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Sodium tetraphenylborate as a phenylating reagent in the palladium-catalyzed phenylation of alkenes and acid chlorides

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Abstract

Sodium tetraphenylborate ($NaBPh_4$) reacts with terminal alkenes in acetic acid at 25°C in the presence of a catalytic amount of palladium(II) acetate together with silver acetate as a re-oxidant to give the corresponding phenylated alkenes in 22–87% yield. It also reacts with acid chlorides in tetrahydrofuran (THF) at 25°C in the presence of a catalytic amount of tetrakis(triphenylphosphine)palladium(0) to give the corresponding phenyl ketones in 51–100% yield. Carbonylation of the borate with 1–30 atm carbon monoxide (CO) in methanol at 25°C in the presence of palladium(II) acetate or sodium chloropalladate (Na_2PdCl_4) affords a low yield (9–30%) of benzophenone and methyl benzoate, a higher pressure favoring the formation of the latter.

1. Introduction

Sodium tetraphenylborate ($NaBPh_4$) has been used as a phenylating agent affording σ-phenyl complexes of various transition metals by the transfer of a phenyl group from boron to metals [1–5]. Phenyl transfer from this reagent to some organopalladium complexes making a new carbon–carbon bond has also been noted [6–8]. From the viewpoint of organic synthesis, however, several recent reports on its use in Pd^0- and/or Pd^{II}-catalyzed reactions are interesting; *i.e.* the phenyl substitution of allylic chlorides [9] and acetates [10] giving allylbenzenes, the synthesis of diaryl substituted norbornanes and norbornenes [11] as well as biaryls [12], the carbonylative cross-coupling of alkyl iodides giving alkyl phenyl ketones [13], and heterocyclic synthesis accompanied by introduction of a phenyl group [14]. We report a Pd^{II}-catalyzed phenylation of alkenes in the presence of a suitable re-oxidant such as silver acetate and Pd^0-catalyzed phenylation of acid chlorides with stable, non-toxic and commercially available $NaBPh_4$. The results of Pd^{II}, Pd^0 or Rh^{III} salt-mediated or -catalyzed carbonylation of the borate itself are also described. The results presented here may lead to the further use of the reagent in organic transformation.

2. Results and discussion

2.1. Reaction of alkenes with $NaBPh_4$

Treatment of $NaBPh_4$ (1 mmol) with ethyl acrylate (1 mmol) in acetic acid (10 ml) in the presence of a catalytic amount of palladium(II) acetate (0.05 mmol) and silver acetate (2 mmol) as a re-oxidant [15] at 25°C for 5 h afforded ethyl cinnamate (0.83 mmol, 83% yield) together with biphenyl (0.06 mmol, 6% yield) as a side product. The reaction also proceeded using ammonium cerium(IV) nitrate (CAN) and potassium persulfate ($K_2S_2O_8$) in place of silver acetate, but the yield of the products was generally lower. The use of copper(II) acetate as a re-oxidant and the use of a palladium(II) chloride–copper(II) chloride system were found to be ineffective for this phenylation. The phenylation did not proceed at all without palladium(II) as catalyst. The use of 0.25 equiv. of both $NaBPh_4$ and of palladium(II) acetate and 1 equiv. of ethyl acrylate (1 mmol) afforded a 39% yield (0.39 mmol) of ethyl cinnamate together with biphenyl (0.15 mmol, 15% yield) based on the substrate. This result indicates that at least two phenyl groups out of four in the borate are available for phenyl transfer and also biphenyl forma-

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tion increases with the increase in the amount of $Pd(OAc)_2$ employed. Triphenylboron (Ph_3B), which may be considered to be formed and to be the most plausible second reactive species under these reaction conditions, was also revealed to work as a phenylating agent. Thus, the reaction of Ph_3B with an equimolar amount of ethyl acrylate under these reaction conditions afforded ethyl cinnamate in 93% yield. The reaction can be applied to various alkenes (**I**) such as methyl acrylate, acrylaldehyde, methyl vinyl ketone, styrene, acrylonitrile, and allylic alcohol and bromide (eqn. (1)); the stereochemistry of the phenylated alkenes (**II**) is always *trans*.

