# Facile Hydrodehalogenation with Hydrogen and Pd/C Catalyst under Multiphase Conditions

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A multiphase system consisting of a hydrocarbon solvent, a strong alkaline solution, and a quaternary onium salt, in the presence of a Pd/C catalyst with hydrogen at atmospheric pressure, allows the rapid and progressive displacement of the chlorine atoms from polyhalogenated benzenes. The onium salt in this case constitutes a third liquid phase in which the reaction takes place. At 50 °C, 1,2,4,5-tetrachlorobenzene is reduced to benzene in 30 min using a Pd/Cl molar ratio of 1/130. Halogenated compounds are partitioned between the hydrocarbon solution and the liquid phase of the phase-transfer agent; rapid removal of HCl adsorbed on Pd/C is effected by neutralization with the alkaline solution. The enhancement of the reaction rate compared with the known methods might be attributed to the facile adsorption of $H_2$ by the catalyst under the reaction conditions. Different reaction rates result in the reduction of the three isomeric chlorotoluenes, whether the reaction is carried out in the presence or absence of the onium salt.

## Introduction

It is well-known that chlorobenzene can be reduced to benzene using various systems.[1a–f] Some of the most relevant and recent methods include the following: hydrodehalogenation with supported palladium catalysts,[2a] palladium on carbon (Pd/C),[2b] palladium complexes,[2c–e] platinum catalysts on spinel[3a] and alumina,[3b] reactive aluminium powders,[3c] and $MgH_2$.[3d] Transfer hydrogenations have also been reported using formate salts[4a–d] and with sodium hypophosphite in protic solvents (i.e., methanol, ethanol, and water).[4e] Transfer hydrogenation with indoline has also been reported.[5]

The utilization of onium salts as phase-transfer (PT) catalysts in hydrodehalogenation reactions has previously been reported;[6a,b] however, the onium salts normally promoted the transfer of anionic species from aqueous to organic phases.

Hydrodehalogenation reactions are usually carried out in polar solvents such as alcohols[7a–d] and DMF[8] because of the low solubility of hydrogen in apolar solvents. High hydrogen pressures are often necessary,[9a–d] even with Pd or Ni as catalysts.

We recently reported[10] that in a two-phase system with sodium hypophosphite as the hydrogen source 1,2,4,5-tetrachlorobenzene (TeCB) was reduced to benzene in 2.5 h at 50 °C in the presence of Aliquat 336 (methyltricaprylammonium chloride) as PT catalyst.

We now wish to report that under the same conditions with molecular hydrogen at atmospheric pressure, the hydrodehalogenation reaction is much faster. Furthermore, the reaction system is simplified; the onium salt, insoluble in both the organic and aqueous phases, is localized in the interfaces, coats the Pd/C catalyst, and constitutes the phase in which the reaction takes place. This new environment may change the rate of the removal of different halogen atoms, resulting in selectivity in the hydrodehalogenation.

## Results

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

All reactions, if not otherwise indicated, were carried out starting with 7.0 mL of a 0.07 M solution of substrate (0.5 mmol), 4.0 mL of aqueous phase solution, 0.032 g of 5% Pd/C (0.015 mmol), and 0.2 mmol of Aliquat 336 (0.085 g). Hydrogen was bubbled at atmospheric pressure through the organic phase at a rate of about 1 mL/min. The reaction flask was thermostated at 50 ± 0.1 °C, and the mixture was magnetically stirred at about 1000 rpm.

† Supported by CNPq, Brazil.

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**Table I. Hydrodehalogenation of TeCB with Pd/C Catalyst and H₂ at Atmospheric Pressure in Different Multiphase Systems[a]**

| en-try | aqueous phase | third liquid phase | t (h) | % convn | TCB | DCBs | PhCl | PhH |
|---|---|---|---|---|---|---|---|---|
| 1 | no | no | 2.00 | 29 | 16 | 5 | | d |
| 2 | H₂O | no | 2.00 | 28 | 17 | 6 | | d |
| 3 | H₂O | Aliquat 336 | 2.00 | 52 | 13 | 8 | 1 | d |
| 4 | KOH (50%) | no | 0.50 | 100 | 4 | 19 | 4 | 73 |
| | | no | 0.92 | 100 | 0 | 1 | 0 | 98 |
| 5 | KOH (50%) | Aliquat 336 | 0.50 | 100 | | 4.0 | | 96 |
| 6 | Ca(OH)₂[c] | Aliquat 336 | 3.00 | 45 | 10 | 2 | | d |

