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Alcohols for the α-Alkylation of Methyl Ketones and Indirect Aza-Wittig Reaction Promoted by Nickel Nanoparticles

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Dedicated to Dr. Cecilio Márquez on the occasion of his retirement

Keywords: Alcohols / Ketone alkylation / Hydrogen transfer / Nickel nanoparticles / Aza-Wittig reactions

Nickel nanoparticles have been found to activate primary alcohols used for the α-alkylation of ketones or in indirect aza-Wittig reactions. These processes involve hydrogen transfer from the alcohol to the intermediate α,β-unsaturated ketone or imine, respectively. All these reactions are carried out in the absence of any ligand, hydrogen acceptor or base under mild reaction conditions. For the first time nickel is employed as a potential alternative to noble-metal-based catalysts in both reactions. A reaction mechanism is proposed on the basis of some deuteration experiments.
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Introduction

The α-alkylation of ketone enolates with alkyl halides is probably the most frequently used method for the synthesis of ketones.[1] In recent years, however, alcohols have emerged as potential alternative alkylating agents of ketones by proper activation with a transition-metal catalyst.[2] This strategy can improve both the atom efficiency and the regioselectivity of the process producing only water as a side product. Until recently, this research was carried out only with catalysts containing some group-8 noble metals, such as ruthenium, iridium, and palladium. For instance, the α-alkylation of aromatic and aliphatic ketones with primary alcohols was successfully accomplished by Cho et al. with both $RuCl_2(PPh_3)_3$[3a] and Pd/C[3b] catalysts at 80–100 °C in dioxane. The presence of a sacrificial hydrogen acceptor (1-dodecene or 1-decene) was, however, mandatory in order to avoid the over-reduction of the alkylated ketone. The non-commercially available complex $RuCl_2(DMSO)_4$ was applied in the absence of a hydrogen acceptor, albeit to the specific α-alkylation of aryl methyl ketones with benzylic alcohols.[4] Wider substrate scope was observed for the heterogeneous palladium catalysts Pd/AlO(OH)[5] (composed of palladium nanoparticles entrapped in aluminum hydroxide) and Pd/viologen[6] (palladium nanoparticles entrapped in a viologen polymer), which could be recycled at the time that the products were obtained in high yields. The presence of stoichiometric amounts of a base (1–3 equiv.) was a common characteristic for the catalytic systems mentioned above. As an exception, however, catalytic amounts of a base (0.1–0.3 equiv.) together with PPh_3 were used in the case of the rather expensive iridium complex $[Ir(COD)Cl]_2$. Interestingly, reactions were performed at 100 °C in the absence of solvent with a varied substrate scope.[7]

The aza-Wittig reaction is another important tool in organic synthesis directed towards the construction of acyclic and cyclic compounds that has experienced a tremendous development in recent years.[8] In this reaction, phosphazenes (iminophosphoranes) react with carbonyl compounds, in an analogous manner to phosphorus ylides in the Wittig reaction, to give C=N bonds. To the best of our knowledge, the conversion of alcohols into *N*-alkylanilines through an indirect aza-Wittig reaction has been carried out only under iridium catalysis by Williams et al.[9] In this research, several benzylic alcohols reacted with *N*-(triphenylphosphoranylidene)aniline in the presence of 2 mol-% of $[IrCl(COD)]_2$, 5 mol-% of 1,1′-bis(diphenylphosphanyl)ferrocene and K_2CO_3 at 110 °C for 24 h. Both the α-alkylation of ketones and the indirect aza-Wittig reactions involve hydrogen transfer[10] from the starting alcohol to the intermediate α,β-unsaturated ketone and imine, respectively. This process has been defined by some authors as a hydrogen autotransfer process[2a] or a process in which hydrogen is borrowed.[2b]

On the other hand, and due to our ongoing interest on the study of active metals,[11] we have developed a mild methodology for the fast synthesis of nickel(0) nanoparticles, from different nickel(II) chloride-containing systems

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in THF, using lithium powder and a catalytic amount of an arene as reducing agent.[12] These nanoparticles found application in many different functional group transformations, including the reduction of a wide variety of functional groups,[13] the highly selective semihydrogenation of alkynes and dienes,[14] conjugate reduction of α,β-unsaturated carbonyl compounds,[15] homocoupling of aryl iodides,[16] and more recently, in the hydrogen transfer reduction of carbonyl compounds[17] and reductive amination of aldehydes.[18] Also recently, we communicated for the first time that nickel, in the form of nanoparticles, can act as a potential alternative to the use of noble-metal-based catalysts for the α-alkylation of ketones with alcohols.[19] These reactions proceed in short reaction times and in the absence of any ligand, hydrogen acceptor or base, under mild conditions.

