed with phenylpolysiloxane using the internal standard technique. For the preparation of (methyl)(aryl)zinc reagents (aryl: C_6H_5, 4-MeC_6H_4, 3-MeC_6H_4, 4-$MeOC_6H_4$, 3-$MeOC_6H_4$, 4-BrC_6H_4), arylzinc chlorides were reacted with methylmagnesium chloride. Arylzinc chloride was prepared by addition of arylmagnesium bromide (10 mmol) to $ZnCl_2$ (10 mmol) in THF (10 ml) at –20 °C and stirring at that temperature for 15 min. To freshly prepared arylzinc chloride (10 mmol), methylmagnesium chloride (10 mmol) was added and the mixture was stirred at –20 °C for another 15 min. For the preparation of (methyl)(aryl)zinc reagents (aryl: 4-$MeOOCC_6H_4$, 3-NCC_6H_4), arylmagnesium bromides were reacted with methylzinc chloride. Arylmagnesium bromide (10 mmol) was prepared by addition of isopropylmagnesium bromide (10.5 mmol) to a solution of aryl iodide (10 mmol) in THF (10 mL) at –30 °C and stirring at that temperature for 1 h to complete the I/Mg exchange. Arylmagnesium bromide (10 mmol) solution was added to methylzinc chloride (10 mmol), which was freshly prepared by addition of methylmagnesium chloride (10 mmol) to $ZnCl_2$ (10 mmol) in THF (10 mL) at –20 °C and the mixture was stirred at that temperature for 15 min. The product ketones were identified by their melting points[77] and ^{1}H NMR spectra.[78–80]

4.1. Typical procedure for nano-NiO catalyzed coupling of (methyl)(aryl)zinc reagents with aroyl chlorides: synthesis of 4-methylbenzophenone

To the freshly prepared mixed (methyl)(phenyl)zinc reagent (10 mmol), nano-NiO (Aldrich, $<$50 nm, 10 mol %, 0.5 mmol, 0.0376 g) was added at –20 °C followed by stirring at that temperature for 15 min. 4-Toluoyl chloride (5 mmol) was then added at –20 °C and the reaction mixture was stirred at room temperature for 2 h. The reaction mixture was hydrolyzed by addition of NH_3/NH_4Cl solution and subsequently extracted with Et_2O. The combined ethereal solutions were washed with dilute HCl solution, dried, and concentrated by rotary evaporation and subjected to silica gel column chromatography with hexane:EtOAc (10:1–5:1) as eluent to give 4-methylbenzophenone. The products were characterized using ^{1}H NMR analysis:

4-Methylbenzophenone: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.8–7.77 (d, 2H, J= 7.2 Hz), 7.74–7.71 (d, 2H, J= 8.0 Hz), 7.60–7.55 (t, 1H, J= 7.2 Hz), 7.50–7.45 (t, 2H, J= 7.6 Hz), 7.30–7.26 (d, 2H, J= 8.0 Hz), 2.44 (s, 3H).

Benzophenone: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82–7.79 (d, 4H, J= 7.6 Hz), 7.61–7.56 (t, 2H, J= 7.4 Hz), 7.51–7.46 (t, 2H, J= 8.0 Hz).

3-Methylbenzophenone: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 (dd, 2H, J= 8 Hz, J = 1.2 Hz), 7.63 (s, 1H), 7.60–7.56 (m, 2H), 7.49–7.45 (t, 2H, J= 7.4 Hz), 7.40–7.33 (m, 2H), 2.41 (s, 3H).

4-Methoxybenzophenone: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (d, 2H, J= 9.2 Hz), 7.75 (d, 2H, J= 6.8 Hz), 7.56 (t, 1H, J= 7.4 Hz), 7.47 (t, 2H, J= 7.4 Hz), 6.96 (d, 2H, J= 9.2 Hz), 3.88 (s, 3H).

3-Methoxybenzophenone: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82–7.79 (m, 2H), 7.59–7.55 (m, 1H), 7.48–7.44 (m, 2H), 7.38–7.32 (m, 3H), 7.13–7.10 (m, 2H), 3.83 (s, 3H).

4,4'-Dimethylbenzophenone: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71–7.69 (d, 4H, J= 8 Hz), 7.28–7.26 (d, 4H, J= 7.6 Hz), 2.44 (s, 6H).

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