Facile Hydrodehalogenation with H₂ and Pd/C Catalyst under Multiphase Conditions. 3. Selective Removal of Halogen from Functionalized Aryl Ketones. 4. Aryl Halide-Promoted Reduction of Benzyl Alcohols to Alkanes

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Operating in a two-phase system [apolar organic solvent and 50% KOH(aq)] at 50 °C, using 5% Pd/C and H₂ at atmospheric pressure, the reduction of halogenated aromatic ketones and benzylic alcohols is considered. In the case of the ketones, the reaction is strongly influenced by the presence of an onium salt, while for the alcohols, the reduction occurs only if an aromatic halide is added as a promoter. In particular, in the presence of Aliquat 336 (methyltricaprylammonium chloride), halogenated ketones are selectively dehalogenated: for instance, in isooctane solvent, 4-chloropropiophenone, 4-bromoacetophenone, and 4,4'-dichlorobenzophenone give the corresponding ketones with selectivity ≥ 95%. No reduction of the carbonyl group is observed. If no onium salt is used, alkylbenzenes are the sole products as occurs when the reduction is carried out over Pd/C in an ethanolic solution under classical conditions. Likewise, the reduction of primary, secondary, and tertiary benzylic alcohols to their corresponding hydrocarbons expressly requires the presence of aromatic halides; these latter undergo a simultaneous hydrodehalogenation to the respective hydrocarbon (for example, *o*-dichlorobenzene to benzene). In the absence of the halide promoter, the reaction takes place only if a halogen is present in the aromatic ring of the alcohol: that is, if haloaryl alcohols are the starting reagents. In this case the halogen is quickly removed from the substrate, so that the corresponding aromatic hydrocarbons are the sole final products.

Introduction

We have previously reported[1,2] that by operating in a multiphase system composed by an aqueous phase and an insoluble hydrocarbon, a facile hydrodehalogenation of aromatic halides occurs at low temperatures (20 or 50 °C) using a Pd/C catalyst and H₂ at atmospheric pressure. Under such conditions, we also reported[2,3] that the presence of a quaternary onium salt allows a remarkable selectivity in the removal of different halogens from the same aromatic ring with both Pd/C and Raney-Ni as catalysts. In addition, sterically hindered alkyl halides [PCB mixture (Aroclor 1254) and tetrachloro-*m*-xylene] are also quickly reduced to the corresponding aromatic hydrocarbons.
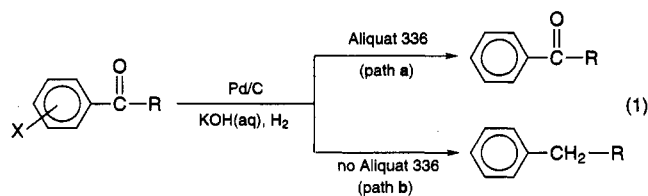
In order to test the applicability of the method with other substrates carrying different functional groups (the reduction of halonitro compounds to amines being already reported by us[1]), we began to investigate the reduction of halogenated (and unhalogenated) aromatic ketones and alcohols.

The dehalogenation and simultaneous reduction of the carbonyl group of halogen-functionalized ketones to give the corresponding aromatic hydrocarbons is well know in literature.[4] In particular, under classical conditions using methanol or ethanol as solvents[5] and 10% Pd/C as the catalyst, the reaction proceeds without any selectivity

either in the halogen removal or in the exclusive reduction of the carbonyl group; that is, no unhalogenated ketones or halogenated alkyl benzenes may be selectively obtained. Aromatic hydrocarbons are the sole final products.

Also, halogenated and unhalogenated benzylic alcohols can be promptly reduced over Pd/C to the corresponding aromatic hydrocarbons.[6]

We report here that operating in a two-phase system, in the presence of Aliquat 336 [(C₈H₁₇)₃N⁺CH₃Cl⁻; methyltricaprylammonium chloride], the reduction of halogenated aromatic ketones over Pd/C in H₂ at atmospheric pressure, affords selectively pure aromatic ketones. Only the dehalogenation takes place while the carbonyl group is kept unchanged (eq 1, path **a**). In contrast, when operating without Aliquat 336 the product is the corresponding alkyl benzene (path **b**)

$$X = Cl \text{ and } Br$$
$$R = -CH_3, -CH_2CH_3, Ph$$

Moreover, under the same multiphase conditions, only haloaryl alcohols afford the corresponding aromatic

