Pergamon

Tetrahedron Letters 42 (2001) 2301–2303

TETRAHEDRON
LETTERS

Regioselective dechlorination of 2,3-dichloronitrobenzene into 3-chloronitrobenzene and regioselective dechlorination–hydrogenation into 3-chloroaniline

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Received 15 January 2001; accepted 18 January 2001

Abstract—Tetrakis(triphenylphosphine)palladium, $Pd(PPh_3)_4$, is an efficient catalyst for the selective dechlorination of 2,3-dichloronitrobenzene into 3-chloronitrobenzene. During the reaction the selectivity is over 90% in a very reproducible manner and the reaction can be stopped at the maximum selectivity. $Pd(PPh_3)_4$ is also a catalyst for the one-pot transformation of 2,3-dichloronitrobenzene into 3-chloroaniline (selectivity >60%). © 2001 Elsevier Science Ltd. All rights reserved.

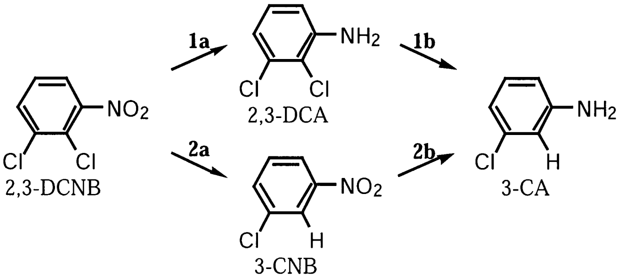
Polychloroarenes are often by-products of industrial reactions and are persistent environmental pollutants which require effective means of disposal.[1] In the last few years many studies have been devoted to the problem of dechlorination of polychloroarenes,[2] which appears to be a necessary step before incineration.[3] However, some chloroarenes are also important chemicals for the manufacture of fertilizers, herbicides, etc….[4] Therefore, from both an economic and environmental point of view, it would be challenging to transform useless, toxic polychloroarenes into chloroarenes that can be used for further chemical synthesis.

2,3-Dichloronitrobenzene (2,3-DCNB) is a by-product of the nitration of 1,2-dichlorobenzene. We have considered the transformation of 2,3-DCNB into 3-chloroaniline (3-CA), which is used for the manufacture of the herbicide chlorpropham. Formally, this transformation can be carried out according to two reaction sequences (Scheme 1). Examination of the literature on the reactions depicted in Scheme 1 led to the following conclusions:

1. The particular case of 2,3-DCNB has never been considered.
2. For what concerns the (1a+1b) sequence, several catalytic systems allow the selective hydrogenation of monochloronitrobenzenes into the corresponding chloroanilines (reaction 1a).[5,6] For this reaction, heterogeneous platinum catalysts seem to be the most efficient.[6] However, the only catalytic systems for reaction (1b) are based on Pd/C in highly acidic media (e.g. aqueous HCl 4 M) in the presence of iodides or Lewis acids (150°C, 20 bars H_2).[7,8] These experimental conditions are prohibitive for an industrial application.
3. For the (2a+2b) sequence, only a few catalytic systems have been tested for the selective dechlorination of chloronitrobenzenes into nitrobenzene. These are palladium-based catalysts, either heterogeneous[9,10] or homogeneous.[11,12]

On the basis of the above data, it was decided to investigate the possible transformation of 2,3-DCNB according to the (2a+2b) sequence:

- either in two steps: since reaction (2b) is possible with platinum-based catalysts (vide supra) the prob-



Scheme 1. The two possible reaction sequences for the transformation of 2,3-DCNB into 3-CA.

Keywords: chloronitroarenes; dechlorination; hydrogenation; palladium catalyst.

