Dehalogenation of polychloroarenes with sodium formate in propan-2-ol catalyzed by $RhCl(PPh_3)_3$

Letter

María A. Atienza,[a] Miguel A. Esteruelas,*[b] Marta Fernández,[a] Juana Herrero[a] and Montserrat Oliván[b]

[a] *Departamento de Química, Universidad de Cantabria, 39005 Santander, Spain*
[b] *Departamento de Química Inorgánica, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza-C.S.I.C., 50009 Zaragoza, Spain. E-mail: maester@posta.unizar.es*

Received (in Strasbourg, France) 5th March 2001, Accepted 20th April 2001
First published as an Advance Article on the web 16th May 2001

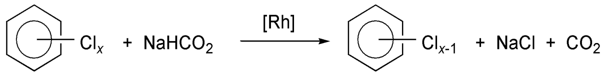
Polychloroarenes can be dehalogenated with sodium formate in propan-2-ol using $RhCl(PPh_3)_3$ as the catalyst. The hydrogenolysis of 1,2,4-trichlorobenzene is selective to 1,2-dichlorobenzene, whereas the hydrogenolysis of 1,3- and 1,4-dichlorobenzene is sequential and selective according to the sequence: chlorobenzene > benzene.

Chloroarenes can be used in organic synthesis as precursors for a wide variety of valuable products.[1] However, their accumulation in the environment implies a serious health hazard.[2] Therefore, from the environmental point of view, the development of simple and economical methods for the reductive dehalogenation of aryl chlorides should be a target with high priority.

A limited number of methods for the hydrogenolysis of chloroarenes containing homogeneous metal catalysts have been reported as a result of the effort in this field.[3] They involve the use of molecular hydrogen,[4] alcohols,[5] cyclic amines,[6] magnesium dihydride,[7] sodium hydride[8] and alkyl Grignard reagents[9] as the hydrogen source.

Among the potential hydrogen sources, formic acid and its salts should occupy a special place since the ease of hydrogen donation is higher than with most donors. This is due to the fact that the stable CO_2 molecule should be formed during the hydrogenolysis. However, its use has been limited to a few systems, mainly heterogeneous. Chlorotoluene has been hydrodehalogenated with formic acid and its salts in the presence of palladium–carbon (10% Pd/C).[10] Milstein and co-workers[11] have reported that *p*-substituted chlorobenzenes undergo efficient homogeneously catalyzed reductive dechlorination to the corresponding arenes, using $Pd(dippp)_2$ as catalyst [dippp = 1,3-bis(diisopropylphosphino)propane] and sodium formate in alcohol or DMF as the hydrogen source. Joó and co-workers[12] have observed that when an aqueous solution of sodium formate is the hydrogen donor and $RuCl(TPPMS)_2$ (TPPMS = *m*-sulfophenyl diphenylphosphine anion) the catalyst, C–X bonds of carbon tetrachloride, chloroform and 1-hexylhalogenides are transformed into C–H bonds. However, under the same conditions, chlorobenzene is inert.

In two recent papers, we have shown that coordination complexes of metals of Groups 8 and 9, chiefly $RhCl(PPh_3)_3$,[13] catalyze the dehalogenation of polychloroarenes with $HSiEt_3$.[14] Now, we report that, in the presence of $RhCl(PPh_3)_3$, polychloroarenes can be dehalogenated not only with $HSiEt_3$ but also with sodium formate in propan-2-ol [eqn. (1)].



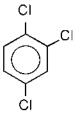
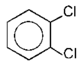
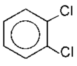
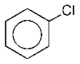
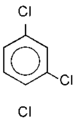
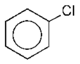
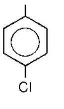
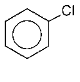
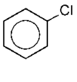
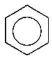
(1)

The catalytic reactions were carried out under reflux using $Rh : C_6H_{6-x}Cl_x$ and $NaHCO_2 : C_6H_{6-x}Cl_x$ molar ratios of 1 : 34 and $x + 1 : 1$, respectively. Under these conditions, the system catalyzes the selective dechlorination of 1,2,4-trichlorobenzene to 1,2-dichlorobenzene and the dechlorination of 1,3- and 1,4-dichlorobenzene to chlorobenzene, which then yields benzene at much slower rates.