*The column header "% Yield[b]" spans TCB, DCBs, PhCl, PhH.*

[a] 4.0 mL of aqueous phase; 7.0 mL of a 0.07 M solution of TeCB; 5% Pd on carbon, 0.032 g (0.015 mmol of Pd). Entries 3, 5, and 6: Aliquat 336, 0.085 g (0.2 mmol). [b] By gas chromatography, compared to the internal standard (*n*-dodecane). [c] 0.15 g. [d] Not determined.

The hydrodechlorination of TeCB was considered (eq 1). The reaction proceeds through all of the less chlori-



(1)
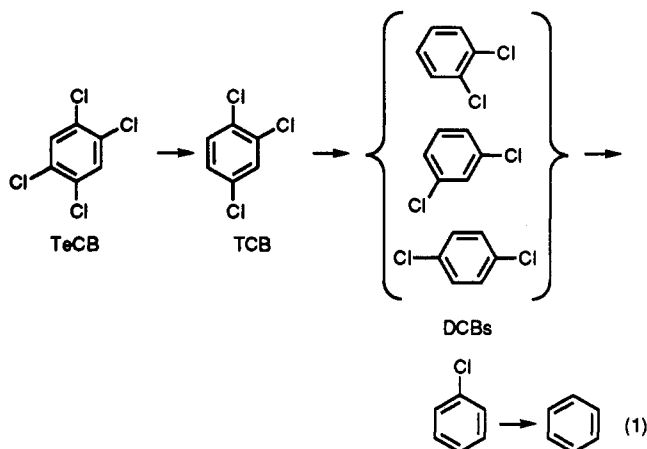
nated compounds, i.e., that is, 1,2,4-trichlorobenzene (TCB), 1,2-, 1,3-, and 1,4-dichlorobenzenes (DCBs) and chlorobenzene.

Table I reports the results of hydrodehalogenation of TeCB in different multiphase systems; the presence of both KOH and the insoluble onium salt, Aliquat 336, improves the conversion of TeCB to benzene. The difference between the reactions carried out just in isooctane solution (entry 1) and in the additional presence of 50% KOH and Aliquat 336 (entry 5) is dramatic. In the fomer case, only 16% of the TeCB had reacted after 30 min, in contrast with a 96% yield of benzene obtained in the latter.

Table II reports the results of hydrodehalogenation reactions for several chlorobenzenes. When considering the reaction rates of Table II, the presence or absence of the onium salt in the reactions does not seem to be conclusive.

The nature of the third insoluble liquid phase is crucial because, as seen in Table III, it can affect the reaction rate significantly. For example, while Aliquat 336 was effective promoting the reaction, other compounds such as V, VI, VIII, and IX completely depressed the reaction rate. The different ratios in the dichlorobenzene (DCB) isomers may be an indication of some selectivity.

The nature of the hydrocarbon solvent also affects the rate: in isooctane and pentane the reaction is faster, while

**Table II. Hydrodehalogenation of TeCB, TCB, 1,2- and 1,4-DCB, and PhCl. ‰ Decrease of the Reagent with the Time Is Reported[a]**

| entry | reagent | third liquid phase (Aliquat 336) | 5 | 10 | 15 | 25 | 30 |
|---|---|---|---|---|---|---|---|
| 1 | TeCB | yes | 54 | | | 92 | 100[b] |
| 2 | TeCB | no | 27 | 43 | 67 | 89 | 100[c] |
| 3 | TCB[d] | yes | 55 | 69 | 80 | 95 | 100[e] |
| 4 | TCB[f] | no | 69 | 98 | 100[g] | | |
| 5 | 1,2-DCB | yes | 68 | 92 | 100[h] | | |
| 6 | 1,2-DCB | no | 50 | 81 | 100[i] | | |
| 7 | 1,4-DCB | yes | 56 | 75 | 87 | 100[j] | |
| 8 | 1,4-DCB | no | 70 | 96 | 100[k] | | |
| 9 | PhCl[l] | yes | 90 | 100 | | | |
| 10 | PhCl | no | 88 | 100 | | | |