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(2) Marques, C. A.; Selva, M.; Tundo, P. *J. Org. Chem.* **1994**, *59*, 3830 (part 2).
(3) Marques, C. A.; Selva, M.; Tundo, P. *J. Mol. Catal.* **1994**, in press.
(4) Mitchell, H.; Lai, Yee-Hing *Tetrahedron Lett.* **1980**, *21*, 2637.
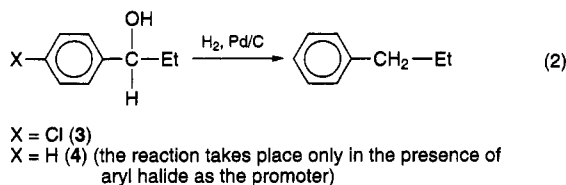(5) Burdeska, K. *Synthesis* **1982**, 940.
(6) Hartung, W. H. *Org. React.* **1953**, *7*, 263 and cited therein references.

Table 1. Hydrodehalogenation of 4-Chloropropiophenone (1) with Pd/C Catalyst under Different Reaction Conditions[a]

entry	Aliquat 336	solvent	T (°C)	t (min)	% conv	PhPr	PhCOEt	4-ClC$_6$H$_4$CH(OH)Et	C$_6$H$_4$CH(OH)Et
1	yes	ethanol[c]	50	15	58	50		8	
				50	100	96		4	
2	no	ethanol[c]	50	10	86	80		6	
				45	99	96		3	
3	yes	isooctane	50	10	86		85		1
				30[d]	100		96		4
4	no	isooctane	50	15	95	94	1		
				25	99	98			1
5	yes	n-pentane	30	20	66		65		1
				45[e]	100		99		1
6	no	n-pentane	30	10	40	35	1		4
				40	100	72	3		25

[a] All reactions were carried out using 7.0 mL of organic solution 0.07 M (0.49 mmol of ketone), 0.032 g (0.0015 mmol) of 5% Pd/C, and 0.085 g (0.20 mmol) of Aliquat 336; molar ratio Pd/Cl 0.031. [b] By gas chromatography. [c] KOH(aq) was replaced by 4.0 mL of ethanol. [d] After 60 min, propiophenone (85), 1-phenyl-1-propanol (15). [e] After 90 min, propiophenone (90), 1-phenyl-1-propanol (10).

hydrocarbons; instead, unhalogenated alcohols are reduced only in the presence of an aryl halide as promoter (eq 2)

X = Cl (3)
X = H (4) (the reaction takes place only in the presence of aryl halide as the promoter)

Results and Discussion

All reactions were carried out in a 25-mL three-necked flask equipped with a condenser and a system for the bubbling of hydrogen.

If not otherwise indicated, they were carried out on 7.0 mL of an isooctane solution of the substrate (0.49 mmol) to be reduced, 4.0 mL of 50% KOH aqueous solution, 0.032 g of 5% Pd/C (0.015 mmol of Pd), and 0.085 g of Aliquat 336 (0.20 mmol). (In the case of benzylic alcohols, no onium salt was used; in fact, when operating with or without Aliquat no appreciable differences were observed.)

Hydrogen was bubbled at atmospheric pressure through the organic phase at a rate of about 1 mL/min; as previously reported,[2] under such conditions, the reaction rates do not depend on the H$_2$ inlet.

The reaction flask was thermostated at 50 ± 0.1 °C (if not otherwise indicated), and the mixture was magnetically stirred at 1000 rpm with a bar 2.5 cm in length and 0.6 cm in diameter.

The reaction course was followed by gas chromatography. Conversions are referred to the internal standard (n-decane).

At first, the reaction of 4-chloropropiophenone 1 was investigated. The results are reported in Table 1. Different solvents and reaction conditions are considered: the reaction being carried out in (i) a classic homogeneous solution (ethyl alcohol; entries 1 and 2); (ii) a two-phase system [aqueous solution—apolar solvent (isooctane and n-pentane); entries 3–4 and entries 5–6, respectively], either with or without Aliquat 336.