$$\underset{(\mathbf{I})}{CH_2{=}CHR} + NaBPh_4 \xrightarrow[\text{AcOH}]{\text{cat. }Pd(OAc)_2/AgOAc} \underset{(\mathbf{II})}{PhCH{=}CHR} \qquad (1)$$

Typical results are summarized in Table 1. In all cases, biphenyl was formed in less than 6% yield as a side product, in addition to the phenylated alkenes.

In the case of allyl bromide, the product was allylbenzene as has been observed in the reactions with phenylmercury(II) [16] and diphenyltellurium(IV) [17] compounds. In this case, the palladium may be eliminated in the +2 oxidation state, [Pd(OAc)Br], and in practice the reaction proceeded catalytically with a Pd^{II} salt even in the absence of silver acetate. In the reaction with allyl alcohol, three kinds of products – cinnamyl alcohol (**II**; R = CH_2OH), 3-phenylpropionaldehyde, and cinnamaldehyde – were obtained, the product distribution being dependent on the reaction time. Thus, cinnamyl alcohol and cinnamaldehyde are the main products for 5 and 20 h, respectively (Table 1). The results may suggest that the initially formed cinnamyl alcohol is oxidized to cinnamaldehyde under the reaction conditions but, unfortunately, separate reactions with cinnamyl alcohol under several similar conditions showed that the alcohol was not oxidized to cinnamaldehyde: thus a scheme for cinnamaldehyde is not yet clear. In the case of 1-octene three products, *trans*-1-phenyl-1-octene(**II**; R = C_6H_{13}), *trans*-1-phenyl-2-octene and 2-phenyl-1-octene were obtained in a ratio of *ca.* 65:20:15 in about 50% yield (Table 1). In a separate experiment, we observed that a similar reaction with triphenylarsine (Ph_3As) gave the same mixture in *ca.* 30% yield [18], the isomer ratio being very close to that obtained here. Since the presence of a phenylpalladium species [PhPdZ] has been proposed in the last reaction [18], the result suggests the presence of a similar species in the $NaBPh_4$ reaction as discussed later.

TABLE 1. Palladium(II)-catalyzed phenylation of alkenes with $NaBPh_4$ [a]

Alkene R in I	Additive (mmol)	Reaction time (h)	Products	Yield(%) [b]
CO_2Et	AgOAc (2)	5	II	83
CO_2Et	AgOAc (1)	20	II	56
CO_2Et [c]	AgOAc (1)	5	II	22
CO_2Et	AgOAc (2)	1	II	47
CO_2Et	CAN [d] (2)	20	II	59
CO_2Et	$K_2S_2O_8$ (2)	20	II	24
CO_2Et	$Cu(OAc)_2$ (2)	5	II	3
CO_2Me	AgOAc (2)	5	II	82
CHO	AgOAc (2)	5	II	55
COMe	AgOAc (2)	5	II	59
Ph	AgOAc (2)	5	II	87
CN	AgOAc (2)	5	II	22
CH_2OAc	AgOAc (2)	5	II	68
CH_2Br	AgOAc (2)	5	$PhCH_2CH{=}CH_2$	42
CH_2Br		20	$PhCH_2CH{=}CH_2$	19
CH_2OH	AgOAc (2)	5	II	34
			$PhCH_2CH_2CHO$	10
			$PhCH{=}CHCHO$	3
CH_2OH	AgOAc (2)	20	II	12
			$PhCH_2CH_2CHO$	12
			$PhCH{=}CHCHO$	32
C_6H_{13}	AgOAc (2)	5	II	33
			$PhCH_2CH{=}CHC_5H_{11}$	10
			$C_6H_{13}(Ph)C{=}CH_2$	8