The formation of acetone is not observed during the hydrogenolysis of these substrates. This suggests that the solvent does not act as a hydrogen source for the process and, in accord with eqn. (1), sodium formate is the only active reducing reagent in the reaction medium.

The yields of the reactions, after 85 min, are given in Table 1. The preferred formation of 1,2-dichlorobenzene during the dehalogenation of 1,2,4-trichlorobenzene suggests that the extraction of the chlorine in position 4 is favored. This agrees well with the fact that the dehalogenation of 1,2-dichlorobenzene is slower than the dehalogenation of the related 1,4-

Table 1 Dehalogenation of polychloroarenes with sodium formate catalyzed by $RhCl(PPh_3)_3$[a]

Substrate	Product	Time/min	Yield (%)
		85	88
		85	3[b]
		85	70
		85	40
		85	5[c]

[a] *Conditions*: $T = 85\,°C$; propan-2-ol (3 ml) as solvent; 2.4 mmol of polycloroarene, 0.07 mmol of $RhCl(PPh_3)_3$, $2.4(x + 1)$ mmol (x = number of chlorine atoms of the polychloroarene) of sodium formate. [b] After 5000 min the yield of the reaction is *ca.* 6%. [c] Under the conditions used for the polychloroarenes, an analyzable quantity of benzene was not observed. The reported yield was obtained when [PhCl] was 4.9 M. After 5000 min the yield of the reaction is *ca.* 8%.

DOI: 10.1039/b102191p

isomer. However, the preferred formation of 1,2-dichlorobenzene is in contrast with previous studies on the oxidative addition of 1,2,4-trichlorobenzene to phosphine–nickel(0) complexes, which show that the addition of the 4-Cl–C bond is less favored than the oxidative addition of the 2-Cl–C bond.[15]

The dehalogenation of 1,2-dichlorobenzene is much slower than the dehalogenation of the 1,3-isomer. This, together with the preferred formation of 1,2-dichlorobenzene from 1,2,4-trichlorobenzene, indicates that the dechlorination of chloroarenes containing chlorines in adjacent positions is more difficult than the dehalogenation of those containing chlorines in non-adjacent positions. This fact is characteristic for catalysts of Groups 8 and 9 and appears to be independent of the hydrogen source,[14] it can be related to the capacity for coordinating to the metal of the chlorine situated in the position adjacent to the activated chlorine.[16]

Since the dehalogenation of 1,2,4-trichlorobenzene is faster than those of the dichlorobenzenes, and the extraction of a chloride from the latter substrates is in both cases faster than the dehalogenation of chlorobenzene, the selective formation of singly dechlorinated products appears to be kinetic in origin, the rate of dehalogenation decreasing with a decrease in the number of the chlorine atoms on the aromatic ring.

In conclusion, the complex $RhCl(PPh_3)_3$ is an active catalyst for the dehalogenation of polychloroarenes with sodium formate in propan-2-ol. The hydrogenolysis is sequential and selective according to the sequence 1,2,4-trichlorobenzene > dichlorobenzene > chlorobenzene.

Experimental

All manipulations were conducted with rigorous exclusion of air. 1,2,4-Trichlorobenzene, 1,2-dichlorobenzene, 1,3-dichlorobenzene, and chlorobenzene were dried by known procedures and distilled prior to use. 1,4-Dichlorobenzene was used without further purification. The complex $RhCl(PPh_3)_3$ was prepared by a published procedure.[17]

Analysis of the products of the reactions was carried out on a Perkin-Elmer Autosystem gas chromatograph equipped with a flame ionization detector, using a FFAP on Chromosorb GHP 80/100-mesh column and *p*-xylene as the internal standard. The oven conditions were 35 °C (hold 4 min) to 180 °C at 20 °C min^{-1} (hold 5 min). The reaction products were identified by comparison of their retention times with those observed for pure samples.