In the absence of the onium salt, no selectivity is observed; operating both in ethyl alcohol and in a two-phase system, propylbenzene is always the sole product (entries 2, 4, and 6). Instead, only in the presence of Aliquat 336 under biphasic conditions, the reaction gives
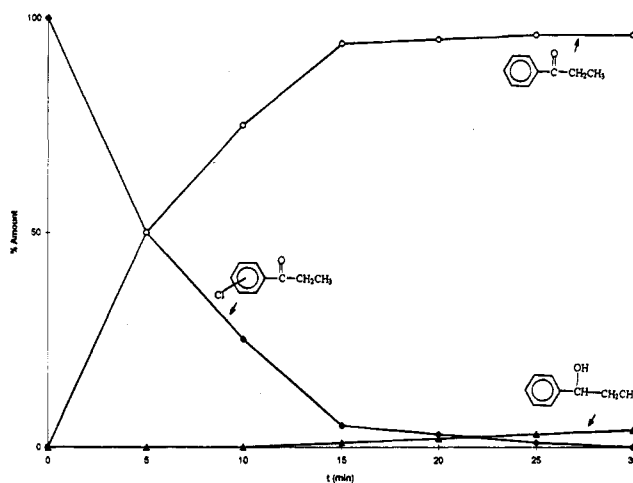
Figure 1. Selective dehalogenation of p-chloropropiophenone to propiophenone with Pd/C catalyst at 50 °C, in the presence of Aliquat 336, in isooctane (from entry 3, Table 1).
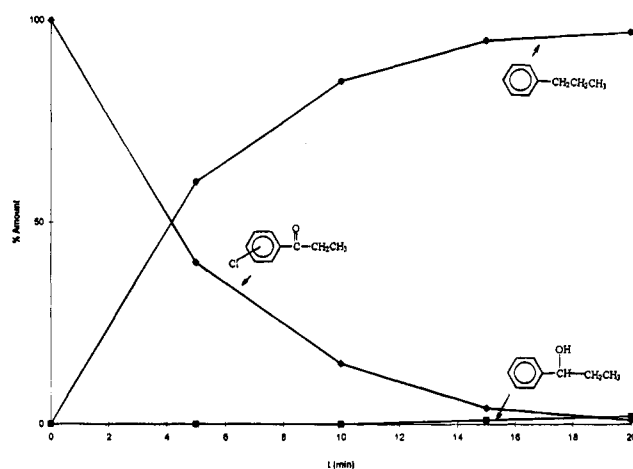
Figure 2. Hydrodehalogenation of p-chloropropiophenone to n-propylbenzene with Pd/C catalyst at 50 °C, without Aliquat 336, in isooctane (from entry 4, Table 1).

the dehalogenated propiophenone in a high yield (entries 3 and 5). Of course, by increasing the reaction time the ketone formed reacts further to give 1-phenyl-1-propanol (entry 3, footnote d and entry 5, footnote e).

The more significant results of Table 1 are shown in Figures 1 and 2; the different selectivities in the reactions of 4-chloropropiophenone (1) under multiphase conditions with and without Aliquat 336 are well depicted.

Table 2. Hydrogenation of Propiophenone (2) and Benzophenone with Pd/C Catalyst under Different Reaction Conditions[a]

entry	substrate	Aliquat 336	solvent	T (°C)	t (min)	conv (%)	products (% yield)[b]
1	propiophenone	yes	isooctane	50	30	15	1-phenyl-1-propanol (15)
					(120)	(60)	1-phenyl-1-propanol (60)
2	propiophenone	no	isooctane	50	90	100	1-phenyl-1-propanol (100)
3	propiophenone	yes	*n*-pentane	30	120	3	1-phenyl-1-propanol (3)
4	propiophenone	no	*n*-pentane	30	120	46	1-phenyl-1-propanol (46)
					(180)	(70)	1-phenyl-1-propanol (70)
5	propiophenone	yes	ethanol[c]	50	50	100	propylbenzene (98); 1-phenyl-1-propanol (2)
6	propiophenone	no	ethanol[c]	50	60	100	propylbenzene (96); 1-phenyl-1-propanol (4)
7	benzophenone	yes	isooctane	50	60	0[d]	
8	benzophenone	no	isooctane[e]	50	90	10	diphenylcarbinol (10)

[a] Hydrogenation was always carried out using 5% Pd/C and H_2 at atmospheric pressure, under the same conditions of Table 1. Entries 1–6, 7 and 8: organic solutions (7.0 mL) were 0.07 M and 0.035 M, respectively (0.49 mmol of propiophenone and 0.245 mmol of benzophenone, respectively). [b] Entries 1–4: *n*-propylbenzene was never formed. [c] KOH(aq) was replaced by 4.0 mL of ethanol. [d] No reaction was observed at all.