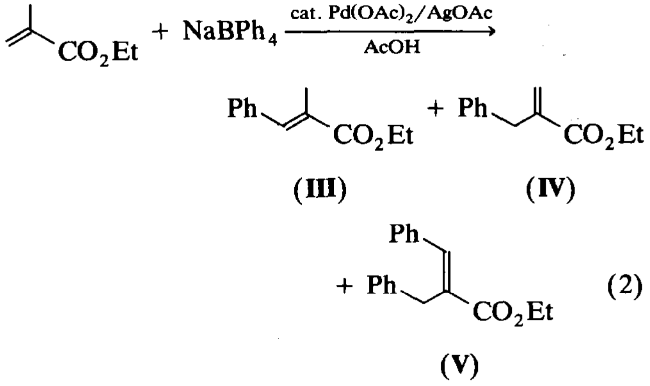
[a] Except as noted, all reactions were carried out with 1 mmol of alkene and $NaBPh_4$, respectively, and 0.05 mmol of $Pd(OAc)_2$ in AcOH (10 ml) at 25°C. [b] Determined by GLC; based on alkene, products are all *trans* and in almost all cases biphenyl (< 6%) was formed. [c] 0.5 mmol of $NaBPh_4$ was used. [d] $(NH_4)_2Ce(NO_3)_6$.

TABLE 2. Phenylation of ethyl methacrylate with $NaBPh_4$ [a]

$Pd(OAc)_2$ (mmol)	$NaBPh_4$ (mmol)	AgOAc (mmol)	Reaction time (h)	Products and yield (%) [b]	(III : IV : V)
0.05	1	2	5	51	(38 : 52 : 10)
0.05	1	2	20	59	(41 : 38 : 21)
0.05	1.5	3	20	75	(35 : 13 : 52)

[a] At 25°C in AcOH (10 ml). [b] Isolated yield based on ethyl methacrylate (1 mmol); isomer distribution is calculated by ^1H NMR.

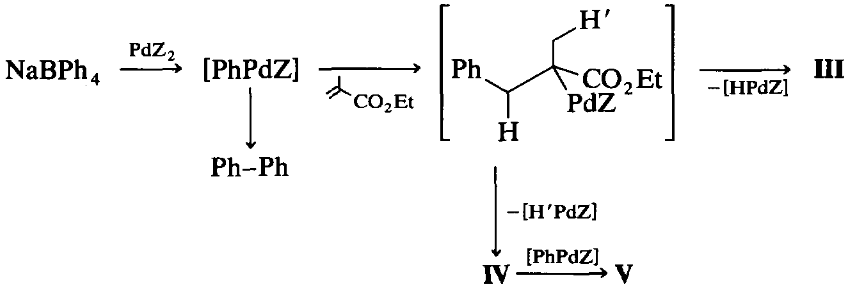
Conversely, the reaction with ethyl methacrylate gave the double phenylated product **V** together with the expected phenylation compounds **III** and **IV** (eqn. (2)). The ratio of **III**, **IV**, and **V** was dependent on the reaction time as well as the amount of $NaBPh_4$ used as shown in Table 2. Since it was not possible to separate these three compounds, the total yield and the distribution of this mixture were analyzed from the intensity of the olefinic protons in the ^1H NMR spectrum (see Experimental section). The distribution of **III** in the products scarcely changed under various reaction conditions, while that of **IV** and **V** changed greatly, the longer reaction time and the use of a larger amount of borate favoring the formation of **V**. The result indicates that **V** was formed via **IV**.



(III) (IV) (V) (2)

It was reported recently that arylmercury compounds react with quinones to give arylated quinones in the presence of a Pd^{II} catalyst [19]. However, treatment of quinone with $NaBPh_4$ under the conditions described so far resulted only in the formation of many unidentified compounds.

