

**Chimica organica.** — *Hydrodehalogenation of polychlorinated aromatics with Pd/C catalyst under multiphase conditions.* Nota di PIETRO TUNDO, CARLOS ALBERTO MARQUES e MAURIZIO SELVA, presentata (\*) dal Socio F. Montanari.

**ABSTRACT.** — Polyhalogenated benzenes, when reacted with hydrogen at atmospheric pressure or sodium hypophosphite and in the presence of Pd/C catalyst in a multi-phase system constituted by a hydrocarbon solvent, a strong alkaline aqueous solution and a quaternary onium salt, allow the rapid and progressive replacement of all the chlorine atoms. Thus, operating with hydrogen at 50°C, 1, 2, 4, 5-tetrachlorobenzene yields benzene after 50 min in 99% yield and using a Pd/Cl ratio of 1/120. The presence of an alkaline medium and a phase-transfer agent is synergic. The enhancement of the reaction rate, compared with the already known methods, has been attributed to the enhanced absorption of hydrogen by the catalyst surface, to partition of halogenated compounds between the hydrocarbon solution and the liquid phase of the phase-transfer agent: and to the rapid removal of HCl absorbed on Pd/C by the alkaline medium. The reaction is effective also with deactivated *p*-methoxyaryl halides.

**KEY WORDS:** Hydrodehalogenation of aromatics; Multiphase reduction system; Pd/C catalyst.

**RISUNTO.** — *Idrodealogenazione catalitica con Pd/C di idrocarburi aromatici policlorurati in un sistema multifasico.* Gli alogenuri aromatici sono facilmente ridotti ai corrispondenti sistemi non alogenati per mezzo di palladio supportato su carbone, quando sono posti a reagire con idrogeno molecolare o ipofosfito di sodio in un sistema multifasico costituito da un idrocarburo alifatico, una soluzione acquosa di KOH e un sale di onio; quest'ultimo, essendo insolubile in entrambe le fasi, ricopre come un film liquido il catalizzatore supportato. In questo modo, operando con idrogeno a 50°C, il 1, 2, 4, 5-tetraclorobenzene ridotto a benzene (99%) in 50 minuti e usando un rapporto Pd/Cl uguale a 1/120. La reazione è efficace anche con i disattivati *para*-metossi sostituiti. L'incremento della velocità di reazione, comparato ai metodi già noti, è attribuito all'aumentato assorbimento di idrogeno sulla superficie del catalizzatore, alla favorita ripartizione dell'aromatico alogenato fra la soluzione idrocarburea e il sale di onio quaternario e alla rapida rimozione dell'acido cloridrico dalla superficie del catalizzatore per mezzo della soluzione concentrata di idrossido di potassio.

#### INTRODUCTION

Hydrodehalogenation reactions of aromatic halides, especially chlorides, are of interest because they allow environmentally problematic compounds to be transformed into the corresponding aromatic hydrocarbons without production of waste.

Moreover, these reactions may be important also from a synthetic point of view: in the reduction of polyhalogenated benzenes to the corresponding less halogenated compounds, regioselectivity may lead to compounds difficult to afford by a direct synthesis. Likewise, the chlorination of benzene (or toluene) always produces considerable amounts of polychlorobenzenes (or polychlorotoluenes), because of the comparable rate constants of the related consecutive reactions. Going backwards may produce in this case the desired less-halogenated compounds.

(\*) Nella seduta del 12 giugno 1992.

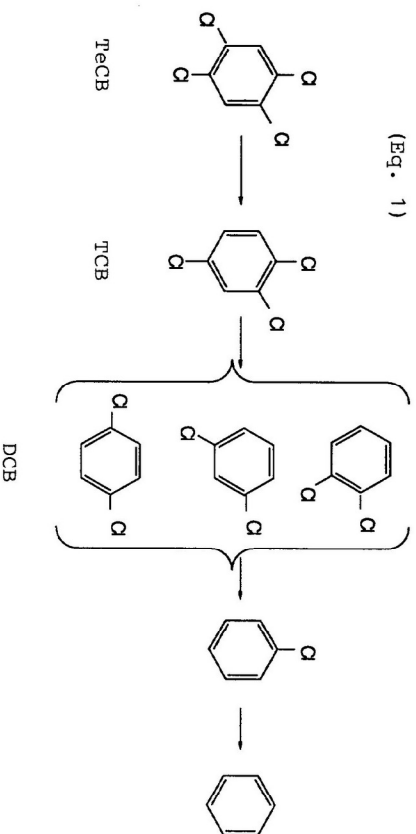
aim to improve reduction rate by developing new reaction conditions: by using classic reduction catalyst like palladium on carbon (Pd/C), here reported is the reduction of mono-, di-, tri- and tetra-chlorobenzenes to less chlorinated compounds and to benzene. This problem is stimulating because many chlorine atoms have to be removed at once. It is well known that chlorobenzene can be reduced to benzene by different systems (Ryländer, 1973; Pinder, 1980; Kiebon and Van Rantwijk, 1977; Pearson and Songstad, 1967). More relevant methods are:

