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IRON-CATALYZED ARYL SELECTIVE ACYLATION OF MIXED DIORGANOZINCS

ÖZGEN ÖMÜR PEKEL AND N. DİDEM KAHYA

Abstract. Iron-catalyzed acylation of mixed alkylarylzincs with aromatic acyl halides in THF provides a new route for aryl-aroyl coupling. This procedure is an atom-economic supplement to transition metal-catalyzed acylation of diorganozincs.

1. Introduction

Aromatic ketones are important building blocks in several natural and active pharmaceutical products. For the synthesis of ketones, the coupling of acyl chlorides with organometallic reagents provides a direct and convenient methodology [1,2] and overcomes some drawbacks of Friedel-Crafts acylation [3]. So far, useful synthetic protocols have been developed for the acylation of mostly Grignard [4-14], organocopper [15,16] and –zinc [17,18] compounds. Acylation of Grignard reagents, RMgX has some restrictions such as the formation of side products including tert-alcohols. In the case of using diorganocuprate reagents, R_2CuM (M=Li, MgX), the problem of the functional group arises. However, diorganozinc, R_2Zn, and monoorganozinc, RZnX reagents are good reaction partners for acylation, not only due to their high tolerance to functional groups but also not the formation of tert-alcohols. The initial reports about the acylation of RZnX and R_2Zn focused on Cu [19] or Pd [20-22] catalysis. In the recent years, steady advances have been made in the acylation of organozinc reagents and due to the high cost-Pd catalysts, inexpensive Co [23-25], Fe [23,26], and Ni [27-30] catalysts also received attention.

Diorganozincs, R_2Zn, are more reactive than organozinc halides, RZnX. However, in the reaction of diorganozincs, only one organic group is transferred to an electrophile, essentially wasting the other R groups. This circumstance is unattractive when the starting organyl halide or organolithium or Grignard reagent

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to be transmettallated is expensive or difficult to prepare and when a large excess of diorganozinc is required to obtain high yield and/or selectivity in their reactions. Mixed diorganozincs, R^1R^2Zn, in which one of the R groups has a lower transfer rate than the other have been developed. Recently, mixed diorganozincs R_RR_TZn which have one transferable R_T together with the residual group R_R have been successfully used in organic synthesis [31-51].

Our group carried out a series of synthetic and mechanistic work [52-57] on the selectivity of organyl groups of mixed diorganozincs, R^1R^2Zn in their C-acyl coupling reactions. We observed that group transferability in the acylation of alkylarylzinc could be controlled using cosolvent, transition metal catalyst, and organic catalyst. We have already reported a transition metal-free protocol for alkyl-aroyl coupling using mixed (alkyl)(aryl)zinc reagents in THF in the presence of *n*-Bu_3P [53]. We found that group selectivity depends on the donor solvent [52] and aryl group transfer takes place in THF:TMEDA (2:1) [54]. Recently, we also reported a new route in the presence of nano-NiO catalysis for aryl-aroyl coupling of (alkyl)(aryl)zincs [57].

However, the percentages of these metals in the earth's crust are extremely small, and their prices are rather expensive. Also, phosphines are unstable in air. So, it is required to handle them in a glove box. As an improvement of these disadvantages, we have focused on using iron compounds as a catalyst, because iron is abundant and less expensive.

Herein we report that inexpensive and non-toxic Fe-catalyzed acylation of (*n*-alkyl)(phenyl)zincs with aromatic benzoyl chlorides provides an alternative atom economic route for the synthesis of diarylketones by acylation of diarylzincs in the presence of transition metal catalysis.

2. EXPERIMENTAL

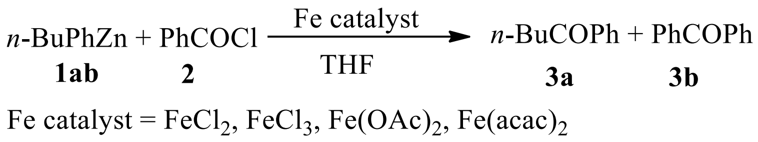
All reactions were carried out in oven-dried glassware under a positive pressure of nitrogen using standard syringe-septum cap techniques [58]. GC analyses were performed on a Thermo Finnigan gas chromatograph equipped with a ZB-5 capillary column packed with phenylpolysiloxane using the internal standard technique.