Table 3. Aromatic Ketones from Selective Hydrodehalogenation of the Corresponding Halogenated Derivatives[a]

entry	substrate	Aliquat 366	t (min)	% conv	products[b] (% yield)			
					ketone	alkane	alcohol	haloalcohol
1	4-bromoacetophenone	yes	15	70	68		2	
			45	100	98		2[c]	
2	4-bromoacetophenone	no	15	30	4	25	1	
			45	100		98	2	
3	2-bromoacetophenone	yes	10	96	95		1[d]	
4	2-bromoacetophenone	no	10	80	58	9	13	
			45	100		97	3	
5	3-chloropropiophenone	yes	10	94	93		1	
			20	100	98		2	
6	3-chloropropiophenone	no	15	82		75	10	2
			30	100		94	6	
7	4,4′-dichlorobenzophenone	yes	15	88	12			66
			30	100	100[e]			
8	4,4′-dichlorobenzophenone	no	30	70	5	3	30	32
			30	100	4	7	88	1[f]

[a] For reaction conditions see Experimental Section: all reactions were carried out at 50 °C using 7.0 mL of an isooctane solution. Entries 1–6, 7 and 8: organic solutions were 0.07 M and 0.035 M (0.49 mmol and 0.245 mmol of the corresponding ketones) with molar ratio Pd/Cl: 0.031 and 0.016, respectively. [b] Ketone, PhCOR; alkane, PhCH$_2$-R; alcohol, PhCH(OH)R (R= CH$_3$, CH$_2$CH$_3$ and Ph in entries 1–4, 5 and 6, and 7 and 8, respectively; haloalcohol, XC$_6$H$_4$CH(OH)R (X= 3-Cl, R= CH$_2$CH$_3$ in entries 5 and 6; X= 4-Cl, R= Ph in entries 7 and 8). [c] After 180 min: 1-phenyl-1-ethanol (32). [d] After 90 min: acetophenone (90); 1-phenyl-1-ethanol (10). [e] After 60 min: benzophenone (90); diphenylcarbinol (10). [f] After 12 h: diphenylmethane (53); diphenylcarbinol (47).

In order to investigate the selectivity observed in Table 1, the reduction of propiophenone (**2**) and benzophenone was carried out in different solvents, either in the presence or in the absence of Aliquat 336. The results are reported in Table 2.

Under multiphase conditions in hydrocarbon solvents, the ketones only give the corresponding alcohols; that is, the reduction of the carbonyl group proceeds selectively to the alcohol formation and no aromatic hydrocarbons are observed (entries 1–4 and 8). However, in the presence of Aliquat 336, the reaction is slowed down considerably (entries 1–2 and 3–4) or even inhibited completely (for benzophenone entries 7–8).

These results agree with those reported in entries 3 and 5 of Table 1; in fact, the presence of the onium salt also lowers the reduction rate of the halo ketone, so that both the corresponding alcohol and the alkyl benzene formation are practically avoided. However, an important difference arises: when operating in the multiphase system, **1** is promptly dehalogenated to **2** (with only a trace amount of the corresponding alcohol: entries 3 and 5, Table 1) or reduced to propylbenzene (entries 4 and 6, Table 1); instead, the reduction of the **2** always selectively gives the alcohol (entries 1–4, Table 2).

On the contrary, under a classical ethanolic phase, **2** is reduced to propylbenzene (entries 5 and 6).

Table 3 shows the general feature of this reaction. In the presence of Aliquat 336, other halogenated ketones are selectively dehalogenated to the corresponding aro-

matic ketones (with selectivity ≥ 95%) using Pd/C under multiphase reaction conditions.