The arylation of alkenes with a putative arylpalladium intermediate [ArPdZ] generated *in situ* from various arylmetal compounds and palladium(II) salts has been investigated extensively [16–25]. It is also known that Pd^{II}-mediated and -catalyzed aromatic substitution of alkene hydrogens involves a similar arylpalladium(II) species generated by direct palladation of aromatic compounds [15,26]. Considering the type of products and their distribution, it is reasonable to assume that the phenylation presented here also involves a reactive phenylpalladium(II) species produced by the interaction between Pd^{II} and a tetraphenylborate anion. The species adds to the carbon–carbon double bond to give an alkylpalladium(II) compound which eliminates a palladium species with vicinal hydrogen to give the products shown in Scheme 1 for ethyl methacrylate. The Pd^0 produced is re-oxidized to Pd^{II} by silver acetate. The fact that a σ-phenyl complex of platinum(IV) is formed in the reaction of $PtCl_6^{2-}$ with $NaBPh_4$ and the complex reacts with acrylic acid to give cinnamic acid [3] supports the above assumption for this reaction pathway.



$$[HPdZ] \longrightarrow HZ + Pd$$

$$Pd + 2AgOAc \longrightarrow Pd(OAc)_2 + 2Ag$$

$$(Z = OAc)$$

Scheme 1.

TABLE 3. Carbonylation of $NaBPh_4$ and biphenyl formation [a]

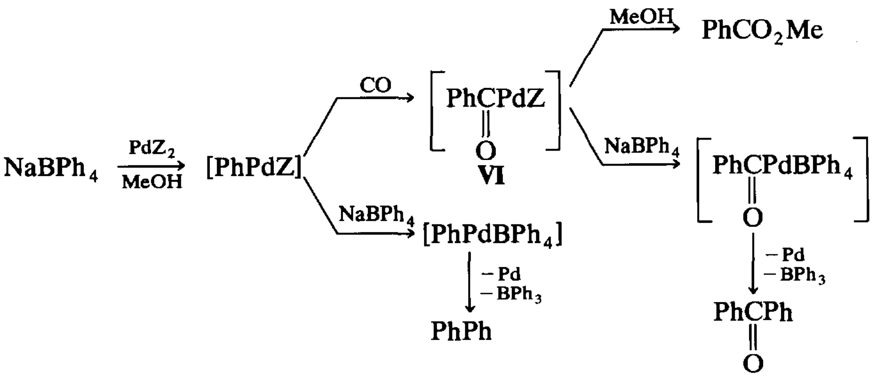
Metal salt (mmol)		CO (atm)	Reaction time (h)	Products and yield(%) [b]		
				$PhCO_2Me$	PhCOPh	PhPh
$Pd(OAc)_2$ [c]	0.5	1	5	11	19	62
$Pd(OAc)_2$ [c]	0.5	30	20	27	1	67
$Pd(OAc)_2$ [d]	0.05	1	5	13	1	5
$Pd(OAc)_2$ [c]	0.5	–	5	–	–	131
Na_2PdCl_4	1	1	5	4	5	46
Na_2PdCl_4	1	30	20	8	1	57
$RhCl_3 \cdot 3H_2O$	1	1	5	5	2	22
$Pd(PPh_3)_4$	0.05	1	5	3	Trace	8
$Pd(PPh_3)_4$	0.05	30	20	Trace	0	1

[a] Except as noted, all reactions were carried out with 1 mmol of $NaBPh_4$ in MeOH (10 ml) at 25°C. [b] Determined by GLC; based on $NaBPh_4$. [c] $NaBPh_4$ (0.5 mmol). [d] 2 mmol of AgOAc was added.