*The column header "t (min)" spans columns 5, 10, 15, 25, 30.*

[a] Aliquat 336, if present, 0.085 g. Conditions of Table I, entry 4 or 5. [b] 96% benzene. [c] 73% benzene. For *b* and *c* data from Table I, entries 5 and 4, respectively. [d] In the presence of 0.1 g of KI, the reaction is much slower; after 2.5 h, conversion was 97% (69% PhH). [e] 94% benzene. [f] In the presence of 0.1 g of KI, the reaction is slower; after 30 min, conversion was 100% (73% PhH). [g] 92% benzene. [h] 100% benzene (within gas chromatography limits). [i] 100% benzene. [j] 100% benzene. [k] 100% benzene. [l] Also reported in Figure 1; this reaction, carried out in *n*-pentane at 30 °C, yielded 100% conversion after 10 min. Hydrodechlorination of a 2.0 M solution of PhCl in isooctane and *n*-pentane is reported in the Experimental Section.

in THF it is slower (Table IV). More apparent in this case, selectivity arises in the ortho/para ratio due to the selective removal of Cl atoms from TCB and/or the different reactivities of DCB isomers in yielding PhCl.

Table V reports the hydrogenation of a few chloro derivatives, nitrobenzene, and hexadeuteriobenzene. Under these conditions, *p*-chlorobromobenzene is selectively reduced to chlorobenzene, since the C–Br bond reacts more rapidly. The reduction of benzyl chloride is difficult (entry 3).

Hydrodehalogenation with Pd/C occurs preferentially with aromatic rather than aliphatic compounds.[2b,4d,11]

In order to investigate the reasons for this enhanced reaction rate some tests were carried out.

Hydrodehalogenations of chloro-, bromo-, and iodobenzene were carried out individually as well as in competitive reaction. The results are reported in Figure 1. When the reactions were carried out separately, the reduction of chlorobenzene closely paralleled that of bromobenzene, while the reduction of iodobenzene was slower. When they were allowed to react competitively, the reduction was highly selective; the reaction was delayed, but iodobenzene reacted first followed by bromobenzene and then chlorobenzene.

A delaying effect was also observed when PhCl was reduced in the presence of KI (See also Table II, footnotes d and f). Clearly, the environment in which the reaction takes place is responsible for this effect: in fact, in the presence of KI, I⁻ is the counteranion of the onium salt, as it occurs in PT catalysis.[12]

The environment in which the reaction occurs can easily be changed and selectivity thus controlled by carrying out the reaction in the presence of different insoluble third phases.

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**Table III. Hydrodehalogenation of TeCB with Hydrogen at Atmospheric Pressure in the Presence of Different Compounds Insoluble in Either Aqueous or Organic Phases[a]**

| entry | | third liquid phase[b] | t (h) | % convn |
|---|---|---|---|---|
| 1 | I | (Aliquat 336: tricaprylylmethylammonium chloride) | 0.50 | 100[c] |
| 2 | II | (hexadecyltrioctadecylammonium bromide) | 1.50 | 63[d] |
| 3 | III | (hexadecyltributylphosphonium bromide) | 1.50 | 100[e] |
| 4 | IV | (hexadecylpyridynium bromide) | 3.00 | 10[f] |
| 5 | V | (benzyltriethylammonium bromide) | 1.50 | no reaction |
| 6 | VI | (tetrabutylammonium hydrogen sulfate) | 2.00 | no reaction |
| 7 | VII | (poly(ethylene glycol) monomethyl ether 550) | 2.50 | 55[g] |
| 8 | VIII | (poly(ethylene glycol) 6000) | 2.50 | no reaction |
| 9 | IX | (poly(propylene glycol) 2000) | 1.50 | no reaction |