General procedure

The dehalogenation reactions were carried out under argon at constant temperature in a two-necked flask fitted with a condenser and containing a magnetic stirring bar. The second neck was capped with a Suba seal to allow samples to be removed by syringe without opening the system. Reaction conditions: $2.4(x + 1)$ mmol (x = number of chlorine atoms of the polychloroarene used) of sodium formate was placed in the flask. 0.07 mmol of $RhCl(PPh_3)_3$ was dissolved in 3 ml of a propan-2-ol solution containing 2.4 mmol of the polychloroarene and 200 μL of *p*-xylene, and added to the flask. The flask was then immersed in an oil bath at 85 °C, and the reaction solution magnetically stirred.

Acknowledgements

We acknowledge financial support from the DGES of Spain (Project PB98-1591) and from the Comisión Mixta Caja Cantabria-Universidad de Cantabria.

References

1 M. Hudlicky, in *Comprehensive Organic Synthesis*, ed. B. M. Trost and I. Fleming, Pergamon, London, 1991, vol. 8, p. 895; T. Imamoto, in *Comprehensive Organic Synthesis*, ed. B. M. Trost and I. Fleming, Pergamon, London, 1991, vol. 8, p. 793; J. March, *Advanced Organic Chemistry*, 4th edn., Wiley, New York, 1992.
2 O. Hutzinger, S. Safe and V. Zitko, *The Chemistry of PCBs*, CRC Press, Cleveland, OH, 1974.
3 V. V. Grushin and H. Alper, *Chem. Rev.*, 1994, **94**, 1047; P. A. Chaloner, M. A. Esteruelas, F. Joó and L. A. Oro, in *Homogeneous Hydrogenation*, Kluwer Academic Publishers, Dordrecht, The Netherlands, 1994, ch. 4, Section 4.12; V. V. Lunin and E. S. Lokteva, *Izv. Akad. Nauk, Ser. Khim.*, 1966, 1609; V. V. Grushin and H. Alper, *Top. Organomet. Chem.*, 1999, **3**, 193.
4 C. J. Love and F. J. McQuillin, *J. Chem. Soc., Perkin Trans. 1*, 1973, 2509; V. V. Grushin and H. Alper, *Organometallics*, 1991, **10**, 1620; D. T. Ferrughelli and I. T. Horváth, *J. Chem. Soc., Chem. Commun.*, 1992, 806.
5 M. E. Cucullu, S. P. Nolan, T. R. Belderrain and R. H. Grubbs, *Organometallics*, 1999, **18**, 1299.
6 H. Imai, T. Nishiguchi, M. Tanaka and K. Fukuzumi, *J. Org. Chem.*, 1977, **42**, 2309.
7 C. Carfagna, A. Musco, R. Pontellini and G. Terzoni, *J. Mol. Catal.*, 1989, **54**, L23.
8 C. Qian, D. Zhu and Y. Gu, *J. Mol. Catal.*, 1990, **63**, L1.
9 R. Hara, K. Sat, W.-H. Sun and T. Takahashi, *Chem. Commun.*, 1999, 845.
10 R. Rajagopal and A. F. Spatola, *J. Org. Chem.*, 1995, **60**, 1347, and references therein.
11 Y. Ben-David, M. Gozin, M. Portnoy and D. Milstein, *J. Mol. Catal.*, 1992, **73**, 173.
12 A. Cs. Bényei, S. Lehel and F. Joó, *J. Mol. Catal. A: Chem.*, 1997, **116**, 349.
13 M. A. Esteruelas, J. Herrero, F. M. López, M. Martín and L. A. Oro, *Organometallics*, 1999, **18**, 1110.
14 J. Díaz, M. A. Esteruelas, J. Herrero, L. Moralejo and M. Oliván, *J. Catal.*, 2000, **195**, 187.
15 D. R. Fahey, *J. Am. Chem. Soc.*, 1970, **92**, 402.
16 R. H. Crabtree, F. W. Faller, M. F. Mellea and J. M. Quirk, *Organometallics*, 1982, **1**, 1361; M. P. García, M. V. Jiménez, A. Cuesta, C. Siurana, L. A. Oro, F. J. Lahoz, J. A. López, M. P. Catalán, A. Tiripicchio and M. Lanfranchi, *Organometallics*, 1997, **16**, 1026.
17 J. A. Osborn and G. Wilkinson, *Inorg. Synth.*, 1990, **28**, 77.