2.2. Reaction of carbon monoxide (CO) with $NaBPh_4$

It is known that some vinyl- and aryl-boric acids and esters react with 1 atm CO in the presence of a palladium(II) [27] and palladium(0) [28] catalyst to give the corresponding carboxylic acids or ketones: namely, a formal CO insertion to a C–B bond occurs with the aid of the Pd catalyst. In order to find out whether a similar carbonylation proceeds with $NaBPh_4$ and to obtain further indirect evidence for the presence of a phenylpalladium species [PhPdZ] proposed in a previous section, we treated the borate with 1 atm CO in methanol in the presence of a stoichiometric amount of $Pd(OAc)_2$ or Na_2PdCl_4 at 25°C for 5 h. The carbonylated compounds, methyl benzoate and benzophenone, were obtained in 30% and 9% yield, respectively, but the major product was biphenyl. The use of a higher pressure of CO (30 atm) did not increase the yield of the carbonylated compounds in which, interestingly, methyl benzoate was almost the sole product. Biphenyl formation occurred more smoothly in the absence of CO. The reaction also proceeded catalytically in $Pd(OAc)_2$ when AgOAc was present as a re-oxidant, the yield of methyl benzoate being 260% based on Pd for a reaction time of 5 h. The transition metal salts such as tetrakis(triphenylphosphine)palladium(0) and rhodium trichloride were revealed to be almost ineffective for the carbonylation. Typical results are shown in Table 3.

The result of a higher yield of biphenyl than carbonylated compounds shows that the phenylpalladium species reacts much faster with another molecule of $NaBPh_4$ than CO even at 30 atm (Scheme 2). Higher pressure of CO might prevent sterically an anion exchange or metathesis of Z by BPh_4^- in VI by coordination of CO on Pd, resulting in almost sole formation of methyl benzoate. Although the details are not yet known, in the catalytic reaction, an acetate anion of AgOAc might play a similar role as CO by occupying



(Z = Cl, OAc)

Scheme 2.

the vacant site of Pd. The reason why the yield of the carbonylated compounds was not increased by increasing the CO pressure remains unexplained.

2.3. Reaction of acid chlorides with $NaBPh_4$

Treatment of $NaBPh_4$ (1 mmol) with benzoyl chloride (1 mmol) in tetrahydrofuran (THF; 10 ml) at 25°C for 20 h in the presence of a catalytic amount of tetrakis(triphenylphosphine)palladium(0) (1 mol%) afforded benzophenone (1 mmol, 100% yield) together with biphenyl (0.15 mmol, 15% yield). The reaction also proceeded with palladium(II) catalysts such as palladium(II) acetate and dichlorobis(triphenylphosphine)palladium(II), although the yield was slightly lower (87–94%), but it did not proceed at all in the absence of the palladium catalyst. In addition, the reaction was strongly dependent on the type of solvent, dichloromethane and acetone being moderately effective (67–72% yield) and acetonitrile and benzene ineffective (18–23% yield). Diethyl ether was shown to be as good as THF as a solvent for benzophenone formation but greater formation of biphenyl was observed than in THF. We applied the reaction to various acid chlorides in THF as a solvent (eqn. (3)); typical results are summarized in Table 4.

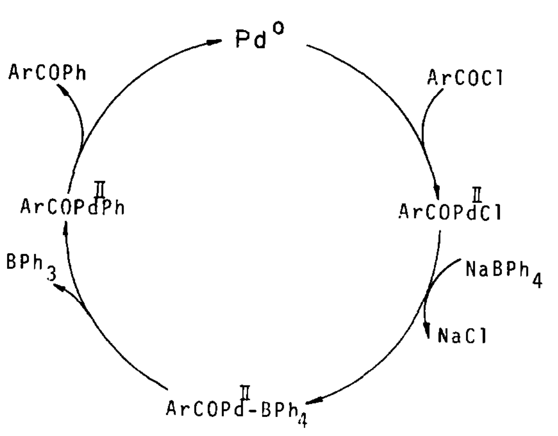
$$\mathrm{RCOCl} + \mathrm{NaBPh_4} \xrightarrow[\text{THF, 25°C}]{\text{cat. Pd}^0} \underset{\textbf{VII}}{\mathrm{RCOPh}} + \mathrm{PhPh} \tag{3}$$

The reaction proceeded effectively especially with aromatic and benzylic acid chlorides. In sharp contrast to the case of phenylation of olefins, Ph_3B was not effective at all for the phenylation of acid chlorides under these reaction conditions.