— Hydrodehalogenation with supported palladium catalysts (Dini *et al.*, 1975), Pd/C (Pandey and Purkayastha, 1982), platin catalysts on spinel (Kasbauer *et al.*, 1988), reactive aluminium powders (Akagah *et al.*, 1985). A few methods have been also reported using hypophosphite as a hydrogen source (Boyer *et al.*, 1985; Boyer, 1986). Also formate salts have been described as a hydrogen donors. In particular Sasson and co-workers (Wiener *et al.*, 1991) has recently reported an efficient reduction system of mono-chlorobenzenes that uses formate salts and Pd/C as a catalyst; they perform the reaction in one phase (methanol or ethanol and water) in which both the inorganic salts and the aromatic halides are solubilised. Sodium hypophosphite has been used in many transfer hydrogenation reactions by Spatola and co-workers (Anwer *et al.*, 1989; Anwer and Spatola, 1975; de Koning, 1975), such as the reduction of nitroaromatics to amines, the dechlorination of aryl chlorides; the hydrogenation of unsaturated C = C bonds, etc. Also in this case, only very polar solvents (C<sub>1</sub> - C<sub>3</sub> alcohols, THF or HMPPT) have been used, because the low solubility of hydrogen in organic solvents.

We have used two immiscible organic and aqueous phases: the organic one is constituted by an inert aliphatic or aromatic hydrocarbon. The use of an aprotic organic phase was required also because 1,2,4,5-tetrachlorobenzene (TeCB), as usually the polychlorinated aromatics, is scarcely soluble in methanol.

## RESULTS

Hydrodehalogenation of TeCB gives at first 1,2,4-trichlorobenzene (TCB) and then, in order, the three dichlorobenzene isomers (DCB), chlorobenzene and benzene (eq. 1).



of hydrogen were utilized: molecular hydrogen itself at atmospheric pressure and sodium hypophosphite; under our conditions, the latter was found to be better than formate salts in transfer-hydrogenation reactions of this type (see later, fig. 1).