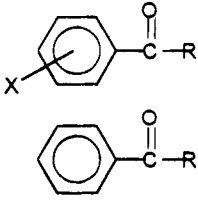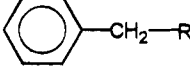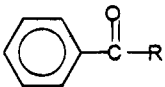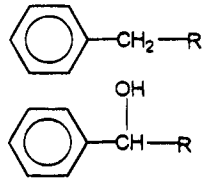The results obtained in the reaction of the ketones are summarized in Scheme 1.

As mentioned before, the fact that the halogenated ketone **1** gives propylbenzene, while the ketone **2** gives the alcohol 1-phenyl-1-propanol (entries 4 and 6, Table 1 and 1–4, Table 2), prompted us to further investigate this unexpected behavior. Thus, we studied the reduction of halogenated and unhalogenated benzylic alcohols, these compounds being intermediates of the reaction of the corresponding ketones.

Table 4 reports the results obtained in the reduction of 1-(4-chlorophenyl)-1-propanol (**3**) and 1-phenyl-1-propanol (**4**). Different reaction conditions are considered: in particular, both classical (in ethanol solvent) and two-phase conditions (in isooctane–water biphasic system) have been explored.

Under both conditions, the reduction of the haloaryl alcohol **3** gives only propylbenzene in a high yield, with just a trace amount of the dehalogenated alcohol **4** (entries 1 and 3, Table 4).

Instead, a significant difference is observed in the reaction of compound **4**; in fact, while in ethanol solvent the reduction still gives propylbenzene as the sole product (entry 2, Table 4), under the biphasic conditions (isooctane/H$_2$O) no reduction occurs at all (entries 4, Table 4). Surprisingly, when an equimolar mixture of the alcohols **3** and **4** is reacted, a quick hydrogenation

Scheme 1. Product Selectivity in the Reduction of Aromatic Ketones under Different Reaction Conditions[a]

Substrates	Products		
	In ethanol	In hydrocarbon solvent	
	with and without Aliquat 336	with Aliquat 336	without Aliquat 336

[a] X = Cl or Br; R = −CH₃ −CH₂CH₃, Ph.

Table 4. Reduction of Benzylic Alcohols and Aromatic Ketones under Different Reaction Conditions[a]

entry	substrate (no.)	solvent	t (min)	% conv	products (% yield)
1	3	ethanol	20	100	propylbenzene (96); 1-phenyl-1-propanol (4)[b]
2	4	ethanol	15	100	propylbenzene (96); 1-phenyl-1-propanol (4)[b]
3	3	isooctane	50	100	propylbenzene (96); 1-phenyl-1-propanol (4)
4	4	isooctane	120	2	propylbenzene (2)
5	3 + 4[c]	isooctane	90	100	propylbenzene[d]
6	1	ethanol	45	99	propylbenzene (98); 1-phenyl-1-propanol (2)[b]
7	2	ethanol	50	100	propylbenzene (97.5); 1-phenyl-1-propanol (2.5)[b]
8[e]	1	isooctane	25	99	propylbenzene (98); 1-phenyl-1-propanol (1)
9[f]	2	isooctane	90	100	1-phenyl-1-propanol (100)

[a] For reaction conditions, see Experimental Section. All reactions were carried out at 50 °C, using 5% Pd/C as the catalyst. A 0.07 M solution (7.0 mL) of the substrate in ethanol or isooctane was employed. [b] The KOH solution was replaced by 4.0 mL of ethanol. [c] Compounds 3 and 4 were used in a 1:1 molar ratio. [d] The calculation of the yield was not possible with respect to compound 3 (or 4); in fact, both compounds 3 and 4 formed n-propylbezene. [e,f] These results are also reported in entry 4, Table 1 and entry 3, Table 2.

of both compounds is observed, along with a simultaneous dehalogenation of 4; propylbenzene is the final product (entry 5, Table 4).

For a convenient comparison, Table 4 also reports the reduction of 1 and 2; both multiphase and classical conditions (ethanol solvent) are considered (entries 8–9, Table 4; see also entries 3–4, Table 1 and 1–2, Table 2).

These results clearly suggest that, under our multiphase conditions, the alcohol reduction can actually take place only if chlorine is present as a substituent in an aromatic ring; otherwise, the reaction is inhibited. In addition, the aromatic chlorine may come from a molecule which is not the alcohol to be reduced; in fact, 1-phenyl-1-propanol (4) is promptly reduced to propylbenzene when 1-(4-chlorophenyl)-1-propanol (3) is added to the reaction mixture (entry 5, Table 4).