TABLE 4. Palladium-catalyzed phenylation of acid chlorides with $NaBPh_4$ [a]

R in RCOCl	$NaBPh_4$ (mmol)	Palladium salt (0.01 mmol)	Products (VII) and yield (%) [b]
Ph [c]	1	$Pd(PPh_3)_4$ [d]	97
Ph	0.5	$Pd(PPh_3)_4$ [d]	60
Ph	0.25	$Pd(PPh_3)_4$ [d]	29
Ph	1	$Pd(PPh_3)_4$	100
Ph	1	$Pd_2(dba)_3$	100
Ph	1	Pd black	3
Ph	1	$Pd(OAc)_2$	87
Ph	1	$Pd(OAc)_2$ [e]	70
Ph	1	$Pd(PPh_3)_2Cl_2$	94
Ph	1	$RhCl_3 \cdot 3H_2O$	3
p-MeC_6H_4	1	$Pd(PPh_3)_4$	91
p-$NO_2C_6H_4$	1	$Pd(PPh_3)_4$	76
CH_3CH_2	1	$Pd(PPh_3)_4$	62
$CH_3(CH_2)_2$	1	$Pd(PPh_3)_4$	54
$PhCH_2$	1	$Pd(PPh_3)_4$	94
Cyclohexyl	1	$Pd(PPh_3)_4$	56
PhCH=CH	1	$Pd(PPh_3)_4$	51

[a] Except as noted, all reactions were carried out with 1 mmol of acid chloride and $NaBPh_4$, respectively, and 0.01 mmol of palladium catalyst in THF (10 ml) at 25°C for 20 h. [b] Determined by GLC; based on acid chloride. In all cases biphenyl (< 15%) was formed. [c] Reaction time (5 h). [d] 0.05 mmol of $Pd(PPh_3)_4$ was used. [e] 1 mmol of Et_3N was added.



Scheme 3.

The reaction seems to proceed as shown in Scheme 3. Oxidative addition of acid chloride to palladium(0) affords acylpalladium(II) chloride. When a palladium(II) catalyst is used, it may be converted into some palladium(0) species under the reaction conditions, probably via a side reaction forming biphenyl. The chloride metathesis with $NaBPh_4$ occurs in the acylpalladium(II) chloride to give the tetraphenylborate salt. The transfer of a phenyl group from the BPh_4 moiety to palladium with concerted elimination of BPh_3 followed by reductive elimination gives the corresponding phenyl ketones. A similar catalytic cycle has already been proposed in the reactions with tetraorganotin [29] and triphenylbismuth [30].

3. Experimental details

^1H and ^{13}C NMR spectra were measured with a JEOL GSX-270 (270 MHz) spectrometer using TMS as an internal standard in $CDCl_3$. Mass spectra were obtained on a Shimadzu QP-2000 spectrometer. GLC analyses were carried out with Hitachi 163 and Shimadzu GC-14A equipped with a EGSS-X (10% on Chromosorb W, 60–80 mesh, 3 mm × 2 m) and CBP10-S25-050 (Shimadzu, fused silica capillary column, 0.33 mm × 25 m, 5.0 μm film thickness) columns, respectively, using nitrogen as the carrier gas. Commercially available organic and inorganic compounds were used without further purification except for the solvent, which was distilled by known methods before use. Except for phenylation products (III–V) from ethyl methacrylate, all commercial compounds were used as authentic samples for the GLC determination. The isolation of pure product was carried out with column chromatography (SiO_2; hexane/ethyl acetate as eluent). A typical experimental procedure is given below.