For the preparation of n-butylphenylzinc reagents, phenylzinc chlorides were reacted with n-butylmagnesium chloride. Phenylzinc chloride was prepared by the addition of phenylmagnesium bromide (2 mmol) to $ZnCl^2$ (2 mmol) in THF (2 ml) at -20 °C and stirring at that temperature for 15 min. To freshly prepared arylzinc chloride (2 mmol), n-butylmagnesium chloride (2 mmol) was added and the mixture was stirred at -20°C for another 15 min.

To the freshly prepared mixed (n-butyl)(phenyl)zinc reagent (2 mmol), Fe catalyst (20 mol % 1 mmol) was added at -20 °C and the mixture was stirred at that temperature for 15 min. If used, cosolvent (or additive) was added. Benzoyl chloride (1 mmol, 0.12ml) was added dropwise at -20 °C. The reaction mixture was stirred at room temperature for 2 h. After the addition of the internal standard, the mixture was hydrolyzed with the NH_3/NH_4Cl solution. The organic phase was analyzed by GC.

3. RESULTS AND DISCUSSION

For the investigation of group selectivity in the iron-catalyzed acylation of (*n*-alkyl)(aryl)zinc reagents (Scheme 1), we chose reaction of (*n*-butyl)(phenyl)zinc with benzoyl chloride in THF as a model reaction based on our previous studies [52-57]. *n*-BuPhZn **1ab** was prepared using Grignard reagents and *n*-butylmagnesium bromide was added to phenylzinc chloride prepared by transmetallation of phenylmagnesium bromide with $ZnCl_2$/THF at -15 °C. We determined the relative transferability of the organyl groups by calculating the GC yields of ketones using authentic samples.



$$\underset{\mathbf{1ab}}{n\text{-BuPhZn}} + \underset{\mathbf{2}}{\text{PhCOCl}} \xrightarrow[\text{THF}]{\text{Fe catalyst}} \underset{\mathbf{3a}}{n\text{-BuCOPh}} + \underset{\mathbf{3b}}{\text{PhCOPh}}$$

Fe catalyst = $FeCl_2$, $FeCl_3$, $Fe(OAc)_2$, $Fe(acac)_2$

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

Firstly, we investigated the effect of reaction conditions on the group selectivity of (*n*-Bu)(Ph)Zn **1ab** in iron-catalyzed acylation with benzoyl chloride **2**. As iron catalysts, $FeCl_2$, $FeCl_3$, $Fe(OAc)_2$ and $Fe(acac)_2$ were used (Table 1). The yield of the uncatalyzed reaction did not exceed 20% with a **3a**:**3b** ratio of 50:50.

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

$$\underset{\mathbf{1ab}}{n\text{-BuPhZn}} + \underset{\mathbf{2}}{\text{PhCOCl}} \xrightarrow[\text{THF, r.t., 2h}]{\text{Fe catalyst}} \underset{\mathbf{3a}}{n\text{-BuCOPh}} + \underset{\mathbf{3b}}{\text{PhCOPh}}$$

Entry	**Fe catalyst / Additive**	**Solvent**	**Total yield, % [b,c]**	**oup selectivity[d] 3a:3b**
1	-	THF	20	50:50
2	$FeCl_2$ (20 mol %)	THF	56	41:59
3	$FeCl_2$ (20 mol %) / LiCl(1 equiv.)	THF	64	56:44
4	$FeCl_3$ (20 mol %)	THF	85	15:85
5	$FeCl_3$ (20 mol %)	THF:NMP(3:1)[e]	62	65:35
6	$FeCl_3$ (20 mol %)	THF:Diglyme(3:1)[e]	15	40:60
7	$FeCl_3$ (20 mol %)	THF:TMEDA(2:1[e]	18	28:72
8	$FeCl_3$ (20 mol %) / $MgCl_2$(20 %)	THF	70	21:79
9	$FeCl_3$(20 mol %/LiCl(20 %)	THF	87	17:83
10	$Fe(OAc)_2$ (20 mol %)	THF	87	15:85
11	$Fe(OAc)_2$ (20 mol %) / LiCl(1equiv.)	THF	74	14:82
12	$Fe(acac)_2$(20 mol %)	THF	57	15:85
13	$Fe(acac)_2$(20 mol %)/LiCl(1equiv.)	THF	52	27:78