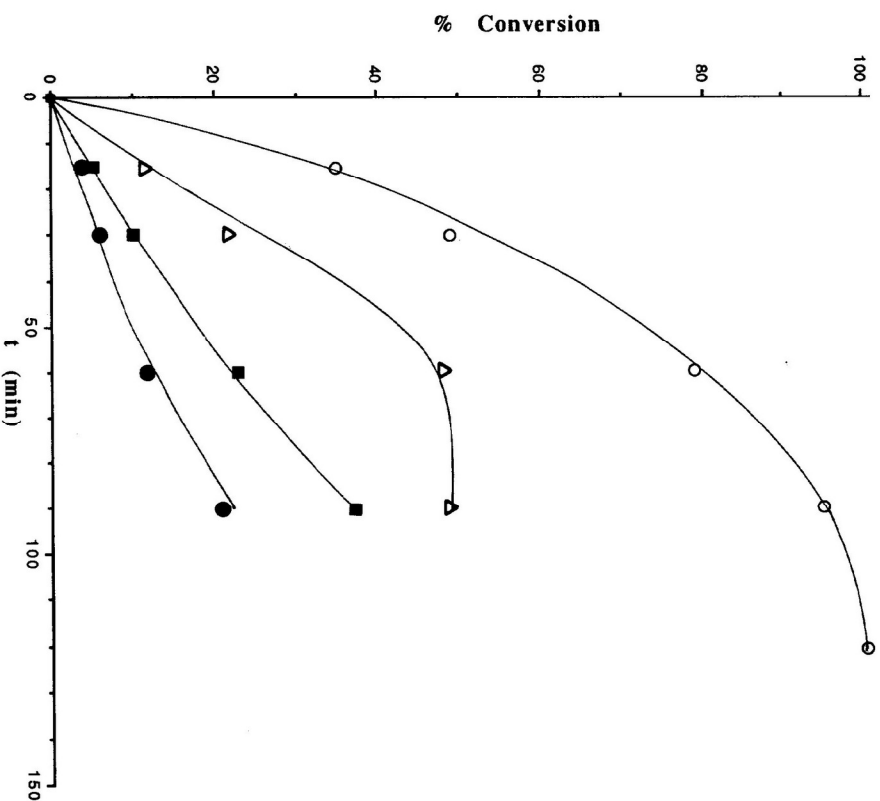


Fig. 1. - Comparison between different hydrogen sources in the hydrodehalogenation of TeCB. Conversion of TeCB accordingly to eq. 1 is reported: ○ NaH<sub>2</sub>PO<sub>2</sub> without Aliquat 336; △ NaH<sub>2</sub>PO<sub>2</sub> with Aliquat 336; ■ HCOONa with Aliquat 336; ● HCOONH<sub>4</sub> with Aliquat 336. For condition, see Experimentals.

Table I reports the hydrodehalogenation of TeCB (eq. 1) in different conditions: the presence of both aqueous KOH and the insoluble phase-transfer (PT) agent (*n* - C<sub>8</sub>H<sub>17</sub>)<sub>3</sub>N<sup>+</sup>CH<sub>3</sub>Cl<sup>-</sup> (Aliquat 336), remarkably improves the conversion of TeCB to benzene. The difference between operating in isooctane solution (entry 1) and in the additional presence of 50% KOH and Aliquat 336 (entry 5) is striking: after 30 min reaction, while in the former case only 14% TeCB was reacted, in the latter one, conversion was complete with 95% benzene yield.

TABLE I. - Hydrodehalogenation of TeCB with Pd/C catalyst and H<sub>2</sub> at atmospheric pressure in different multiphase systems<sup>(a)</sup>.

Entry	Aqueous phase	PT agent	t(h)	% Conv.	% Yield	PhH <sup>(c)</sup>		
						TCB	DCB <sup>(b)</sup>	PhCl
1	—	—	2	29	16	5	—	—
2	H <sub>2</sub> O	—	1.3	35	15	14	1	—
3	H <sub>2</sub> O	Aliquat 336 <sup>(d)</sup>	2	56	12	20	1	—
4	KOH (50%)	—	0.5	92	10	14	7	64
5	KOH (50%)	Aliquat 336 <sup>(d)</sup>	0.5	100	—	5.0	—	95

<sup>(a)</sup> In a 25 mL three necked flask thermostated at 50 ± 0.1°C and connected with a system for addition of hydrogen, a mixture of 4.0 mL of KOH 50% aqueous solution, 0.032 g of 5% Pd/C (0.015 mmol of Pd), 2.0 mL of isooctane and 0.085 g (0.20 mmol) of Aliquat 336 were magnetically stirred at about 1000 rpm. 7.0 mL of a 0.07 M solution of TeCB in isooctane (0.5 mmol) were added. Aliquat 336 is situated on Pd/C, between the two phases.

<sup>(b)</sup> o/p ratio = 5; m-dichlorobenzene, trace amount.

<sup>(c)</sup> By gas-chromatography, compared to the internal standard (*n*-dodecane).

<sup>(d)</sup> (n-C<sub>8</sub>H<sub>17</sub>)<sub>3</sub>N<sup>+</sup>CH<sub>3</sub>Cl<sup>-</sup>.

The reaction promoted by NaH<sub>2</sub>PO<sub>2</sub> · H<sub>2</sub>O, HCOONa and HCOOH<sub>4</sub>, in the presence and in the absence of a PT catalyst, is reported in fig. 1. In these cases, in order to provide a constant hydrogen generation, 0.2 g of NaH<sub>2</sub>PO<sub>2</sub> · H<sub>2</sub>O were added each 30 min; in fact, when the hydrodehalogenation rate isn't fast enough, the reaction may stop, since the decomposition of hypophosphite effected by palladium, being faster in comparison, causes the hydrogen to cease at all. Figure 1 clearly shows that the reaction is faster in the presence of a PT agent.

