Palladium-catalyzed reactions of arylboron compounds with carboxylic acid chlorides

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Reactions of sodium tetraarylborates and arylboronic acids with acyl chlorides in the presence of palladium salts afford non-symmetrical ketones in high yields under mild conditions.

Key words: cross-coupling, organoboron compounds, palladium, synthesis of ketones, acyl chlorides.

Cross-coupling of organoboron compounds with organic electrophiles catalyzed by palladium and nickel complexes (the Suzuki reaction) is currently one of the most attractive methods for the formation of new carbon—carbon bonds, which is widely used in organic synthesis.[1] In water or water-organic solvent mixtures, the Suzuki reaction is very effectively catalyzed by palladium salts PdX_2 containing no phosphine ligands.[2] "Ligand-free" palladium was successfully used as a catalyst for reactions of sterically hindered tris(1-naphthyl)borane with aryl halides and diaryliodonium salts.[3] It was interesting to apply this approach to the synthesis of non-symmetrical ketones by reactions of organoboron compounds with acyl chlorides as electrophilic reagents. This approach has been employed[4] for acyldeboration of sodium tetraphenylborate with various RCOCl in THF in the presence of $Pd(PPh_3)_4$ at 25 °C. However, under these conditions, only one phenyl group of Ph_4BNa is involved in the reaction. Later, it was shown that arylboronic acids[5] and triorganoboranes[6] can also be used in cross-coupling with acyl chlorides under similar conditions. Earlier, we found that in the presence of ligand-free palladium, sodium tetraarylborates and arylboronic acids react with acyl chlorides under very mild conditions to give non-symmetrical ketones in high yields.[7] According to the published data,[8] the Suzuki reaction catalyzed by phosphine complexes of palladium requires more drastic conditions and proceeds more slowly. In the present work, the synthetic aspects of this reaction and some of its specific features are described in detail.

Results and Discussion

1. Acyldeboration of sodium tetraarylborates

In a search for the optimum reaction conditions in anhydrous organic solvents, we synthesized benzophenone from Ph_4BNa and PhCOCl using various catalysts, bases, and solvents (Scheme 1, Table 1). In the presence of 1 mol. % $Pd(OAc)_2$ and Na_2CO_3 (1.5 equiv.), the reaction smoothly proceeded at room temperature in acetone, 1,4-dioxane, DMF, and THF to give benzophenone in 79—96% yield over 4 to 6 h (see Table 1, entries 1—4). With $PdCl_2$ as the catalyst, the reaction time was 8 h and the yield decreased to 74% (entry 5). It should be emphasized that in the presence of Na_2CO_3, all the four Ph groups of Ph_4BNa are involved in the reaction (as distinct from the previous data[4]).

Scheme 1

i. [Pd], Na_2CO_3, 20 °C.

In dichloromethane, chloroform, benzene, and toluene, even in the presence of a base and a phase-transfer catalyst (5 mol. % Bu_4NBr), the yield of benzophenone does not exceed 24%, which suggests that acyldeboration involves only one Ph group of Ph_4BNa. A possible reason is that these solvents poorly solvate Na_2CO_3, which impedes its reaction with organoboron compounds (see Table 1, entries 6—9). Coordination of the base to the boron atom is the key factor that determines the efficiency of the cross-coupling of organoboron compounds with electrophilic agents.[9]

Other bases (K_2CO_3, K_3PO_4, $Ba(OH)_2$, and Ag_2CO_3) can also be used (entries 10—13); in the presence of $Ba(OH)_2$, the reaction is completed in 4 h to give benzophenone in quantitative yield (entry 13). In all cases, all of the four Ph groups of sodium tetraphenylborate are transferred. In the absence of a base, the yield of the ketone is 23%, which suggests the transfer of only one Ph

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Table 1. Effects of the solvent, base, and catalyst on the reaction of benzoyl chloride with sodium tetraphenylborate[a]