A further support to this consideration comes from Figure 2, where it may be clearly seen that in the reduction of 4-chloropropiophenone, the intermediate alcohol, 1-phenyl-1-propanol, accumulates in detectable quantities only after the chlorinated aryl ketone is nearly consumed. Actually, this may be due to the fact that the chlorinated aryl ketone may act as a promoter for the reduction of the alcohol. (Authors with to thank a referee for this suggestion.)

Bearing this in mind, we considered the possibility of a general utilization of aryl halides as promoters in the reduction of benzyl alcohols to aromatic hydrocarbons. Thus, operating under multiphase conditions (isooctane/H₂O), the reduction of 4 was carried out by using a number of different aryl halides as promoters. Table 5 reports the results.

The reduction of the alcohol 4 to propylbenzene proceeds with all the tested aryl halides while these latter are simultaneously hydrodehalogenated to the corresponding aromatic hydrocarbons. Better results are obtained with chlorobenzene and o-dibromo- and o-dichlorobenzene which can also be used in catalytic amounts (alcohol–halide in a 1:0.2 molar ratio, respectively; entries 6–8). 2-Chloro-p-xylene is also an efficient promoter of the alcohol reduction when a stoichiometric amount is employed (entries 3–5).

In any case, as soon as the sacrificial aryl halide is completely comsumed during the reaction, the reduction of 4 stops immediately. This is shown for example, when o-dibromobenzene is used as the promoter. After 90 min of reaction, the alcohol conversion stopped at 86% when the aromatic halide was totally reacted (entry 7). Likewise, in the case of chlorobenzene, the complete disappearance of the promoter stopped the reaction at 94% conversion. However, the alcohol reduction can be promptly started again and completed by adding the same or another halide promoter (see for example, entry 3, Table 6).

Also, alkyl halides may be used as promoters in the reduction of 4, but the reaction time becomes much longer; for example, when a catalytic amount of 1-bromooctadecane was used, the alcohol conversion is 78% after 480 min of reaction (entry 9).

Under multiphase reaction conditions in the presence of o-dichlorobenzene, the reduction of different benzyl alcohols was also carried out; in particular, primary, secondary, and tertiary alcohols were considered. Table 6 reports the results.

Table 5. Reduction of 1-Phenyl-1-propanol (4) to n-Propylbenzene under Multiphase Conditions Using Different Aromatic Halides as Promoters (P)[a]

entry	promoter (P)[b]	molar ratio (4:P)	t	conv (%)	products (% yield)
1	p-chloroethylbenzene	1:1	360	(4) 100	propylbenzene (100)
				(P) 70	ethylbenzene (70)
2	2-chloro-m-xylene	1:1	150	(4) 44	propylbenzene (44)
				(P) 7	m-xylene (7)
3	2-chloro-p-xylene	1:1	60	(4) 98	propylbenzene (98)
				(P) 12	p-xylene (12)
4	2-chloro-p-xylene	1:0.1	420	(4) 90	propylbenzene (90)
				(P) 81	p-xylene (81)
5	2-chloro-p-xylene	1:0.2	270	(4) 99	propylbenzene (99)
				(P) 68	p-xylene (68)
6	o-dichlorobenzene	1:0.2	60	(4) 98	propylbenzene (98)
				(P) 100	benzene (100)
7	o-dibromobenzene	1:0.2	10	(4) 40	propylbenzene (40)
				(P) 99	benzene (84); bromobenzene (15)
			90[c]	(4) 86	propylbenzene (86)
				(P) 100	benzene (100)
8	chlorobenzene	1:0.2	10	(4) 91	propylbenzene (91)
				(P) 83	benzene (83)
			30[c]	(4) 94	propylbenzene (94)
				(P) 100	benzene (100)
9	1-bromooctadecane	1:0.2	180	(4) 35	propylbenzene (35)
				(P) 35	octadecane (35)
			480	(4) 78	propylbenzene (78)
				(P) 51	octadecane (51)

[a] All reactions were carried out at 50 °C, using 5% Pd/C; a 0.07 M isooctane solution of 4 was always employed. The molar ratio Pd/A was 0.031. [b] A total of 7.0 and 3.0 mL of isooctane solution of the promoters were added (entries 1-3 and 4-9, respectively). [c] After 120 min and 60 min, the % amount of propylbenzene was unchanged: 86 and 94%, respectively.