Figure 2 shows the hydrodechlorination of TeCB by hydrogen under different multiphase systems: without a water solution, with and without KOH, with and without Aliquat 336. The highest rate was observed in the system containing either the phase-transfer agent and the strong KOH aqueous solution.

Figure 3 describes the course of the reaction 1: it was performed in the presence of KOH an Aliquat 336. The rapid reduction of TeCB and the subsequent formation of benzene are here well evidenced<sup>(1)</sup>.

Hydrodehalogenation reaction of a few polyhalogenated benzenes is reported in table II; the results have been obtained after that an activation period of 1.5 h was passed; the compounds manifest different reactivities, that may change with the time. The data are not easily elucidable by kinetic treatments, maybe because the compounds progressively formed during the hydrogenation compete with the starting aryl halide on the surface of the insoluble catalyst. This may explain how the reactivity of TeCB and PhCl may change with the progress of the reaction (after 15 min, reaction rate seems much higher than after 5 min).

<sup>(1)</sup> Compared to the internal standard, mass balance of benzene was < 100 % may be because the former

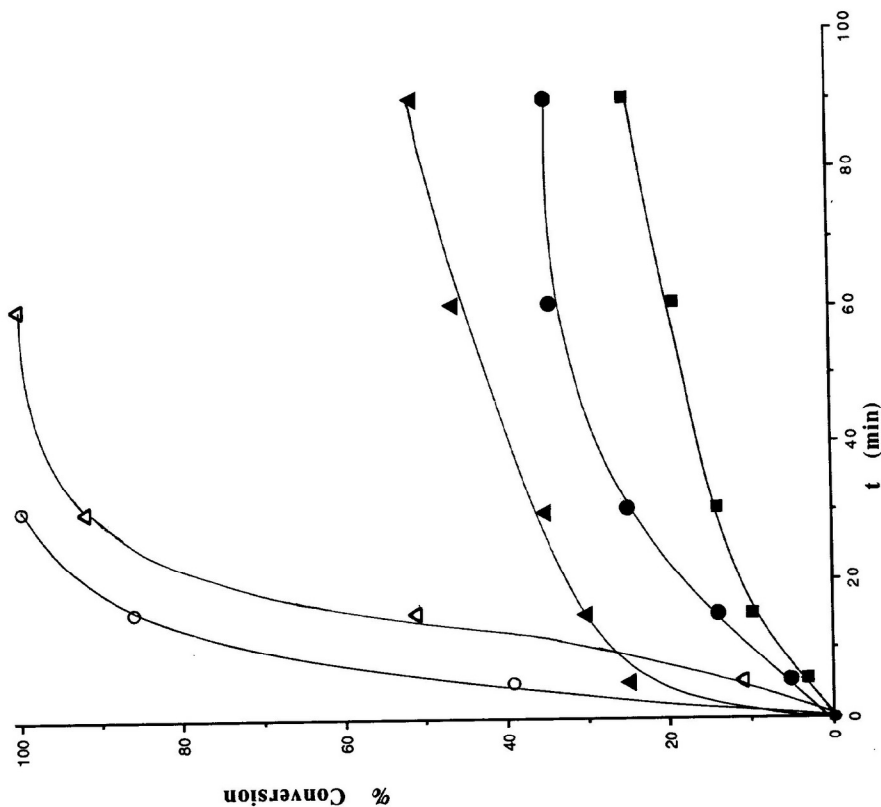


Fig. 2. - Hydrodehalogenation of 1,2,4,5-tetrachlorobenzene with H<sub>2</sub> (for conditions, see table I, entry 5 and Experimentals) with and without the PT Agent, with and without 50% aq. KOH solution. ○ % with Aliquat 336 and KOH 50%; △ % with Aliquat 336, water and KOH 50%; ▲ % with water (no KOH 50%) and Aliquat 336; ● % without Aliquat 336, water and KOH 50%; ■ % with water, without Aliquat 336 and KOH 50%.

The reduction of a massive amount (14.0 mmoles) of chlorobenzene by using 0.001 molar equivalents of Pd and 18 mmoles of KOH is reported in Experimentals.

In order to preliminarily investigate the mechanism, the influence of different factors affecting the reaction were studied.