Entry	Solvent	Base	Catalyst	τ/h	Yield[b] (%)
1	Acetone	Na_2CO_3	$Pd(OAc)_2$	6	96
2	THF	Na_2CO_3	$Pd(OAc)_2$	5	79
3	DMF	Na_2CO_3	$Pd(OAc)_2$	4	86
4	1,4-Dioxane	Na_2CO_3	$Pd(OAc)_2$	6	85
5	Acetone	Na_2CO_3	$PdCl_2$	8	74
6	Dichloromethane[c]	Na_2CO_3	$Pd(OAc)_2$	40	19
7	Chloroform[c]	Na_2CO_3	$Pd(OAc)_2$	40	22
8	Benzene[c]	Na_2CO_3	$Pd(OAc)_2$	40	20
9	Toluene[c]	Na_2CO_3	$Pd(OAc)_2$	40	24
10	Acetone	K_2CO_3	$Pd(OAc)_2$	6	94
11	Acetone	K_3PO_4	$Pd(OAc)_2$	5	93
12	Acetone	$Ba(OH)_2$	$Pd(OAc)_2$	5	84
13	Acetone	Ag_2CO_3	$Pd(OAc)_2$	4	96
14	Acetone	—	$Pd(OAc)_2$	5	23
15	Acetone	Na_2CO_3	$PdCl_2(PPh_3)_2$	40	21
16	Acetone	Na_2CO_3	$PdCl_2$(dppf)	40	18
17	Acetone	Na_2CO_3	$Pd(dba)_2$	40	15
18	Acetone	Na_2CO_3	Pd black[d]	40	—

[a] PhCOCl (1 mmol), a base (1.5 mmol), Ph_4BNa (0.25 mmol), a solvent (5 mL), and a catalyst (1 mol. %), 20 °C, argon.
[b] Preparative yield.
[c] In the presence of Bu_4NBr (0.05 mmol, 5 mol. %).
[d] Powder (particle size 0.1—0.5 mm).

group (entry 14). Nearly the same yield of benzophenone was attained[4] in THF with $Pd(PPh_3)_4$ as the catalyst, but the reaction time was 20 h.

Unsatisfactory results were obtained in the presence of $Pd(dba)_2$ (dba is dibenzylideneacetone) and Pd black (entries 17, 18), although Pd black is known[2b] to effectively catalyze the cross-coupling of 3-iodobenzoic acid with $PhB(OH)_2$ (20 °C, 3 h, 80%).

Phosphine complexes of palladium, $PdCl_2(PPh_3)_2$ and $PdCl_2$(dppf), which are widely used in various versions of the Suzuki reaction,[1] proved to be significantly less efficient as precursors of a catalyst than ligand-free palladium (entries 15, 16). The reaction products are benzophenone (yield 18—21%, corresponding to the transfer of only one Ph group of sodium tetraphenylborate) and benzoic anhydride, which undergoes no further conversions.

We found that acyldeboration can be substantially accelerated by adding water in the case of slowly hydrolyzable acyl chlorides (Table 2). For instance, the reaction of PhCOCl with Ph_4BNa in anhydrous acetone is completed in 6 h (see Table 2, entry 1), while its duration in 80—90% aqueous acetone is 1 to 1.5 h (see Table 2, entries 2—4). At a water content of 50 vol. %, the reaction is completed in 15 min. Surprisingly, even in water, in which benzoyl chloride is virtually insoluble, the reaction proceeds more rapidly than in dry acetone (see Table 2, entry 5).

In the presence of water, the reaction rate and the yield are only slightly sensitive to the nature of an organic solvent. For instance, in homogeneous water—THF and water—DMF mixtures (see Table 2, entries 6, 7), the reaction occurs as in aqueous acetone, and benzophenone is obtained in quantitative yield in 1 h. In contrast, in the two-phase toluene—water system (see Table 2, entry 8) even in the presence of a phase-transfer catalyst, the yield of the ketone is substantially lower, probably because of hydrolysis as a side reaction.

The use of other bases (K_3PO_4 and $Ba(OH)_2$) does not change the reaction pattern significantly (see Table 2, entries 12, 13). The reaction occurs also without any base (entry 14).

Note that benzoic anhydride is also formed in all reactions carried out in aqueous media, probably as a result of the partial hydrolysis of PhCOCl (see Table 2).

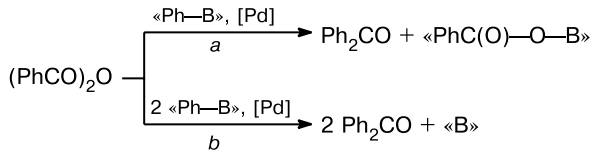
The amount and subsequent transformations of benzoic anhydride depend on the type of the Pd catalyst. In the presence of $PdCl_2(PPh_3)_2$, $Pd(dba)_2$, and Pd black, benzoyl chloride forms benzoic anhydride very rapidly (in 15—20 min) and quantitatively, while benzophenone is detected in trace amounts. Then, benzoic anhydride reacts with organoboron compounds "Ph—B" over 4—5 h (entries 9—11) to give benzophenone in 48—56% yield (with respect to the starting benzoyl chloride; Scheme 2, pathway *a*); this is a virtually quantitative yield with respect to one acyl group of benzoic anhydride.