[a] Reaction conditions are those of entry 5, Table I. [b] TeCB: II–IX = 1:0.1 molar ratio (1:0.2 in the case of Aliquat 336). [c] Ortho/para ratio in DCBs: about 5; m-dichlorobenzene, trace amount. [d] Ortho/para ratio in DCBs: about 2; m-dichlorobenzene, trace amount. [e] No DCBs; 4% of PhCl. [f] 9% of TCB; 1% of only o-dichlorobenzene. [g] Ortho/para ratio in DCBs: about 5; m-dichlorobenzene, trace amount.
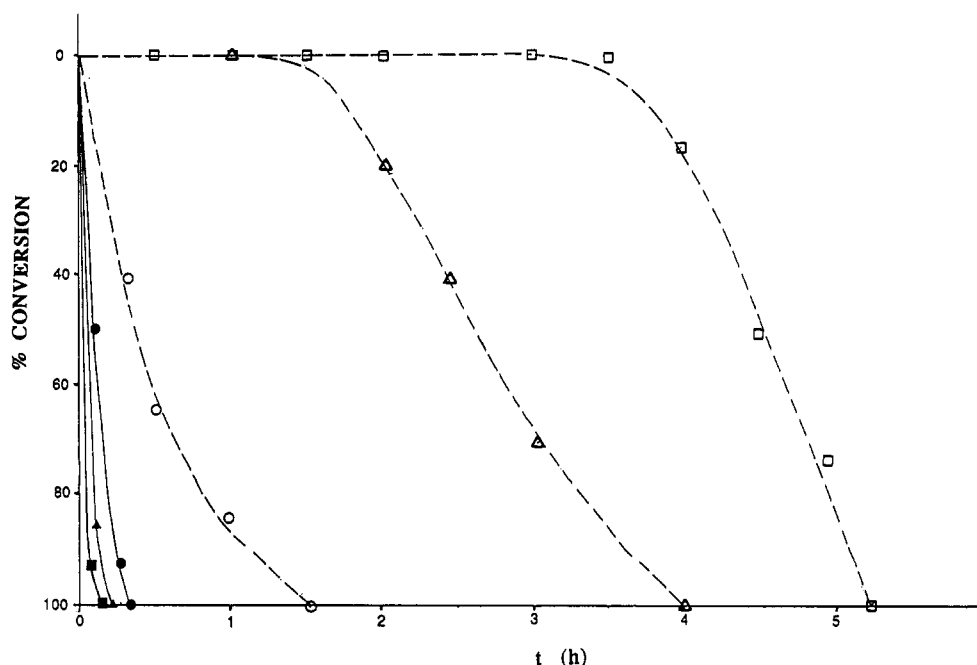


**Figure 1.** Hydrodehalogenation of PhI, PhBr, and PhCl to benzene (for conditions, see Experimental Section and Table I, entry 5) with hydrogen and Pd/C Catalyst. Full line: noncompetitive reactions of ■ PhBr, ▲ PhCl, and ● PhI. Dotted line: competitive reaction between ○ PhI, △ PhBr, and □ PhCl.

**Table IV. Hydrodehalogenations of TeCB in Different Solvents and in the Presence of Aliquat 336[a]**

| | | | | % yield | | | |
|---|---|---|---|---|---|---|---|
| entry | solvent | t (h) | % convn | TCB | DCBs | PhCl | PhH |
| 1 | isooctane | 0.50 | 100 | 0 | 5[b] | 0 | 95 |
| 2 | n-pentane[c] | 1.00 | 100 | 0 | 2[d] | 0 | 98 |
| 3 | cyclohexane | 1.75 | 100 | 2 | 1[d] | 0 | 97 |
| 4 | cyclooctane | 1.50 | 98 | 0 | 2[d] | 0 | 96 |
| 5 | benzene | 1.50 | 100 | 0 | 4[e] | 0 | 96 |
| 6 | THF[f] | 3.00 | 94 | 2 | 8[g] | 2 | 82 |

[a] Reaction conditions are those of entry 5, Table I. [b] Ortho/para ratio, about 5; m-dichlorobenzene, trace amount. [c] Reaction carried out at 30 °C. [d] Only o-dichlorobenzene. [e] Ortho/para ratio, about 4; m-dichlorobenzene, trace amount. [f] Aliquat 336 is soluble in THF. [g] Ortho/para ratio, about 7; m-dichlorobenzene, trace amount.