A few solvents were tested. Table III reports the reduction of TeCB with hypophosphite in isooctane, cyclohexane and benzene and in the presence of 50% aq. KOH solution. The highest rate was achieved in the apolar isooctane. Benzene itself was a profitable solvent under such conditions; it's interesting to observe that in benzene the reaction does not go on so fast toward the complete reduction, but it appears to originate some selectivity in mono- and di-halogenated products.

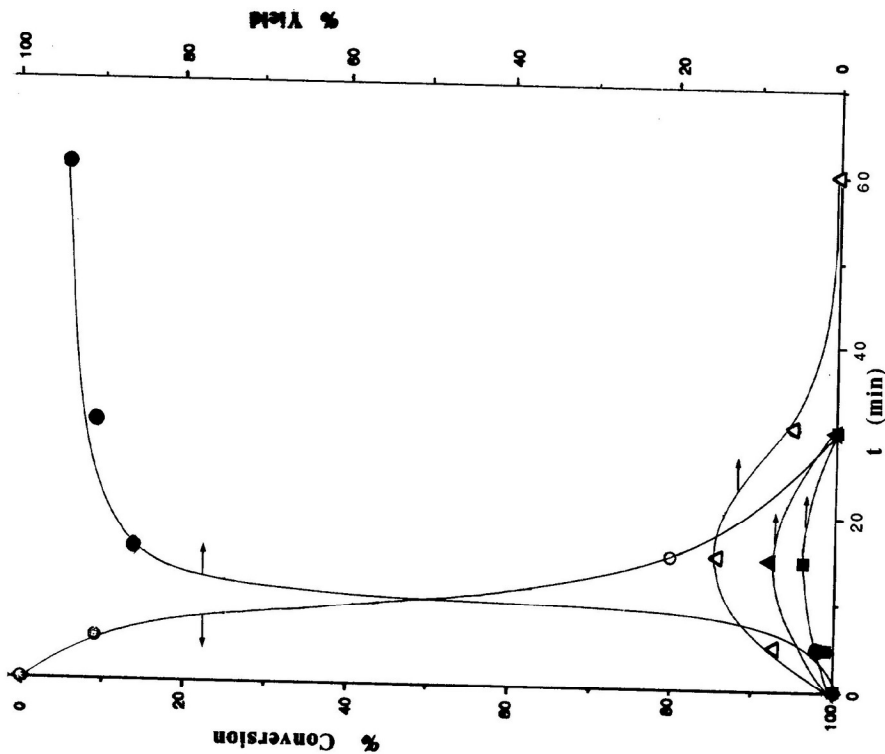


Fig. 3. — Course of the reduction of 1, 2, 4, 5-tetrachlorobenzene with  $H_2$  (for conditions, see table I, footnote a, entry 5 and Experimentals).  $\circ$  % 1, 2, 4, 5-tetrachlorobenzene;  $\Delta$  % 1, 2, 4-trichlorobenzene;  $\blacktriangle$  % 1, 2- and 1, 4-dichlorobenzene;  $\blacksquare$  % chlorobenzene;  $\bullet$  % benzene.

TABLE II. — Hydrodehalogenation of TeCB, TCB, 1, 2-, 1, 4-DCB and PhCl with hydrogen. (% Decrease of the reagent with the time is reported)<sup>(a)</sup>.

Entry	Reagent	t (min)	5	10	15	25	30
1	TeCB	8	—	86	—	—	100 <sup>(b)</sup>
2	TCB	36	59	95	100	100	100 <sup>(c)</sup>
3	1, 2-DCB	22	39	56	86	97	97 <sup>(d)</sup>
4	1, 4-DCB	54	76	90	100	100	100 <sup>(e)</sup>
5	PhCl	32	68	98	100	100	100 <sup>(f)</sup>

<sup>(a)</sup> All data, but TeCB, were obtained after 1.50 h of conditioning without the aryl halide. Conditions are those of entry 5, Table I.  
<sup>(b)</sup> 95% benzene.  
<sup>(c)</sup> 96% benzene.  
<sup>(d)</sup> 90% benzene.  
<sup>(e)</sup> 91% benzene.  
<sup>(f)</sup> 97% benzene.

TABLE III. — Influence of solvent in the hydrodehalogenation of TeCB with hypophosphite as a hydrogen source.