Table 6. Reduction of Different Benzylic Alcohols under Multiphase Conditions Using o-Dichlorobenzene as the Promoter (P)[a,b]

entry	substrate (A)	t (min)	conv (%)	products (% yield)
1	2-phenyl-2-propanol	60	(A) 100	2-phenylpropane (100)
			(P) 100	benzene (100)
2	benzyl alcohol	420	(A) 91	toluene (91)
			(P) 70	benzene (68); chlorobenzene (2)
3	diphenylcarbinol	300[c]	(A) 60	diphenylmethane (60)
			(P) 100	benzene (100)
		540	(A) 94	diphenylmethane (94)
			(P) 50	benzene (50)

[a] All reactions were carried out at 50 °C, using 5% Pd/C. Entries 1-2 and entry 3: 0.07 M and 0.035 M isooctane solution of the substrates were employed, respectively. For reaction conditions, see Experimental Section. The substrate and promoter were used in a 1:0.2 molar ratio. [b] No reduction takes place at all if no promoter was added. [c] After 300 min, o-dichlorobenzene was furtherly added: the final substrate/promoter molar ratio was 1:0.4.

All the tested alcohols give the corresponding hydrocarbons, although in the case of diphenyl carbinol, the higher steric hindrance results in a prolonged reaction time (entry 3). However, if the tertiary and secondary alcohols have only one aryl group, they react much more rapidly than the primary ones (compare entry 6 in Table 5 and entry 1 in Table 6 with entry 2 in Table 6).

Scheme 2 summarizes the results obtained in the reduction of compounds **3** and **4**.

Conclusions

Aryl Ketones. When operating in a two-phase system, Aliquat 336 plays a decisive role in the dehalogenation of the haloaromatic ketones; a selective removal of halogen(s) from the aromatic ring occurs without any reduction of the carbonyl group. This effect may be due to the fact that, as we previously reported,[2] in an apolar solvent, the polar onium salt is adsorbed on the surface of the metal catalyst and thus may constitute the medium in which the reaction actually takes place.

In this way, the presence of the onium salt influences both the reaction outcome and selectivity.

Instead, this effect is lost in ethanol, where the complete solubility of the Aliquat 336 in the solvent results in the lack of its peculiar adsorption on the Pd/C surface.

Benzylic Alcohols. Under multiphase conditions (apolar solvent–aqueous alkaline solution), the presence of an aromatic halide is expressly required for the Pd-catalyzed reduction of benzylic alcohols to the respective aromatic hydrocarbons. However, the role of the aryl halides in the reaction mechanism remains an open question.

To our knowledge, this is the first time that the reduction of benzyl alcohols over Pd/C is promoted by an aryl halide. The reaction seems to proceed through a preliminary oxidative addition of the aryl halide over Pd/C.[7-10] However, it is not clear why the promoter can be used in small amounts (alcohol/promoter in a 1:0.2 molar ratio) and why the easier the aryl halide reduction is, the easier the reduction of the alcohols is as well.

As previously reported,[1,2] the steric hindrance of the aryl halides plays a decisive role in the hydrodehalogenation rate, but it is still not well understood how this may influence the alcohol reduction. From a mechanistic point of view, this reaction certainly requires a more detailed study; in fact, the action of sacrifical aryl halides
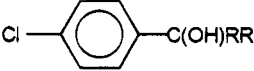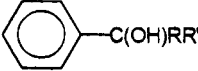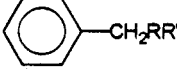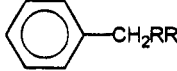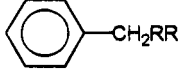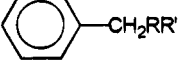
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Scheme 2. Product Selectivity in the Reduction of Aromatic Alcohols under Different Reaction Conditions[a]

[a] R = H, R′ = –CH$_2$CH$_3$; R = R′ = H; R = R′ = –CH$_3$; R = H, R′ = Ph.

may open the way to new investigation and utilizations of the Pd/C catalyst.

Despite the different nature of the aromatic ketones and alcohols, their Pd-catalyzed reduction here reported represents a significant example of a marked change in selectivity caused by the addition of an inhibitor (Aliquat 336), or of promoters (aryl halides).