The fact that there are several consecutive reactions in the reduction of TeCB, TCB, and DCB may hide the selectivity of a single step. However, in the reduction to toluene of the three isomeric chlorotoluenes, selectivity is more evident.

These results are reported in Table VI. In the absence of Aliquat 336, reactivity of the chlorotoluenes was in the order meta > para > ortho; in the presence of Aliquat 336 the reaction rate was ortho > meta > para. The addition of KI further changes the nature of the onium salt,

**Table V. Hydrodehalogenation of Different Compounds[a]**

| entry | substrate | t (min) | % convn |
|---|---|---|---|
| 1 | p-chlorobromobenzene | 50 | 100[b] |
| 2 | p-chloroaniline | 80 | 100[c] |
| 3 | benzyl chloride | 180 | 97[d] |
| 4 | 1-chloronaphthalene | 60 | 100[e] |
| 5 | methyl benzyl ether | 180 | no reaction |
| 6 | nitrobenzene | 120 | 95[f] |
| 7 | hexadeuteriobenzene[g] | 120 | no reaction[h] |

[a] Conditions of entry 5, Table I: 7.0 mL of a 0.07 M (0.05 mmol) isooctane solution of the corresponding compound. Analyses were carried out by gas chromatography with n-dodecane as the internal standard. [b] After 30 min, 93% conversion to chlorobenzene; after 35 min, 69% chlorobenzene and 31% benzene; after an additional 15 min, conversion to benzene was complete. [c] To aniline. [d] To toluene. [e] To naphthalene. [f] 95% aniline and 5% azobenzene. [g] In n-pentane at 30 °C. [h] By GC/MS analysis.

decreasing the rate and affecting the selectivity: the three chlorotoluenes reacted differently (entries 3 and 4 of Table VI).

## Discussion

As far as we know, under the conditions reported, the hydrodechlorination of polychlorinated benzenes with Pd/C catalyst was very fast, faster than previously

Table VI. Competitive Hydrodehalogenation of the o-, m-, and p-Chlorotoluene to Toluene in the Presence and the Absence of Aliquat 336[a]

| entry | third liquid phase | t (min) | % convn[b] | remaining chlorotoluene isomers (ortho:meta:para ratio)[b] |
|-------|-------------------|---------|-----------|-----------------------------------------------------------|
| 1 | no | 10 | 54 | 1.00:0.59:0.79 |
|   |    | 40 | 91 | 1.00:—:0.35 |
| 2 | Aliquat 336 | 10 | 38 | 1.00:1.57:1.77 |
|   |    | 30 | 80 | 1.00:1.74:4.28 |
| 3 | Aliquat 336 + 0.2 g KI | 120 | 32 | 1.00:0.85:1.03 |
| 4 | Aliquat 336 + 1.5 g KI | 180 | 5.8 | 1.00:0.90:0.94 |
| 5 | hexadecyltributylphosphonium bromide | 180 | 56 | 1.00:1.10:1.71 |
| 6 | poly(ethylene glycol) monomethyl ether 550 | 60 | 15 | 1.00:0.85:1.00 |

[a] Reaction conditions are those of entry 5, Table I. Starting solution: 7.0 mL of isooctane containing o-, m-, and p-chlorotoluenes in 1:1:1 molar ratio each at 0.10 M concentration. [b] By gas chromatography, with n-dodecane as internal standard.

reported. Only a few minutes are required for the reduction of 1,2,4,5-tetrachlorobenzene to benzene, using a Pd/Cl ratio = 1/130.

The reactions carried out with Aliquat 336 (or in the presence of the compounds reported in Table III) appear to consist of a double organic and aqueous phase separated by a third phase which contains the supported solid catalyst Pd/C. In the absence of a third insoluble phase, Pd/C is dispersed in the organic–aqueous phase mixture.