Entry	Solvent	t(h)	% Conv.	% Yield		
				TCB	DCB	PhH
1	Cyclohexane	3.0	90	10	13	65
2	Benzene	3.5	98	18	42 <sup>(a)</sup>	12
3	Isooctane	2.5	100	—	5	95

For conditions, see Experimentals.  
<sup>(a)</sup> o/p ratio = 7; m - dichlorobenzene, trace amount.

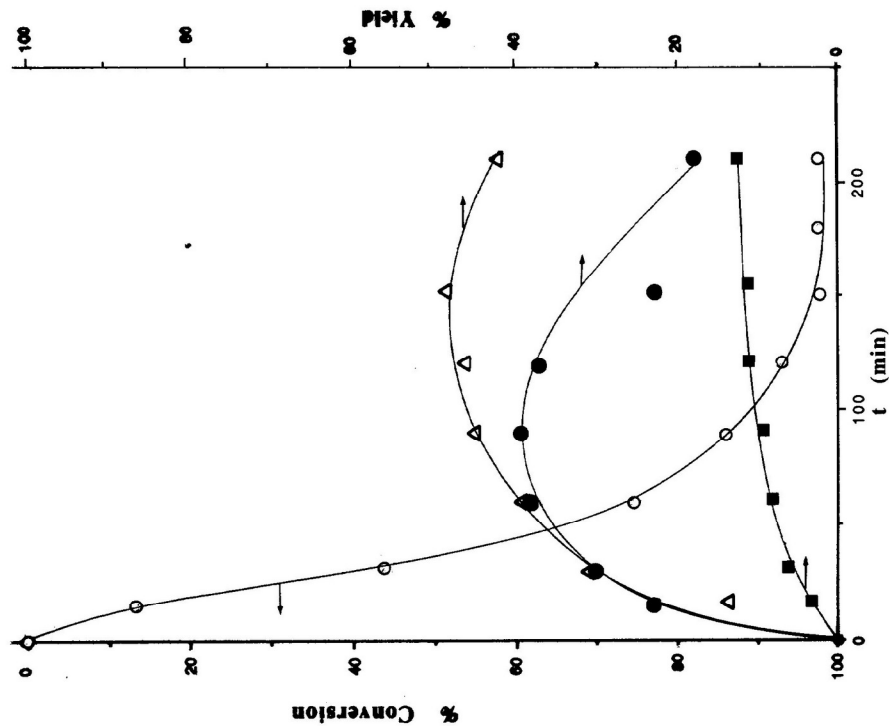


Fig. 4. — Course of the reduction of 1, 2, 4, 5-tetrachlorobenzene with  $NaH_2PO_2$  in benzene solvent. For conditions see Experimentals.  $\circ$  % 1, 2, 4-trichlorobenzene;  $\Delta$  % 1, 2, 4-trichlorobenzene;  $\bullet$  % 1, 2- and



Figure 4 better shows that *o*- and *p*-dichlorobenzene react slower, so that benzene may be used to obtain selectively such compounds from other polychlorinated benzenes.

The reaction is effective also with the less-activated *para*-methoxy-halogenated benzenes; either chloro- or bromo-derivatives easily yielded anisole: as reported in table IV, the reactivities of *para*-chloroanisole, *para*-bromoanisole, chlorobenzene and bromobenzene are comparable, but the *p*-methoxy-substituted compounds are a bit less reactive.

TABLE IV. - % Decrease of reagent vs. time in some dehalogenations carried out with hypophosphite.

Entry	Reagent	time (min)		
		5	10	20
1	Chlorobenzene <sup>(a)</sup>	13	22	97
2	<i>p</i> -Chloroanisole <sup>(b)</sup>	7	15	90
3	Bromobenzene <sup>(a)</sup>	37	79	100
4	<i>p</i> -Bromoanisole <sup>(b)</sup>	35	67	100

For reaction conditions, see Experimentals.

<sup>(a)</sup> Reaction product: benzene.

<sup>(b)</sup> Reaction product: anisole.

## DISCUSSIONS

As reported in table I and figs. 1, 2, a composite system made of different phases promotes the hydrodehalogenation reaction of TeCB to benzene, if the reaction is performed in the presence of aqueous solutions of KOH. In fact, operating in only one phase of isooctane (table I, entry 1), the reaction is considerably slower: high concentrations of KOH allow the reaction to yield benzene in a few time at 50 °C.