From a synthetic point view, these results may open the way to a new approach in organic synthesis for the utilization of halogens in aromatic rings as protective groups for functionalized aromatic ketones adding new perspectives in the selective reduction of benzylic alcohols.

Experimental Section

All reagents and solvents were ACS grade and were used without further purification. The 5% Pd/C was from Fluka, Art. No. 75992; its surface area was 700–800 m^2/g. GC analyses were performed on a Varian GC 3400 using a fused silica capillary column (30 m × 0.25 mm) with SPB-5 as the liquid phase (film thickness 0.25 μm). GC/MS analyses were performed on a HP 5971 mass detector coupled to a HP 5890 gas chromatograph fitted with a 30 m × 0.25 mm DB5 capillary column.

The 1-(4-chlorophenyl-1-propanol, 1-phenyl-1-propanol, 1-phenyl-2-propanol, and diphenylcarbinol were prepared by reduction of the corresponding ketones, according to the following procedure.[11]

A mixture of the ketone, NaBH$_4$ (in a 1:1 molar ratio, respectively), and ethanol as the solvent (15 mL) was stirred for 30 min at rt. Then, the solvent was removed by rotary evaporation. The residue was diluted with water (5 mL), acidified with HCl (5%, 1 mL), and extracted with diethyl ether (3 × 10 mL). The combined extracts were finally dried over Na$_2$SO$_4$.

The structure of the obtained alcohols **3-6** was confirmed by mass spectroscopy and the corresponding GC/MS spectra are here reported.

1-(4-Chlorophenyl)-1-propanol (3) (99% pure by GC, 94% yield): mass spectrum (70 eV) m/z (relative intensity) 172 (4), 170 (M$^+$, 12), 142 (32), 140 (100), 139 (6), 115 (7), 113 (18).

1-Phenyl-1-propanol (4) (98% pure by GC, 95% yield): mass spectrum (70 eV) m/z (relative intensity) 136 (M$^+$, 14), 107 (100), 105 (6), 79 (47), 77 (23), 51 (6).

1-Phenyl-2-propanol (5) (99% pure by GC, 94% yield): mass spectrum (70 eV) m/z (relative intensity) 136 (M$^+$, 3), 93 (8), 92 (100), 91 (74), 65 (14).

Diphenylcarbinol (6) (98% pure by GC, 97% yield): mass spectrum (70 eV) m/z (relative intensity) 184 (M$^+$, 30), 183 (12), 165 (11), 107 (11), 106 (10), 105 (100), 79 (37), 78 (28), 77 (65), 51 (23).

General Procedure for the Hydrodehalogenation of Aromatic Ketones (Table 1–3 and Figures 1 and 2) and Hydrodehalogenation/Reduction of Halogenated and Unhalogenated Benzylic Alcohol (Table 4–6). In a 25-mL three-necked round-bottoned flask thermostated at the reaction temperature (50 or 30 ± 0.1 °C) and connected with a system for the addition of hydrogen, a mixture of aqueous KOH solution (4.0 mL; 50%), 5% Pd/C (0.032 g; 0.015 mmol of Pd), and Aliquat 336 (0.085 g; 0.20 mmol) was magnetically stirred at 1000 rpm. A volume of 7.0 mL of the specific organic solution (0.07 M of the substrate in the corresponding solvent), containing n-decane as the internal standard was added. Hydrogen was bubbled at atmospheric pressure into the organic phase at about 1 mL/min.

In the case of 4,4′-dichlorobenzophenone, benzophenone, and diphenylcarbinol the reagent amounts were halved and dissolved by ultrasound in isooctane solvent (0.035 molar concentration: entries 7 and 8, Table 2; 7 and 8, Table 3; and entry 3, Table 6).

If not otherwise indicated, in the case of benzylic alcohols the promoter was added into the organic solution at time zero (as soon as the alcohol reduction was started); when a stoichiometric amount was used (entries 1–3, Table 5), 7.0 mL of an isooctane solution of the specific aryl halide was added. Instead, when catalytic amounts were employed (entries 4–9, Table 5), the promoters were diluted in 3.0 mL of the specific solvent and added to the reaction mixture.

(11) Brown, N. G. *Org. React.* **1951**, *6*, 469.