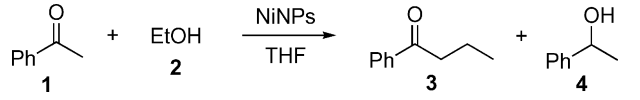
We wish to report herein a more detailed study on the α-alkylation of ketones with alcohols promoted by nickel nanoparticles, including a mechanistic proposal based on some deuterium labelling experiments, as well as the application of these nanoparticles to the indirect aza-Wittig reaction to give *N*-alkylated anilines.

Results and Discussion

The nickel(0) nanoparticles (NiNPs) were generated from anhydrous nickel(II) chloride, lithium powder and a catalytic amount of DTBB (4,4′-di-*tert*-butylbiphenyl) in THF at room temperature, and used in the α-alkylation of acetophenone with ethanol as a model reaction (Table 1). We first optimised the amount of ethanol, the yield of butyrophenone (**3**) increasing progressively with the amount of ethanol (entries 1–3). In these cases, however, important amounts of 1-phenylethanol, from the reduction of the starting ketone, were obtained. The best result was obtained with a large excess of ethanol (entry 4) and stoichiometric amounts of both nickel and lithium at 76 °C, the reaction being completed in only 2 h. In one of the experiments, 2 mmol excess of lithium were added in order to know whether the lithium ethoxide in situ generated had any effect on the reaction course. A decrease in the yield was observed together with the formation of the reduced starting ketone (entry 5). Two attempts to use the NiNPs in catalytic amounts resulted in much slower reactions that did not go to completion (entries 6 and 7). Product **3** was formed even at room temperature (entry 8) albeit with a low conversion and long reaction time. It is worthy to note that, in contrast to other catalytic systems, we did not observe the formation of the alcohol derived from the reduction of **3**.

We tried to extend this methodology to other ketones and alcohols (Table 2). Thus, valerophenone could be obtained in a short reaction time and good yield by alkylation of acetophenone with *n*-propanol (entry 2), under the same reaction conditions used for ethanol (entry 1). It is noteworthy that, to the best of our knowledge, this is the first time that both ethanol and *n*-propanol have been used as alkylating agents of ketones. The reasons can be found in their lower reactivity, compared to the benzylic alcohols, or in the reaction temperatures applied that exceeded those of their boiling points. Ethanol and *n*-propanol were used in large excess because they are cheap and volatile, 4 equiv. was found to be the optimum amount for other alcohols. Phenethyl alcohol was another aliphatic primary alcohol tested in the alkylation of acetophenone to give 1,4-diphenylbutan-1-one in moderate yield (entry 3). Acetophenone was also subjected to the alkylation reaction with several benzylic alcohols. Thus, the reaction with benzyl alcohol furnished dihydrochalcone in high yield (entry 4), while moderate-to-good yields were obtained for 4-chlorobenzyl alcohol, 4-methoxybenzyl alcohol, and furan-2-ylmethanol (entries 5–7). Acetophenone derivatives bearing electron-donating or electron-withdrawing groups were also alkylated with benzyl alcohol. 4-(Trifluoromethyl)acetophenone reacted faster than 4-methoxyacetophenone due probably to the higher acidity of the methyl hydrogens in the former ketone (entries 8 and 9). It must be pointed out that 0% yield of the alkylated ketone in entry 8 was obtained by using the complex $RuCl_2(DMSO)_4$.[4] Interestingly, the alkylation reaction could be also applied to a variety of alkyl methyl ketones with benzyl alcohol, albeit the reaction with aliphatic non-benzylic alcohols failed. The reaction times and yields were shown to be dependent on the ketone structure. Thus, the linear alkyl-substituted methyl ketones (entries 10 and 11) reacted faster than the branched alkyl-substituted (entries 12 and 13), the best yield being achieved in the case of 5-methylhexan-2-one (entry 12). In those cases in which the yields were lower, the resulting ketones could be separated from the starting ketones by column chromatography, which, in addition, could be recovered. An attempt to dialkylate acetone with benzyl alcohol gave a mixture of the mono- and dialkylated ketones in 23 and 27% isolated yields, respectively (entry 14). Finally, the alkylation of the α,β-unsaturated ketone (*E*)-non-3-en-2-one with benzyl alcohol afforded the corresponding saturated alkylated ketone in good yield (entry 15). In this case, the