Table 2. Reaction of benzoyl chloride with Ph_4BNa in aqueous organic media[a]

Entry	Solvent	Base	Catalyst	τ/h	Yield[b] (%)
1	Acetone	Na_2CO_3	$Pd(OAc)_2$	6	96
2	Acetone—water (4 : 1)	Na_2CO_3	$PdCl_2$	1	95
3	Acetone—water (10 : 1)	Na_2CO_3	$PdCl_2$	1.5	93
4	Acetone—water (1 : 1)	Na_2CO_3	$PdCl_2$	0.25	98
5	Water	Na_2CO_3	$PdCl_2$	5	98
6	THF—water (4 : 1)	Na_2CO_3	$Pd(OAc)_2$	1	96
7	DMF—water (4 : 1)	Na_2CO_3	$Pd(OAc)_2$	1	96
8	Toluene—water (2 : 1)	Na_2CO_3	$Pd(OAc)_2$	1	67[c]
9	Acetone—water (4 : 1)	Na_2CO_3	$PdCl_2(PPh_3)_2$	5	56
10	Acetone—water (4 : 1)	Na_2CO_3	$Pd(dba)_2$	4	55
11	Acetone—water (4 : 1)	Na_2CO_3	Pd black[d]	5	48
12	Acetone—water (4 : 1)	K_3PO_4	$PdCl_2$	1	97
13	Acetone—water (4 : 1)	$Ba(OH)_2$	$PdCl_2$	1	96
14	Acetone—water (4 : 1)	—	$PdCl_2$	5	29

[a] PhCOCl (1 mmol), Ph_4BNa (0.25 mmol), a base (1.5 mmol), a catalyst (1 mol. %), a solvent (5 mL), 20 °C, argon.
[b] Preparative yield.
[c] In the presence of Bu_4NBr (0.05 mmol, 5 mol. %).
[d] Powder (particle size 0.1—0.5 mm).

Scheme 2

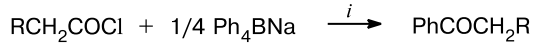


Acidification of the reaction mixture with HCl results in the formation of benzoic acid in 40—45% yield.

In the presence of ligand-free palladium, benzoyl chloride is completely converted into benzophenone (90%) and benzoic anhydride (~10%) in 5 min. After 1 h, the yield of benzophenone becomes nearly quantitative, and benzoic acid is detected in trace amounts (<1%) (entry 2). These data suggest that the reaction of benzoic anhydride with the phenylboron compound "Ph—B" catalyzed by ligand-free palladium proceeds in a non-trivial manner with involvement of both benzoyl groups (Scheme 2, pathway *b*).

Under the optimum conditions found (acetone, Na_2CO_3, 1 mol. % $Pd(OAc)_2$, 20 °C), Ar_4BNa easily reacts with acid chlorides of alkanoic, α,β-unsaturated, and substituted benzoic and heterocyclic acids (Table 3). Alkanoic acid chlorides react most rapidly (Scheme 3) to

Scheme 3



i. [Pd], 5—20 min, 84—100%.

R = *n*-C_6H_{13}, PhO

Table 3. Synthesis of aryl ketones from RCOCl and Ar_4BNa*

Entry	Ar	RCOCl	τ/h	Yield** (%)
1	Ph	C_6H_5COCl	6	96
2	Ph	4-$CH_3C_6H_4COCl$	5.5	84
3	Ph	2-BrC_6H_4COCl	5	92
4	Ph	4-BrC_6H_4COCl	5	86
5	Ph	3-$NO_2C_6H_4COCl$	2.5	64
6	Ph	(*E*)-PhCH=CHCOCl	3	96
7	Ph	CH_2=$C(CH_3)COCl$	1	66
8	Ph	2-Furoyl chloride	1	88
9	Ph	2-Thenoyl chloride	1	95
10	Ph	*n*-$C_7H_{15}COCl$	5 min	98
11	Ph	$C_6H_5OCH_2COCl$	20 min	84
12	4-MeC_6H_4	3-$NO_2C_6H_4COCl$	2.5	61
13	4-MeC_6H_4	4-$CH_3C_6H_4COCl$	6	86
14	4-$EtOC_6H_4$	3-$NO_2C_6H_4COCl$	1.5	59

* PhCOCl (1 mmol), Ar_4BNa (0.25 mmol), Na_2CO_3 (1.5 mmol), $Pd(OAc)_2$ (1 mol. %), acetone (5 mL), 20 °C, argon.
** Preparative yield.