Under our conditions, hypophosphite was a more active hydrogen source (fig. 1); it is not a matter of decomposition rate of hypophosphite compared to formate, as sodium formate was decomposed by Pd/C at the same rate than hypophosphite. However, it is necessary that decomposition rate to hydrogen is comparable with hydrodehalogenation reaction because a rapid decomposition would waste the hydrogen source.

The other peculiarity is the promoting presence of PT agents. They, being insoluble in either aqueous phase or isooctane, cover the surface of the Pd/C, thus mediating the anion exchange with the aqueous solution and the sorption of the compound to be dehalogenated from the hydrocarbon solution. In spite of the complex exchange and partition phenomena, the reactions performed in the presence of a PT agent were faster than in its absence (fig. 2).

Noticeably, benzene is almost quantitatively formed at the end of the reaction and no nucleophilic displacement reactions were observed on polychlorinated benzenes, not even on TeCB.

## FACTORS THAT AFFECT THE REACTION

As shown in fig. 2, both the presence of a PT agent and concentrated KOH aqueous solution are necessary in order to enhance substantially the reaction rate.

The solvent markedly effects the reaction completion. The apolar solvent improves strongly hydrodehalogenation reaction, more than less apolar solvents like benzene or methanol (table III and fig. 4). The reasons of such behavior are not clearly evident; exchange phenomena between the solvent and the liquid PT agent and/or formation of unusual interfaces between the different phases might play a role. They may be responsible also of the different behavior of the reaction carried out in benzene and isooctane. In fact, as shown in table III, in benzene solvent the hydrodehalogenation of TeCB seems to be more selective toward the dichlorobenzenes, owing to the fact that hydrodehalogenation of the latter is more difficult than TeCB.

It has been reported that hydrodehalogenation of chlorobenzene by Pd/C proceeds toward the dissociation absorption of the molecule on the surface which is followed by the addition of hydrogen (Coq *et al.*, 1986). This mechanistic explanation may require that interphase phenomena are important. Moreover, it may explain the strong effect of KOH: the produced HCl, yet adsorbed on the surface, is quickly removed by strong alkaline media, so allowing a faster regeneration of the catalyst surface. Under such an interpretation the PT agent may have its promoting role in wetting the carbon surface, meantime transferring alkaline anions from the aqueous phase to the insoluble catalyst (Tundo, 1991; Starks and Liotta, 1978; Montanari *et al.*, 1982; Dehmlow and Dehmlow, 1983).

It is interesting that, in spite of strong alkaline solution, only reduction products are obtained and no nucleophilic substitution takes place, not even on TeCB.

With the aim of clarifying if the activation of the catalyst was due to a higher adsorption of hydrogen in such multi-phase conditions or if the strong aq. KOH solution, with the aid of PT agent, would quicker remove hydrogen chloride originated from the hydrogenation of Ar-Cl bonds, adsorption of hydrogen was measured in the presence of different reaction systems. It has been observed that no absorption of hydrogen occurs in the absence of Pd/C catalyst (neither isooctane, nor KOH, nor PT agent); but, operating at 50 °C and under the reaction conditions, 4 mL of H<sub>2</sub> (room temperature) were absorbed by isooctane, KOH, and Pd/C, 4 mL by isooctane and Pd/C and 7 mL by isooctane, KOH, Pd/C and Aliquat 336 system.

This higher hydrogen uptake corresponds to about 40 H/Pd atoms; the further consumption of 40 mL of hydrogen which occurs during 50 min reaction of TeCB (entry 5, table I) well corresponds to the hydrogen needed for the complete reduction of the four chlorine atoms to benzene.

Such result also indicates that the reaction might proceed through the dissociative adsorption of Ar-Cl on the catalyst surface, from which aq. KOH removes the adsorbed HCl; so, regeneration of the catalyst may be the step controlling the reaction rate: PT agent, which interfaces Pd/C with the two immiscible phases, might provide a faster

### CONCLUSIONS

The conditions here reported for hydrodehalogenation reaction, characterized by a multiphase system, allow the complete dehalogenation of TeCB to benzene in few minutes of reaction at 50 °C, and using 0.03 molar equivalents of Pd/C catalyst, or less. Molecular hydrogen was the most active reagent, but hypophosphite was also suitable; the latter may be used when one wants to avoid hydrogen from the reaction during the process.