[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 **3** 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] NMP=N-methylpyrrolidine, Diglyme=Diethylene glycol dimethyl ether, TMEDA= Tetramethylenediamine.

As can be seen from Table 1, all iron catalysts are not successful in group selective coupling of **1ab** with **2** in THF. The catalysis reaction of 20 mol% $FeCl_2$ at room temperature resulted in a medium yield (56%) with a poor group selectivity (Table 1, entry 2) (*n*-Bu transfer:Ph transfer ratio=41:59). Using LiCl as an additive led to a somewhat higher yield (Table 1, entry 3); however, the reaction did not occur in the presence of $n\text{-}Bu_3P\text{-}FeCl_2$. Catalysis of 20 mol% $FeCl_3$ in a two-hour reaction at room temperature increased the coupling yield (85%) and Ph selectivity (*n*-Bu transfer:Ph transfer ratio=15:85) (Table 1, entry 4). Increasing the reaction time changing the catalyst amount to 10-25% decreased the yield to 78-80% but did not change the Ph selectivity. Varying the temperature (0 ºC or 60 ºC) led to a significant decrease in the yield. The effect of cosolvent was also investigated, however the use of NMP (N-methylpyrrolidine) and especially diglyme (diethylene glycol dimethyl ether) or TMEDA (tetramethylenediamine) gave quite low yields (Table 1, entries 5-7). Interestingly, the *n*-butyl group:phenyl group transfer ratio decreased in THF:TMEDA compared to that found in THF:NMP. The addition of $MgCl_2$ resulted in lower yield (70%) and lower Ph selectivity although the reaction medium is not Mg-free (Table 1, entry 8). However, the addition of LiCl did not make a change in the yield and Ph selectivity (Table 1, entry 9). Under optimized conditions, Fe $(OAc)_2$-catalysis (20 mol % catalyst, room temperature, and two-hour reaction) gave a quite high yield (87%) and Ph selectivity (*n*-Bu transfer: Ph transfer rate=15:85) (Table 1, entry 10) and these results are the same as those obtained in the presence of $FeCl_3$ catalysis (Table 1, entry 4).

Using LiCl as an additive lowered the yield to 74%, however, it did not change the Ph selectivity (Table 1, entry 11). Coupling in the presence of $Fe(acac)_2$ did not provide higher yield and Ph selectivity in the absence and presence of LiCl additive (Table 1, entries 12 and 13).

Our experimental results show that the best iron catalysts for Ph selective coupling of (*n*-Bu)(Ph)Zn **1ab** with benzoyl chloride **2** seemed to be $FeCl_3$ and $Fe(OAc)_2$. Before deciding between $FeCl_3$ and $Fe(OAc)_2$, as the most active catalyst(s) in the benzoyl coupling of (*n*-butyl)(phenyl)zinc **1ab**, we compared the atom economic utility of **1ab** 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 the methyl group as a residual group instead of the *n*-butyl group in the (*n*-alkyl)(phenyl)zinc **1ab** to find a higher yield and the phenyl selectivity of acylation. The backgrounds yields for uncatalyzed benzoylation of mixed diorganozincs **1ab** were found to be 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 observed that the acylation yield of the Ph group in (*n*-Bu)(Ph)Zn **1ab** is about the same with the acylation yield of Ph_2Zn $\mathbf{1b_2}$ in the presence of $FeCl_3$ catalysis (Table 2, entries 4 and 5). In the presence of $Fe(OAc)_2$ catalysis, the acylation yield of Ph group in (*n*-Bu)(Ph)Zn **1ab** was found pretty higher than that in Ph_2Zn. These results confirmed the atom-economic character of (*n*-Bu)(Ph)Zn **1ab** in the iron-catalyzed acylation with **2**. The use of (Me)(Ph)Zn **1bc** as the mixed organozinc in the acylation resulted in much lower yield than that of (*n*-Bu)(Ph)Zn **1ab** in the presence of $FeCl_3$ catalysis (Table 3, entries 4 and 6) and $Fe(OAc)_2$ catalysis (Table 2, entries 7 and 9).