Table 1. Reaction of acetophenone with ethanol promoted by NiNPs in THF under different conditions.[a]



Entry	Ni [mmol]	Li [mmol]	EtOH	*T* [°C]	*t* [h]	Product [%][b] 3	4	1
1	1	2	2 mmol	76	4	28	47	21
2	1	2	4 mmol	76	15	52	37	10
3	1	2	8 mmol	76	15	55	43	–
4	1	2	4 mL	76	2	81	–	–
5	1	4	4 mL	76	2	67	23	–
6	0.1	2	4 mL	76	15	19	–	81
7	0.2	2	4 mL	76	15	45	–	55
8	1	2	4 mL	r.t.	24	7	–	77

[a] **1** (1 mmol) and **2** were added to a suspension of the NiNPs generated from $NiCl_2$, lithium powder, and a catalytic amount of DTBB (5%) in THF at room temp. [b] GLC yield.

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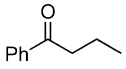
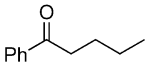
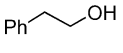
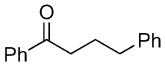
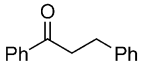
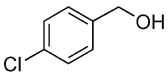
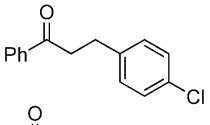
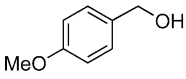
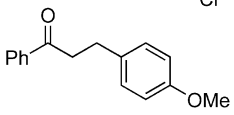
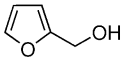
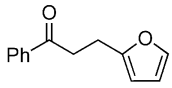
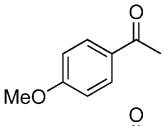
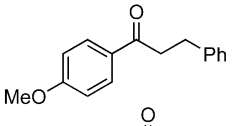
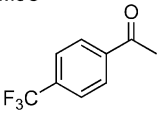
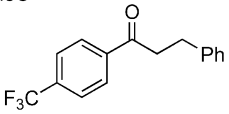
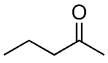
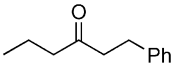
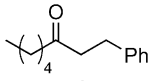
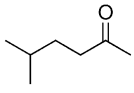
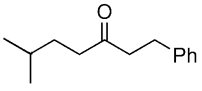
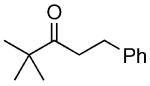
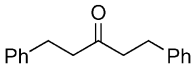
Table 2. α-Alkylation of ketones with primary alcohols promoted by Ni nanoparticles.[a]

Entry	Ketone	Alcohol	*t* [h]	Product	Yield[b] [%]
1		EtOH[c]	2		81 [66]
2		*n*PrOH[c]	2		84 [68]
3			4		68 [40]
4			6		92 [85]
5			7		70 [41]
6			8		84 [71]
7			6		53 [46]
8			6		77 [51]
9			3		71 [42]
10			8		[36]
11			6		52 [59]
12			20		96 [86]
13			24		56 [22]
14			4		[27][d]
15			3		78 [76]

[a] Ketone (1 mmol), alcohol (4 mmol), NiNPs (1 mmol), THF, 76 °C. [b] GLC yield, isolated yield in parenthesis. [c] 4 mL of alcohol. [d] The monoalkylation product 4-phenylbutan-2-one was isolated in 23% yield.

conjugate reduction in the expected product seems to be very favoured since it was observed even when using an equimolecular amount of the alcohol.