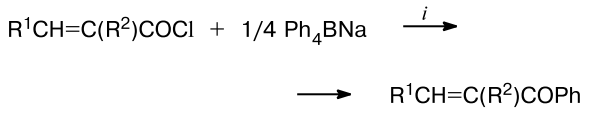
give alkyl phenyl ketones in high yields in 5 to 20 min (see Table 3, entries 10, 11).

Reactions with α,β-unsaturated acid chlorides are completed in 1 to 3 h affording the corresponding ketones in quantitative yields (Scheme 4).

2-Furoyl and 2-thenoyl chlorides also easily react with Ph_4BNa (Scheme 5).

Aroyl chlorides containing electron-donating and weak electron-withdrawing substituents react with Ph_4BNa without difficulty (see Table 3). However, the yields of aryl 3-nitrophenyl ketones from 3-nitrobenzoyl chloride

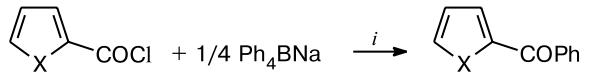
Scheme 4



i. [Pd], 1—3 h, 92—96%.

R^1 = Ph, R^2 = H; R^1 = H, R^2 = Me

Scheme 5



i. [Pd], 1 h, 88—95%.

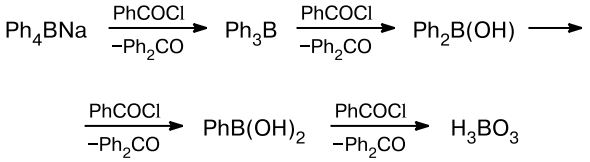
X = O, S

are somewhat lower (59—64%), and 3-nitrobenzoic acid is detected in the reaction mixture upon its workup.

In the reactions of 2- and 4-bromobenzoyl chlorides, the bromine atoms remain unaffected, and the corresponding bromobenzophenones were obtained in high yields (see Table 3, entries 3, 4).

It is noteworthy that all possible intermediates of the acyldeboration of Ph_4BNa, namely, Ph_3B, $Ph_2B(OH)$, and $PhB(OH)_2$, were detected as transient species in the reaction mixtures by TLC (Scheme 6). Obviously, they also serve, once formed, as sources of the phenyl group for acyldeboration.

Scheme 6



2. Acyldeboration of arylboronic acids

Arylboronic acids are the most stable and most accessible organoboron compounds. For this reason, we studied their reactions with carboxylic acid chlorides.

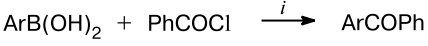
The acyldeboration of arylboronic acids with benzoyl chloride was carried out in aqueous 75% acetone in the presence of 1 mol. % $PdCl_2$ and Na_2CO_3 in an inert atmosphere at 20 °C. Under these conditions, aryl- and hetarylboronic acids easily react with benzoyl chloride to give substituted benzophenones and aryl hetaryl ketones in high yields (Scheme 7, Table 4). For instance, the reactions of PhCOCl with isomeric tolylboronic acids are completed in 1.5 to 2 h and afford 2-, 3-, and 4-methylbenzophenones in 79—95% yields (entries 1, 2, 6).

Table 4. Synthesis of non-symmetrical ketones from benzoyl chloride and arylboronic acids $ArB(OH)_2$[a]

Entry	Ar	τ/h	Preparative yield (%)
1	2-MeC_6H_4	2	80
2	3-MeC_6H_4	1.5	95
3[b]	3-MeC_6H_4	72	59
4[c]	3-MeC_6H_4	28	79
5[d]	3-MeC_6H_4	80	79
6	4-MeC_6H_4	2	79
7	3-NO_2-4-MeC_6H_4	1	96
8	5-Bromo-2-thienyl	1	85
9	5-Formyl-3-thienyl	1.5	76

[a] PhCOCl (1 mmol), $ArB(OH)_2$ (1.05 mmol), Na_2CO_3 (1.5 mmol), $PdCl_2$ (1 mol. %), acetone—water (3 : 1, 5 mL), 20 °C, argon.
[b] $PdCl_2(PPh_3)_2$ (1 mol. %).
[c] In dry acetone.
[d] In dry THF.