TABLE 2. Coupling of *n*-Bu_2Zn **1a₂**, Ph_2Zn **1b₂** and (Me)(Ph)Zn **1bc** with benzoyl chloride **2** in THF in the presence of $FeCl_3$ and $Fe(OAc)_2$catalysts.[a]

$$\underset{\mathbf{1}}{R^1R^2Zn} + \underset{\mathbf{2}}{PhCOCl} \xrightarrow[\text{THF, r.t., 2h}]{\text{Fe catalyst}} R^1COPh + R^2COPh$$

Entry	R^1, R^2, catalyst	Total yield, % [b,c]	Group selectivity [d] $R^1COPh:R^2COPh$
1	n-Bu, n-Bu	90	-
2	Ph, Ph	66	-
3	n-Bu, Ph	20	50:50
4	n-Bu, Ph, $FeCl_3$ (20 mol %)[e]	85	15:85
5	Ph, Ph, $FeCl_3$ (20 mol %)	82	-
6	Me, Ph, $FeCl_3$ (20 mol %)	64	0:100
7	n-Bu, Ph, $Fe(OAc)_2$ (20 mol %)[e]	87	15:85
8	Ph, Ph, $Fe(OAc)_2$ (20 mol %)	48	-
9	Me, Ph, $Fe(OAc)_2$ (20 mol %)	62	0:100

[a] The reactions were carried out using 1 mmol of benzoyl chloride **2** and 2 mmol of **1a₂**, **1b₂** or **1bc**. A mol % amount of catalyst was indicated.
[b] The sum of GC yields of R^1COPh and R^2COPh.
[c] All the data are the average of at least two experiments.
[d] The ratio of GC yields of R^1COPh and R^2COPh.
[e] Taken from Table 1.

4. Concluson

In conclusion, we have shown that selective acylation of aryl groups in $FeCl_3$ or $Fe(OAc)_2$ catalyzed reactions of mixed n-alkyl phenylzincs reagents with aromatic acyl halides in THF is an efficient method for the synthesis of diarylketones.

We have demonstrated that

(i) This route provides a new simple and atom economic alternative to transition metal-catalyzed acylation of diarylzinc reagents.

(ii) Fe catalysts are inexpensive and non-toxic, so this procedure is a supplement to Ni catalyzed acylation of mixed n-alkyl phenylzincs.

(iii) These findings provide another support for Erdik's hypothesis of the dependence of group selectivity of mixed diorganozincs on the reaction parameters [52-57].

ÖZET

Karışık alkilarilçinkoların THF'deki aromatik açil halojenürlerle demir katalizli açillenmesi, aril-aroil eşleşmesi için yeni bir yöntemdir. Bu yöntem, diorganoçinkoların geçiş metali katalizli açillenmesine atom-ekonomik bir alternatiftir.

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Current Address: ÖZGEN ÖMÜR PEKEL: Department of Chemistry, Ankara University, 06100 Ankara, TURKEY
E-mail Address: oomur@science.ankara.edu.tr
ORCID: https://orcid.org/0000-0003-3833-4447

Current Address: N. DİDEM KAHYA (Corresponding author): Department of Chemistry, Ankara University, 06100 Ankara, TURKEY
E-mail Address: kahya@ankara.edu.tr
ORCID: https://orcid.org/0000-0001-9255-0867