Such high activity of Pd catalyst may open the way to new applications. In fact it may be valuable from an industrial point of view that, after the chlorination of benzene, polyhalogenated by-products are converted to less chlorinated benzenes in benzene solvent; this would allow the next batch chlorination to be carried out without production of any waste.

Moreover, such results allow a very fast hydrodehalogenation reaction with a facile work-up of the reaction mixture: the reaction is carried out at atmospheric pressure and at low temperature.

### EXPERIMENTAL SECTION

#### Materials.

All the reagents were commercially available and were used without further purification. 5% Pd/C was by Fluka (Art. N. 75992).

#### General Procedure: reactions with hydrogen (table I and figs. 2, 3).

In a 25 mL three necked flask thermostated at  $50 \pm 0.1^\circ\text{C}$  and connected with a system for the addition of hydrogen, a mixture of 4.0 mL of 50% KOH aqueous solution, 0.032 g of 5% Pd/C (0.015 mmol of Pd), 2.0 mL of isooctane and 0.085 g (0.20 mmol) of Aliquat 336 were magnetically stirred at about 1000 rpm. In case of a conditioning period, the mixture was stirred for 1.5 h.

7.0 mL of isooctane solution of the aryl halide (0.07 M, 0.5 mmoles) containing *n*-dodecane as internal standard were added.

The reaction course was followed by gas-chromatography, by comparison with authentic samples; conversions were referred to the internal standard.

#### General Procedure: reactions with hypophosphite (table III and figs. 1, 4).

In a 20 mL Ermenmeyer flask equipped with a condenser and thermostated at  $50^\circ\text{C} \pm 0.1^\circ\text{C}$ , 7.0 mL of a solution of 0.07 M of TeCB in isooctane (0.5 mmol) containing *n*-dodecane as internal standard, 4.0 mL of KOH 50% aqueous solution, 0.032 g of 5% Pd/C (0.015 mmol of Pd) and 0.085 g (0.20 mmol) of Aliquat 336 were magnetically stirred at about 1000 rpm. 0.20 g (1.9 mmol) of  $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$  were added every 30 min.

In the experiences carried out with formiate salts as hydrogen sources (fig. 1), 0.20 g of sodium formate or 0.20 g of ammonium formate were added every 30 min. Other

The reaction course was followed gas-chromatographically, by comparison with authentic compounds; conversions were referred to the internal standard.

#### Reduction of 1,2,4-trichlorobenzene, 1,4 and 1,2-dichlorobenzene and chlorobenzene with hydrogen (table II).

The same conditions just used for reduction of TeCB were used for TeCB, *ortho*- and *para*-DCB and PhCl. That is, starting from 7.0 mL of 0.07 M isooctane solution of the corresponding aryl chlorides, and containing *n*-dodecane as the internal standard. The reactions were carried out with 4.0 mL of (50%) aqueous KOH solution, 0.032 g of 5% Pd/C (0.015 mmol of Pd) and 0.085 g of Aliquat 336 and were magnetically stirred at about 1000 rpm. 0.20 g (1.9 mmoles) of  $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$  were added every 30 min.

Reactions were followed by gas-chromatography; conversions were determined by comparison with the internal standard.

#### Dehalogenation of chlorobenzenes, bromobenzenes and their *p*-methoxy derivatives (table IV).

Starting from 7.0 mL of 0.07 M isooctane solutions of the corresponding aryl halides, and containing *n*-dodecane as the internal standard, the reactions were carried out with 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; they were magnetically stirred at about 1000 rpm. 0.20 g (1.9 mmol) of  $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$  were added every 30 min. Analyses were carried out by gas-chromatography.

#### Benzene from chlorobenzene and hydrogen with 0.001 molar equivalents of Pd.

In a 25 mL three necked flask thermostated at  $50 \pm 0.1^\circ\text{C}$  and connected with a system for the addition of hydrogen, a mixture of 4.0 mL of 50% KOH aqueous solution (18 moles), 0.032 g of 5% Pd/C (0.015 mmol of Pd), 2.0 mL of isooctane and 0.085 g (0.20 mmol) of Aliquat 336 were magnetically stirred at about 1000 rpm.

7.0 mL of a 2.0 M solution of PhCl in isooctane (14.0 mool) containing *n*-dodecane as internal standard (10 mmol) were added.

The reduction to benzene was complete after 7.5 h.

### ACKNOWLEDGEMENTS

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