Scheme 7



i. [Pd], 20 °C, up to 96%.

It was demonstrated with the reaction of benzoyl chloride with 4-methyl-3-nitrophenylboronic acid as an example that the NO_2 group remains intact during the reaction (see Table 4, entry 7).

Because of very mild conditions of acyldeboration, thenoylboronic acids with such substituents as bromine and a formyl group can be successfully used in cross-coupling (entries 8, 9).

As in the reactions of sodium tetraphenylborate, the reaction rate and yield significantly decrease when phosphine complexes of palladium are used as catalysts.

Unlike Ph_4BNa, arylboronic acids in anhydrous media react much more slowly than in aqueous solvents (*cf.* entries 2, 4, 5). It should be noted that the reaction of PhCOCl with $PhB(OH)_2$ in toluene in the presence of 5 mol. % $Pd(PPh_3)_4$ at 100 °C for 16 h affords benzophenone in 80% yield.[5a]

To involve arylboronic acids in reactions with reactive, easily hydrolyzable acyl chlorides, optimum reaction conditions in anhydrous media should be found. For this purpose, we studied model reactions of benzoyl chloride with 4-tolylboronic and 4-fluorophenylboronic acids in the presence of 1 mol. % $Pd(OAc)_2$ and various bases (Table 5). Sodium carbonate, which acts well in reactions with Ph_4BNa, does not provide high yields (entry 1). Trialkylamines or pyridine (*i.e.*, the bases forming soluble adducts with boric acid under these conditions) increase the reaction rate and the yield of the ketone. As in aque-

Table 5. Reactions of arylboronic acids with benzoyl chloride in anhydrous media[a]

Entry	Arylboronic acid	Base	τ/h	Yield[b] (%)
1	4-$MeC_6H_4B(OH)_2$	Na_2CO_3	48	32
2[c]	4-$MeC_6H_4B(OH)_2$	Na_2CO_3	24	74
3	4-F-$C_6H_4B(OH)_2$	CH_3COONa	150	67
4	4-F-$C_6H_4B(OH)_2$	NaF	150	57
5	4-$MeC_6H_4B(OH)_2$	CH_3COONa	48	81
6	4-$MeC_6H_4B(OH)_2$	NaF	48	72
7[d]	4-$MeC_6H_4B(OH)_2$	NaF	5 min	64
8	4-$MeC_6H_4B(OH)_2$	Ag_2O	16	24
9[e]	4-$MeC_6H_4B(OH)_2$	Triethylamine	1	5
10[e]	4-$MeC_6H_4B(OH)_2$	Tributylamine	12	74
11[e]	4-$MeC_6H_4B(OH)_2$	Pyridine	4	14

[a] PhCOCl (1 mmol), $ArB(OH)_2$ (1.05 mmol), a base (1.5 mmol), $Pd(OAc)_2$ (1 mol. %), dry acetone (5 mL), 20 °C, argon.
[b] Preparative yield.
[c] In dry DMF.
[d] Without a solvent in a microwave oven (radiation power 300 W).
[e] In the presence of 3 mmol of the base.

ous organic media, the reaction in anhydrous solvents is mainly impeded by the formation of benzoic anhydride, even with thoroughly dried reagents. Under these conditions, the resulting anhydride seems to be inert in oxidative addition and is isolated as a by-product.

The most convenient system for acyldeboration in anhydrous media is dry acetone and tributylamine as a base (see Table 5, entry 10). More basic but less bulky triethylamine and pyridine are less suitable under these conditions since they rapidly react with PhCOCl to give acetone-insoluble adducts $PhCOCl \cdot Et_3N$ and $PhCOCl \cdot Py$, respectively. In this case, the yield of the ketone is low (see Table 5, entries 9, 11). The use of sodium fluoride or acetate increases the yield of the ketone. However, the reaction time is noticeably larger and the degree of hydrolytic cleavage of the acid chloride changes considerably and is irreproducible, and the yield of the product is also irreproducible.

Thus, non-symmetrical aromatic ketones were synthesized in high yields from easily accessible starting reagents, namely, arylboron compounds and carboxylic acid chlorides. The high catalytic activity of palladium salts in aqueous organic media makes the method economically attractive. The optimum conditions are mild, which allows functionalized substrates to be employed in this reaction.