We tried to compare our ketone alkylation method with others previously reported in the literature.[3–7] The alkylation of acetophenone with benzyl alcohol was the only example commonly studied in all these reports. As it is shown in Scheme 1, our procedure led to a high isolated yield of dihydrochalcone under the mildest reaction conditions and in a relatively short reaction time. The fact that no over-reduced product was detected, together with the absence of any ligand, hydrogen acceptor, or added base, as well as the use of common THF as a solvent, are additional advantages. The alkylation of alkyl methyl ketones with aliphatic non-benzylic alcohols is, however, better accomplished with the palladium and iridium catalysts. Although the use of stoichiometric instead of catalytic amounts of nickel is a weakness of this methodology, we

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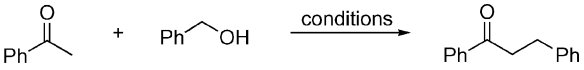
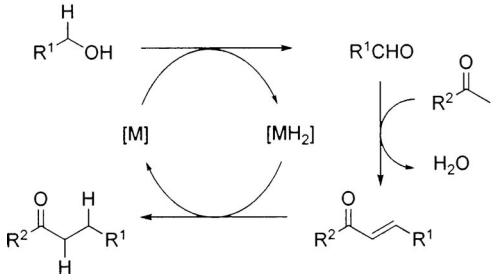
must take into account that nickel is 100-fold cheaper than ruthenium (referred to the corresponding chlorides, Aldrich), the latter being the cheapest noble metals shown below.



$RuCl_2(PPh_3)_3$, KOH, 1-dodecene, dioxane	80 °C, 20 h	82%[3a]
$[Ir(COD)Cl]_2$-PPh_3, KOH, solvent-free	100 °C, 4 h	86%[7]
Pd/C, KOH, 1-decene, dioxane	100 °C, 20 h	66%[3b]
Pd/AlO(OH), K_3PO_4, toluene	80 °C, 8 h	92%[5]
$RuCl_2(DMSO)_4$, KOH, dioxane	80 °C, 24 h	72%[4]
Pd/viologen, $Ba(OH)_2 \cdot H_2O$, 7 equiv. H_2O	100 °C, 24 h	82%[6]
NiNPs, THF	76 °C, 6 h	85%

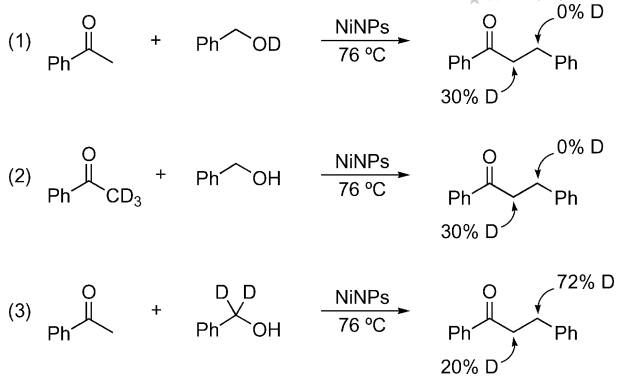
Scheme 1. Reaction of acetophenone with benzyl alcohol in different catalytic systems.

The reaction mechanism of the herein described reactions has been scarcely studied. In general, the α-alkylation of ketones with primary alcohols is formally explained by a sequence of reactions involving: (a) dehydrogenation of the alcohol to give the aldehyde and the metal dihydride, (b) base-promoted aldol condensation between the aldehyde and ketone, followed by dehydration, to furnish the α,β-unsaturated ketone, and (c) chemoselective reduction of the α,β-unsaturated ketone by hydrogen transfer from the metal dihydride giving the alkylated ketone (Scheme 2).[3,7]



Scheme 2. Formal mechanism for the α-alkylation of ketones with alcohols.

$RuCl_2(DMSO)_4$/KOH/dioxane is the only system for which the reaction mechanism has been studied in detail.[4b] Thus, based on deuteration experiments, the authors concluded that, after the aldol reaction, the reduction of the carbon–carbon double bond in the α,β-unsaturated ketone occurred through a Michael-type process involving a ruthenium enolate. In the case of our methodology with the NiNPs the scenario is quite different since the reaction is considered to take place under heterogeneous conditions, and consequently, it is more difficult to study. Nonetheless, we carried out a series of experiments with different deuterium-labelled components of the reaction that could provide any evidence about the reaction mechanism. In particular, we studied the reaction of acetophenone with benzyl alcohol-OD ($PhCH_2OD$), α,α,α-trideuterioacetophenone ($PhCOCD_3$) with benzyl alcohol, and acetophenone with α,α-dideuteriobenzyl alcohol ($PhCD_2OH$) under the above reaction conditions (Scheme 3).