During the reactions in the presence of Aliquat 336, two phenomena occur simultaneously: (i) partition of the aromatic compounds between the organic phases and (ii) regeneration of the Pd/C catalyst from the byproduct HCl via neutralization with the concentrated aqueous alkaline solution.

This new multiphase system, in spite of its apparent complexity, may produce favorable effects on both the rate and selectivity of the reaction (Tables I and II).

The nature of this third liquid phase which lies between the organic and aqueous phases and which coats the Pd/C catalyst plays a primary role. In fact, not all of the insoluble compounds promote the reaction. Instead, poly(ethylene glycols) and onium salts with short chains depress the reaction rate considerably (Table III). The reason for such different behavior is not clear at the moment. The organic solvent used is also important; while very similar, the apolar solvents of Table IV nevertheless have different effects on the reaction rate and on its selectivity (compare the ortho/para ratio of DCBs).

The data of both Tables III and IV suggest that the hydrodechlorination environment is crucial. The effect of the solvent on the hydrodehalogenation reaction has long been well-known.[4a,13] In our case, the onium–salt phase may also contain dissolved organic solvent, constituting the actual environment in which the reaction takes place. The best combination seems to be Aliquat 336–isooctane (Table IV).

As previously reported in the hydrodehalogenation reactions, the reduction of aromatic halides is faster than the corresponding aliphatic ones.[2b,4d,11] Table V further shows that aryl bromides react faster than the corresponding chlorides, since p-bromochlorobenzene is first selectively reduced to chlorobenzene.[4b] Under these conditions, no H–D exchange takes place (entry 7, Table V).

It has been reported that the hydrodehalogenation of the aryl halides follows the order PhI > PhBr > PhCl with Pd complexes[2e] and Raney-Ni[14a,b] as catalysts whereas

with Pd/C this order is reversed.[2d,4b] The peculiarity of the reaction is selectively reducing aromatic halides in the order PhI > PhBr > PhCl is depicted in Figure 1. It is known that such compounds are selectively adsorbed by Pd/C in the same order (PhI > PhBr > PhCl), so that only when the previous compound has been reduced can the reduction of the next one begin. The differences in operating in the presence of I⁻ are clearly evident in the reactions plotted in Figure 1. In fact, Figure 1 also suggests that the presence of I⁻ anions delays the reaction by disabling the catalyst centers. Reductions of PhCl and PhBr were faster alone than after the PhI reaction had taken place.

The effect of the addition of KI to the reaction mixture is highly evident when Aliquat 336 is present (Table II, footnotes d and f). I⁻ is selectively transferred into the Aliquat 336 phase increasing its concentration at the reaction site. While the presence of I⁻ anion slows the reaction rate, it also changes the selectivity of the catalyst (Table VI) by changing the nature of the environment in which the reaction occurs.

No absorption of hydrogen occurred in the absence of a Pd/C catalyst (neither isooctane, nor KOH, nor PT agent); however, at 50 °C and under the reaction conditions of Table I, 4 mL of $H_2$ (room temperature) were absorbed by isooctane and Pd/C,[15] 4 mL by isooctane, KOH, and Pd/C, and 7 mL by the isooctane, KOH, Pd/C, and Aliquat 336 system. This higher hydrogen uptake (7 mL) corresponds to about 40 H/Pd atoms and may explain the high reaction rate. The further consumption of 40 mL of hydrogen during the 30 min reaction of TeCB (entry 5, Table I) corresponds to the hydrogen needed for the complete removal of the four chlorine atoms of TeCB.

It has been reported that the hydrodehalogenation of chlorobenzene by Pd/C proceeds through the dissociative adsorption of the molecule on the surface[16] followed by the addition of hydrogen. The interactions between the liberated hydrohalide acids with Pd must also be considered.[17] Both the circumstances require that the interphase phenomena be important and explain the effect of KOH. The HCl adsorbed on the surface is neutralized by the strong alkaline medium, allowing the regeneration of the catalyst surface. The PT catalyst may play a promoting role in both wetting the carbon surface and

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(15) In alkene-free isooctane; it was obtained by treatment with concd sulfuric acid and with acidic permanganate solution. Hydrogen was bubbled before the addition of Pd/C, in order to remove the oxygen.