3.1. General procedure for the phenylation of alkenes with $NaBPh_4$

A mixture of sodium tetraphenylborate (0.342 g, 1 mmol), alkene (1 mmol), palladium(II) acetate (0.011 g, 0.05 mmol), silver acetate (0.334 g, 2 mmol), and an appropriate amount of internal standard (generally bibenzyl) in acetic acid (10 ml) was stirred at 25°C for 5 h or 20 h. The precipitated black solid was filtered off and the filtrate was poured into a saturated aqueous NaCl solution (100 ml), extracted with methylene chloride (50 ml × 2), and washed with aqueous $NaHCO_3$. The extracts were washed with water, dried over $MgSO_4$, and analyzed by GLC.

In the case of ethyl methacrylate (for 5 h), three kinds of phenylated alkenes were isolated as a mixture (0.101 g, 51% yield) using column chromatography (eluent, ethyl acetate/*n*-hexane 1:5 (v/v %)) and identified by their ^1H NMR, ^{13}C NMR, and GC-MS spectra. Similarly, the reaction using ethyl methacrylate (1 mmol), $Pd(OAc)_2$ (0.05 mmol), $NaBPh_4$ (1.5 mmol), and AgOAc (3 mmol) at 25°C for 20 h afforded 0.171 g (75% yield) of the mixture. The molar ratio was determined from the peak areas of the olefinic protons in the ^1H NMR spectrum. Typical spectroscopic data are as follows. ^1H NMR: **III** δ 2.11 (d, 3H, allylic CH_3), 7.69 (q, 1H, vinylic); **IV** 3.62 (s, 2H, benzylic), 5.42 (q, 1H, vinylic), 6.22 (s, 1H, vinylic); **V** 3.95 (s, 2H, benzylic), 7.93 (s, 1H, vinylic). ^{13}C NMR (C=O): δ 166.86, 168.09, 168.62. MS *m/z* (rel. intensity): **III** 190 (M^+, 52), 161 (20), 145 (64), 117 (100), 116 (87), 115 (91), 91 (33), 40 (24), 39 (22); **IV** 190 (M^+, 31), 145 (25), 144 (30), 117 (70), 91 (34), 58 (20), 39 (22); **V** 266 (M^+, 28), 220 (42), 193 (37), 192 (100), 191 (37), 159 (25), 115 (73), 91 (47).

3.2. Typical procedure for the carbonylation of $NaBPh_4$

Sodium tetraphenylborate (0.171 g, 0.5 mmol), palladium(II) acetate (0.112 g, 0.5 mmol), and bibenzyl (0.032 g, 0.176 mmol; an internal standard for GLC) were placed in a 30 ml round-bottom flask (with a septum inlet) and the system was flushed with CO from a balloon connected to the flask. Dry methanol (10 ml) was then injected by a syringe, and the mixture stirred for 5 h at 25°C. The precipitate was filtered off and the filtrate was poured into a saturated aqueous NaCl solution (10 ml) and extracted with methylene chloride (50 ml × 2). The extracts were washed with water and dried over $MgSO_4$. GLC analysis revealed the presence of methyl benzoate (0.055 mmol, 11%), benzophenone (0.095 mmol, 19%) and biphenyl (0.31 mmol, 62%).

The reaction using 30 atm CO was carried out similarly in a stainless steel autoclave with mechanical stirring.

3.3. General procedure for the phenylation of acid chloride with $NaBPh_4$

A mixture of sodium tetraphenylborate (0.342 g, 1 mmol), acid chloride (1 mmol), tetrakis(triphenylphosphine)palladium(0) (0.012 g, 0.01 mmol), and an appropriate amount of an internal standard in tetrahydrofuran (10 ml) was stirred at 25°C for 20 h. The precipitate was filtered off and the filtrate was poured into a saturated aqueous NaCl solution (100 ml) and extracted with methylene chloride (50 ml × 2). The extracts were washed with water, dried over $MgSO_4$, and analyzed by GLC.

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