Scheme 3. Deuterium labelling experiments in the α-alkylation of acetophenone with benzyl alcohol.

In the two first experiments, deuterium incorporation was only observed at the α-position of the carbonyl group in the product dihydrochalcone. Interestingly, the same deuterium percentage was obtained in both cases. From these results in can be inferred that, in spite of the fact that no external base was added, small amounts of the lithium metal used for the generation of the NiNPs could react with the alcohol, forming a catalytic amount of the corresponding alkoxide. This alkoxide could generate the acetophenone enolate, which by a fast deuteration (protonation) and deuterium-hydrogen scrambling would lead to an equilibration mixture. The fact that no deuterium incorporation was observed at the beta position of dihydrochalcone in the experiment with $PhCH_2OD$ is in agreement with the equilibration mixture being achieved for the starting ketone before the alkylation (see comments on the third experiment), together with the possibility of a primary isotopic effect in the scrambled alcohol dehydrogenation step.

In a third experiment, the alkylation of acetophenone with $PhCD_2OH$ yielded dihydrochalcone with 20 and 72% D incorporation at the α- and β-positions, respectively. This result is very much in agreement with the reaction mechanism depicted in Scheme 4. According to this mechanism, the oxidation of $PhCD_2OH$ would give the deuterated benzaldehyde PhCDO and nickel hydride-deuteride species. Aldol condensation followed by dehydration would lead to β-deuterated chalcone, which would undergo reduction by deuterium-hydrogen transfer from nickel. If we consider that statistically the two modes of addition of D-H to the carbon–carbon double bond are equally possible, then a 1:1 mixture of the regioisomeric dideuterated products would be obtained. The overall deuterium incorporation at the α- and β-positions of the product is very close to that observed experimentally. In view of these results, we can propose a general dihydride-type reaction mechanism in which the two hydrogen atoms of the alcohol (the α-C–H to the O atom and the O–H) become equivalent after being transferred to the metal. This proposal is consistent with the results obtained in the hydrogen-transfer reduction of carbonyl compounds promoted by NiNPs using 2-propanol as hydrogen donor, where the same type of mechanism was proposed.[17a]

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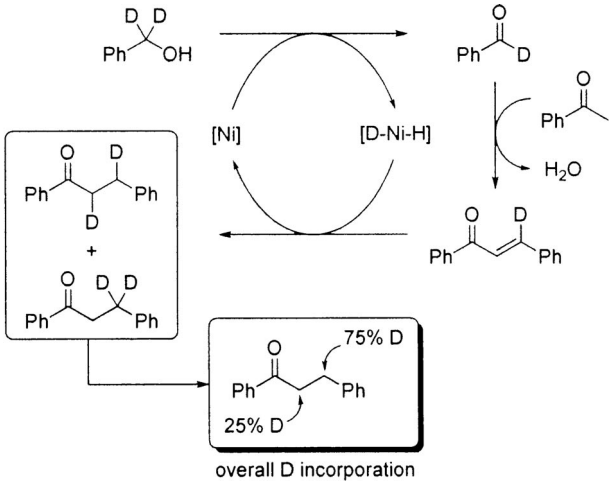


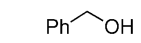
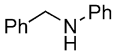
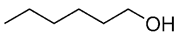
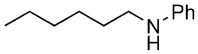
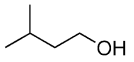
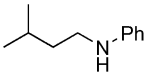
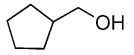
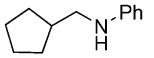
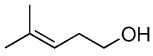
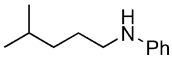
Scheme 4. Theoretical deuterium incorporation in the α-alkylation of acetophenone with $PhCD_2OH$ based on a dihydride-type mechanism.

Based on a similar type of chemistry, we also studied the reactivity of the NiNPs in the indirect aza-Wittig reaction. In this case, a series of primary alcohols were treated with commercially available *N*-(triphenylphosphoranylidene)aniline, under similar reaction conditions as those described for the α-alkylation of ketones (Table 3). In general, longer reaction times were needed to afford the corresponding *N*-alkylanilines in modest yields. A variety of representative primary alcohols were studied, benzyl alcohol reacting faster probably due to the more favoured formation of the intermediate benzaldehyde (entry 1). Other substrates such as linear alkyl- (entries 2 and 3), branched alkyl- (entry 4), or cycloalkyl-substituted (entry 5) alcohols gave the expected secondary amines in isolated yields around 50%. In the case of 4-methylpent-3-en-1-ol, the saturated alkyl-substituted *N*-(4-methylpentyl)aniline was obtained (entry 6). It is worthy of note that, so far, this type of reaction had only been reported under iridium catalysis.[9] Although the yields achieved with the NiNPs are lower than those with complex $[IrCl(COD)]_2$, the substrate scope is wider, the reaction conditions are milder and the reaction system is simpler.