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simultaneously transferring alkaline anions from the aqueous phase forward to the insoluble catalyst by a PT process.[18]

The hydrodehalogenation reactions reported here yield only the parent aromatic hydrocarbon exclusively: in the presence of the strong alkaline medium and PT agent, no aromatic substitutions were observed, not even on the TeCB.

## Conclusions

This paper details an alternative approach to the replacement of methanol or ethanol in hydrodehalogenation reactions. Furthermore, the hydrodehalogenation is characterized by a facile workup of the reaction mixture. The reaction is carried out at atmospheric pressure and at low temperature.

The importance of effecting the reaction in apolar solvents may be emphasized by an example: in the chlorination of benzene, highly chlorinated benzenes are also produced. In this case, a reaction system which catalytically reduces polychlorinated benzenes to less chlorinated ones, in benzene solvent, may permit the next chlorination reaction to be carried out without any waste.

Hydrodehalogenation reactions of aromatic chlorides are of interest because they allow environmentally problematic compounds to be transformed into the corresponding aromatic hydrocarbons. Furthermore, this reaction may produce halogenated aromatics otherwise difficult to obtain by a direct synthesis.

Studies are underway to further correlate the nature of the organic phase which coats of the Pd/C catalyst with the reactivity of the halogen atoms in order to provide high hydrodehalogenation selectivities and to apply such results to other hydrogenolysis reactions.

It will be interesting to investigate the behavior of group VIII metal complexes in this system.

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## Experimental Section

All reagents and solvents were ACS grade and were used without further purification.

**General Procedure** (Tables I–V and Figure 1). In a 25-mL three-necked flask thermostated at 50 ± 0.1 °C and connected with a system for the addition of hydrogen was stirred a mixture of 4.0 mL of 50% KOH aqueous solution, 0.032 g of 5% Pd/C (0.015 mmol of Pd; Fluka, Art. N. 75992), and 0.085 g (0.20 mmol) of Aliquat 336 magnetically at about 1000 rpm.

Seven mL of the organic solution (0.07 M, 0.5 mmol) of the aryl halide (or the other compounds of Table V) containing *n*-dodecane as internal standard was added.

Hydrogen was bubbled at atmospheric pressure in the organic phase at about 1 mL/min.

The reaction course was followed by gas chromatography, by comparison with authentic samples. Conversions were referred to the internal standard. GC analyses were performed on a Varian GC 3400 (30 m, SPB-5 capillary column, FID detector, 140 °C, 0 min, with subsequent heating at 10 °C/min to 270 °C where it was held for 5 min).

**Competitive Reactions of the Isomeric Chlorotoluenes (Table VI).** 7.0 mL of an isooctane solution of *o*-, *m*-, and *p*-chlorotoluene (each at 0.1 M concentration) containing *n*-dodecane as internal standard were added to the mixture of entry 5, Table I. *n*-Dodecane was used as internal standard.

**Competitive Hydrodehalogenation Reaction (PhI, PhBr, and PhCl, Figure 1, Dotted Lines).** Seven mL of an isooctane solution of the aryl halides (PhCl, PhBr, PhI, each at 0.07 M concentration) and containing *n*-dodecane as internal standard was added to the mixture of entry 5, Table I.

**Benzene from Chlorobenzene with 0.001 Molar Equiv of Pd.** In a 25-mL three-necked flask thermostated at 50 ± 0.1 °C and connected with a system for the addition of hydrogen was stirred a mixture of 4.0 mL of 50% KOH aqueous solution, 0.032 g of 5% Pd/C (0.015 mmol of Pd), and 0.085 g (0.20 mmol) of Aliquat 336 magnetically at about 1000 rpm.

Seven mL of a 2.0 M solution of PhCl in isooctane (14.0 mmol) containing *n*-decane as internal standard (10 mmol) was added. The reduction to benzene was complete after 4.30 h.

The same reaction was then carried out, but in *n*-pentane solvent and at 30 °C. Conversion to benzene was 99% after 4.0 h.