Experimental

^1H NMR spectra were recorded on a Bruker AM-400 spectrometer (400 MHz) in $CDCl_3$ and DMSO-d_6. Chemical shifts were measured with reference to residual protons of the solvents. Arylboronic acids and sodium tetraarylborates were prepared according to known procedures[10] from the corresponding organomagnesium or -lithium compounds and $B(OMe)_3$. Carboxylic acid chlorides were prepared from carboxylic acids and $SOCl_2$.[11] Solvents were purified using standard procedures.

Reactions of acyl chlorides with sodium tetraarylborates in anhydrous media. Benzoyl chloride (0.12 mL, 1 mmol), $NaBPh_4$ (0.09 g, 0.26 mmol), dry Na_2CO_3 (0.159 g, 1.5 mmol), dry acetone (5 mL), and $PdCl_2$ (or $Pd(OAc)_2$) (0.0022 g, $1 \cdot 10^{-5}$ mol L^{-1}, 1 mol. %) were placed in a Schlenk vessel in an argon atmosphere. The reaction mixture was stirred at ≈20 °C for 6 h. The course of the reaction was monitored by TLC (Silufol UV-254; hexane—ether, 4 : 1). After the reaction was over, the mixture was diluted with water (20—25 mL) and the products were extracted with ether (3×15 mL). The combined organic extracts were dried with $CaCl_2$ and the solvent was removed to give benzophenone (0.174 g, 96%).

The above procedure was used to study the effects of the solvent, base, and catalyst on the reaction of Ph_4BNa with PhCOCl (see Table 1) and to carry out the reactions of Ar_4BNa with RCOCl (see Table 3).

Reaction of benzoyl chloride with Ph_4BNa in aqueous organic media. Benzoyl chloride (0.12 mL, 1 mmol), $NaBPh_4$ (0.09 g, 0.26 mmol), aqueous 0.15 *M* Na_2CO_3 (1 mL), acetone (4 mL), and aqueous 0.1 *M* $PdCl_2$ (0.1 mL) were placed in a Schlenk vessel in an argon atmosphere. The reaction mixture was stirred at ≈20 °C for 1 h. The reaction mixture was worked up as described above to give benzophenone (0.172 g, 95%).

Reactions of PhCOCl with Ph_4BNa in other aqueous organic media were carried out analogously (see Table 2).

A similar procedure was used to synthesize non-symmetrical phenyl ketones from benzoyl chloride and arylboronic acids, with the exception that $NaBPh_4$ is replaced by an arylboronic acid (1.05 mmol) (see Table 4).

Syntheses of non-symmetrical phenyl ketones by the reactions of benzoyl chloride with arylboronic acids in an anhydrous medium. Benzoyl chloride (0.12 mL, 1 mmol), 4-tolylboronic acid (0.1426 g, 1.05 mmol), dry acetone (5 mL), tributylamine (0.36 mL, 1.5 mmol), and $Pd(OAc)_2$ (0.0022 g) were placed in a Schlenk vessel in an argon atmosphere. The reaction mixture was stirred at ≈20 °C for 12 h. The course of the reaction was monitored by TLC (Silufol UV-254; hexane—ether, 4 : 1). After the reaction was over, the mixture was diluted with water (20—25 mL) and the products were extracted with ether (3×15 mL). The combined organic extracts were washed with dilute HCl (1 : 4) (3×15 mL) and dried with $CaCl_2$. The solvent was removed to give 4-methylbenzophenone (0.145 g, 74%).

An analogous procedure was used to study the effects of the solvent and the base on the reactions of PhCOCl with arylboronic acids (see Table 5).

All the compounds obtained were characterized by ^1H NMR spectra, melting points, and elemental analysis data. Analytical samples of solid compounds were prepared by recrystallization from hexane or a hexane—acetone mixture. Analytical samples of liquid compounds (at room temperature) were prepared by passing their ethereal solutions through a layer of silica gel (2 cm) with subsequent removal of the solvent. 2,4-Dinitrophenylhydrazones of the ketones were prepared as follows.[12] Conc. H_2SO_4 (0.5 mL) was slowly added to a suspension of 2,4-dinitrophenylhydrazine (0.4 g) in 10 mL of ethanol. The mixture was heated until the solution became transparent, and a ketone (~0.2 g) was added to the hot solution. After 2 to 10 min, 2,4-dinitrophenylhydrazone precipitated on cooling.