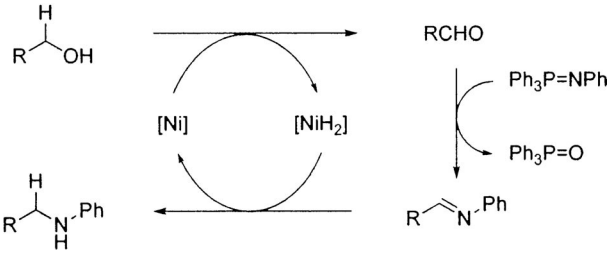
Based on the above mechanistic proposal, a similar reaction pathway can be invoked for the indirect aza-Wittig reaction (Scheme 5). In this case, the in situ generated aldehyde would undergo an aza-Wittig reaction with *N*-(triphenylphosphoranylidene)aniline to give the corresponding imine. Trace amounts of the imine have been detected in some of the experiments. Reduction of the imine by hydrogen transfer from the alcohol mediated by the NiNPs would provide the expected *N*-alkylated aniline. The transfer hydrogenation of imines, generated in situ from amines and aldehydes (reductive amination), has been recently reported by us under the catalysis of NiNPs and using 2-propanol as a hydrogen source.[18]

Finally, we compared the reactivity of the NiNPs with two common and commercially available nickel catalysts, Raney Ni and Ni/Al_2O_3, in the above described reactions.

Table 3. Indirect aza-Wittig reaction of alcohols with *N*-(triphenylphosphoranilidene)aniline.[a]

Entry	Alcohol	t [h]	Product	Yield[b] [%]
1		2		45
2	EtOH[c]	15		45
3		30		56
4		15		50
5		30		40
6		20		35

[a] Alcohol (1 mmol), Ph_3P=NPh (1.1 mmol), NiNPs (1 mmol), THF, 76 °C. [b] Isolated yield. [c] 2 mmol of EtOH were used.



Scheme 5. General reaction pathway for the indirect aza-Wittig reaction of alcohols with *N*-(triphenylphosphoranylidene)aniline.

The starting materials were recovered unchanged in the alkylation reaction of acetophenone with benzyl alcohol, either with Raney Ni or with Ni/Al_2O_3, under the reaction conditions reported for the NiNPs (THF, 76 °C, 24 h). A mixture of products, including aniline (8%), the starting alcohol (56%), the corresponding imine (4%) and amine (2%), was obtained in the indirect aza-Wittig reaction of benzyl alcohol with *N*-(triphenylphosphoranylidene)aniline using Raney Ni, whereas no reaction was observed with Ni/Al_2O_3.

Conclusions

We have reported, for the first time, the use of nickel for the activation of primary alcohols in the α-alkylation of ketones and in the indirect aza-Wittig reaction. The nickel metal used, in the form of nanoparticles, has shown to be a potential alternative in these reactions to noble-metal catalysts such as those derived from palladium, ruthenium, or iridium. A variety of acetophenones have been successfully alkylated with aliphatic and benzylic alcohols to give the corresponding products in moderate-to-high yields. It is noteworthy that ethanol and *n*-propanol have been used for the first time as alkylating agents in this reaction. The alky-

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lation of alkyl methyl ketones was, in general, less efficient and could only be applied to benzylic alcohols. The NiNPs have also found application in the indirect aza-Wittig reaction of alcohols with an iminophosphorane, leading to *N*-alkylated anilines in moderate yields but with a wider substrate scope, milder reaction conditions, and simpler reaction system than under iridium catalysis. Deuterium labelling experiments have brought some evidence about a dihydride-type reaction mechanism operating in these reactions. Furthermore, the NiNPs have shown to be superior to other common nickel catalysts in the two processes described herein, which, in addition, proceed in the absence of any hydrogen acceptor, ligand, or added base.

Experimental Section

General Remarks: Anhydrous nickel(II) chloride (Aldrich), lithium powder (MEDALCHEMY S. L.), and DTBB (4,4′-di-*tert*-butylbiphenyl, Aldrich) were commercially available. All the starting materials were commercially available of the best grade (Aldrich, Acros, Alfa Aesar) and were used without further purification. THF was directly used without any purification (Fluka, 99.9%). All reactions were carried out under an Ar atmosphere. Benzyl alcohol-OD ($PhCH_2OD$) was prepared by stirring benzyl alcohol with an excess of deuterium oxide for 1 h, followed by extraction with diethyl ether, drying with anhydrous magnesium sulfate and solvent evaporation. α,α,α-Trideuterioacetophenone ($PhCOCD_3$) was prepared by hydrogen-deuterium exchange with D_2O in the presence of KOH at room temperature.[20] α,α-Dideuteriobenzyl alcohol ($PhCD_2OH$) was prepared by reduction of methyl benzoate with lithium aluminum deuteride in THF at 0 °C.[21] Flash column chromatography was performed using silica gel 60 of 40–60 microns.

General Procedure for the α-Alkylation of Ketones with Primary Alcohols: Nickel(II) chloride (130 mg, 1 mmol) was added over a suspension of lithium (14 mg, 2 mmol) and DTBB (13 mg, 0.05 mmol) in THF (2 mL) at room temperature under argon. The reaction mixture, which was initially dark blue, changed to black indicating that the NiNPs suspension was formed. After 10 min, the corresponding alcohol (4 mmol for benzyl alcohols, 4 mL for EtOH and *n*-PrOH) and the ketone (1 mmol) were consecutively added. The reaction mixture was warmed up to 76 °C and monitored by GLC-MS until total or steady conversion of the starting material. The resulting suspension was diluted with Et_2O (20 mL), filtered through a pad containing celite, and the filtrate was washed with 2 M HCl (2 × 20 mL) and dried with $MgSO_4$. The residue obtained after removal of the solvent (15 Torr) was purified by column chromatography (silica gel, hexane/EtOAc) to give the pure alkylated ketone.

Butyrophenone, valerophenone, and 4-phenylbutyrophenone were characterised by comparison of their physical and spectroscopic data with those of commercially available samples (Aldrich). 1,3-Diphenylpropan-1-one,[3b] (4-chlorophenyl)-1-phenylpropan-1-one,[22] 3-(4-methoxyphenyl)-1-phenylpropan-1-one,[22] 3-(furan-2-yl)-1-phenylpropan-1-one,[22] 1-(4-methoxyphenyl)-3-phenylpropan-1-one,[23] 1-(4-trifluoromethylphenyl)-3-phenylpropan-1-one,[24] 1-phenylhexan-3-one,[25] 1-phenyloctan-3-one,[26] 6-methyl-1-phenylheptan-3-one,[27] 1-phenyl-4,4-dimethylpentan-3-one,[28] 1,5-diphenylpentan-3-one,[22] and 1-phenyldecan-3-one,[6] were characterised by comparison of their physical and spectroscopic data with those described in the literature.

General Procedure for the Indirect Aza-Wittig Reaction of Alcohols with *N*-(Triphenylphosphoranilidene)aniline: *N*-(Triphenylphosphoranilidene)aniline (389 mg, 1.1 mmol) and the corresponding alcohol (1 mmol) were consecutively added to the NiNPs suspension, prepared as described for the α-alkylation of ketones. The reaction mixture was warmed up to 76 °C and monitored by GLC-MS until total or steady conversion of the starting material. The resulting suspension was diluted with Et_2O (20 mL), filtered through a pad containing celite, and the filtrate was dried with $MgSO_4$. The residue obtained after removal of the solvent (15 Torr) was purified by column chromatography (silica gel, hexane/EtOAc) to give the pure *N*-alkylaniline.

N-Benzylaniline, *N*-ethylaniline, *N*-hexylaniline, and *N*-isopentylaniline were characterised by comparison of their physical and spectroscopic data with those of commercially available samples (Aldrich). *N*-(Cyclopentylmethyl)aniline[29] and *N*-(4-methylpentyl)-aniline[30] were characterised by comparison of their physical and spectroscopic data with those described in the literature.

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