Benzophenone, m.p. 47—48 °C (Ref. 13: m.p. 48—49 °C). 2,4-Dinitrophenylhydrazone, m.p. 237—238 °C (Ref. 13: m.p. 238 °C).

2-Methylbenzophenone, oil. 2,4-Dinitrophenylhydrazone, m.p. 184—189 °C (Ref. 14: m.p. 184—190 °C).

3-Methylbenzophenone, oil. 2,4-Dinitrophenylhydrazone, m.p. 221—222 °C (Ref. 14: m.p. 221 °C).

4-Methylbenzophenone, m.p. 59—60 °C (Ref. 14: m.p. 59—60 °C). 2,4-Dinitrophenylhydrazone, m.p. 204—205 °C (Ref. 13: m.p. 202 °C).

4-Fluorobenzophenone, m.p. 46—48 °C (Ref. 14: m.p. 48.2—48.7 °C). 2,4-Dinitrophenylhydrazone, m.p. 230—231 °C (Ref. 15: m.p. 230—233 °C).

2-Bromobenzophenone, oil (Ref. 14: m.p. 42 °C). ^{1}H NMR (DMSO-d_6), δ: 7.45—7.80 (m, 6 H, C_6H_4Br, *m*-H (Ph)); 7.85—7.95 (m, 3 H, *o*- and *p*-H (Ph)).

4-Bromobenzophenone, m.p. 80—82 °C (Ref. 14: m.p. 82 °C).

3-Nitrobenzophenone, m.p. 92—94 °C (Ref. 14: m.p. 92 °C).

Chalcone (benzylideneacetophenone), m.p. 57—58 °C (Ref. 14: m.p. 58 °C). 2,4-Dinitrophenylhydrazone, m.p. 242—245 °C (Ref. 13: m.p. 244 °C).

2-Methyl-1-phenylprop-2-en-1-one, oil (Ref. 16: oil). ^{1}H NMR (DMSO-d_6), δ: 2.05 (s, 3 H, Me); 6.01 (s, 1 H, $=CH_2$); 6.19 (s, 1 H, $=CH_2$); 7.33—7.42 (m, 5 H, Ph).

2-Benzoylfuran, oil (Ref. 14: oil; Ref. 17: m.p. 42—44 °C). ^{1}H NMR (DMSO-d_6), δ: 6.79 (br.s, 1 H, 4-H (Fur)); 7.40—7.55 (m, 4 H, 3-H (Fur), *m*- and *p*-H (Ph)); 8.01—8.07 (m, 3 H, 5-H (Fur), *o*-H (Ph)).

2-Benzoylthiophene, m.p. 54—56 °C (Ref. 18: m.p. 55—56 °C). ^{1}H NMR (DMSO-d_6), δ: 7.21 (br.s, 1 H, 4-H (thienyl), J = 1.2 Hz); 7.50—7.70 (m, 7 H, 3- and 5-H (thienyl, Ph)).

1-Phenyloctan-1-one, oil. ^{1}H NMR (DMSO-d_6), δ: 0.88 (t, 3 H, Me, J = 7.1 Hz); 1.25—1.30 (m, 10 H, 3,4,5,6,7-CH_2); 2.90 (t, 2 H, 2-CH_2, J = 7.0 Hz); 7.50 (m, 3 H, *m*- and *p*-H (Ph)); 7.95 (d, 2 H, *o*-H (Ph), J = 7.8 Hz). 2,4-Dinitrophenylhydrazone, m.p. 120—122 °C (Ref. 19: m.p. 122 °C).

2-Phenoxy-1-phenylethan-1-one, oil (Ref. 20: m.p. 71—72 °C). ^{1}H NMR (DMSO-d_6), δ: 5.32 (s, 2 H, CH_2O); 6.85—6.95 (m, 3 H, *o*- and *p*-H (PhO)); 7.40—7.60 (m, 5 H, *m*-H (PhO), *m*- and *p*-H (PhCO)); 8.00 (d, 2 H, *o*-H (PhCO), J = 7.7 Hz).

4-Methyl-3-nitrobenzophenone, m.p. 129—130 °C (Ref. 14: m.p. 130—132 °C).

2-Benzoyl-5-bromothiophene, m.p. 35—38 °C (Ref. 21: m.p. 38—39 °C).

4-Benzoylthiophene-2-carbaldehyde, m.p. 75—77 °C (Ref. 22: m.p. 74—75 °C).

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