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PII: S0040-4039(01)00103-4

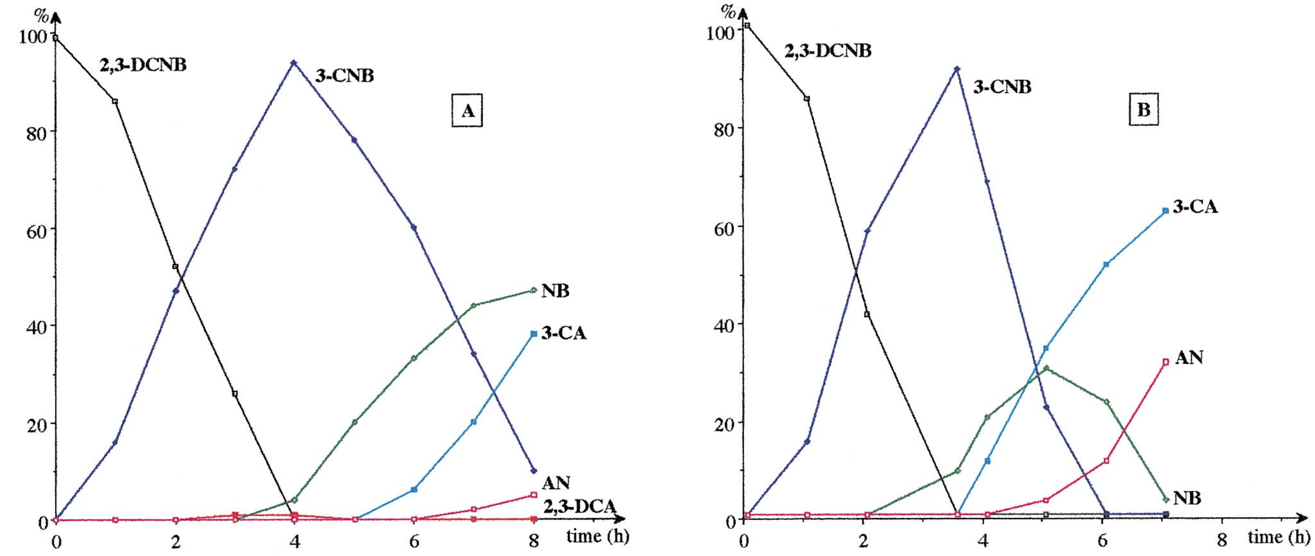

Figure 1. Dechlorination of 2,3-DCNB with 15% $Pd(PPh_3)_4$ (curves A) and 8% $Pd(PPh_3)_4$ (curves B).

lem was to find a regioselective dechlorination of 2,3-DCNB into 3-chloronitrobenzene (3-CNB).

- Or in one-step: in this case, no literature data could direct the choice of a catalytic system.

In a preliminary study, six palladium-based catalytic systems, either heterogeneous (Pd/C, Pd/Al_2O_3, PVP-$PdCl_2$) or homogeneous ($Pd(OAc)_2/PEt_3$, $Pd(OAc)_2/PCy_3$), $Pd(PPh_3)_4$) were tested for the transformation of 2,3-DCNB under 1 atm hydrogen pressure. Monitoring the reactions by GC analysis indicated that, among the six palladium catalysts considered, $Pd(PPh_3)_4$ exhibits the more promising selectivity for the dechlorination of 2,3-DCNB into 3-CNB.

When a solution of 2,3-DCNB (6.2 mmol) in DMF (15 mL) in the presence of AcOK (7.5 mmol) and $Pd(PPh_3)_4$ is heated from 20 to 120°C (internal temperature 116±2°C, reached in 0.3 h) under hydrogen (1 atm), GC and GC–MS analyses indicate the highly selective formation of 3-CNB which is later transformed into nitrobenzene (NB), 3-CA or aniline (AN), depending on the catalyst concentration (vide infra). No loss of material is observed (GC calibration with anisole).

When the $Pd(PPh_3)_4$ concentration is 15% (mol/mol), 2,3-DCNB is consumed within 4 h. At that moment, the selectivity in 3-CNB is 94%. When the catalyst concentration is reduced to 8%, the selectivity in 3-CNB after total consumption of 2,3-DCNB is 91%. The above selectivities proved to be reproducible within 1–2% variations, depending on the exact time of sampling. The corresponding curves are shown in Fig. 1.

Curves A: up to 50% conversion (2 h), the reaction is fully selective. Small amounts of 2,3-DCA are formed, but never exceed 1–2%. After 3 h, NB is slowly formed. When 2,3-DCNB is totally consumed (4 h), the reaction medium contains 3-CNB (94%), 2,3-dichloroaniline (2,3-DCA) (1%) and NB (4%), corresponding to the maximum selectivity obtained with this catalyst. Later, 3-CNB is transformed into NB and 3-CA. AN forms slowly only after 6 h reaction.

Curves B: up to total conversion of 2,3-DCNB, the reaction occurs in the same manner as with 15% catalyst (curves A) to give de 3-CNB (91%) and NB (9%), with slightly lower selectivity than above. The difference only appears later: nitro groups are more rapidly hydrogenated, 3-CNB into 3-CA and NB into AN. 2,3-DCA is never detected. The most interesting result is that, after 7 h under these conditions, the percentage of 3-CA reaches 62%, which is the best result for the one-pot transformation of 2,3-DCNB into 3-CA. Preparative runs on ca. 10 g of 2,3-DCNB indicated that the same selectivities are observed.

Unexpectedly, when the catalyst concentration is decreased to 1%, the transformation of 2,3-DCNB is no more selective. Large proportions of AN and 3-CA are formed before total conversion of 2,3-DCNB. For instance, after 3 h reaction, GC analysis indicates the following product distribution: 2,3-DCNB (11%), 2,3-DCA (6%), 3-CA (15%), 3-CNB (21%), NB (9%), AN (30%). A similar observation has been mentioned by Ohta et al. for the dechlorination of 4-chloronitrobenzene with the same catalyst.[12] At the beginning, $Pd(PPh_3)_4$ selectively dechlorinates 2,3-DCNB to 3-CNB, but after some turnovers hydrogenation occurs. These observations suggest that there is a change in the state of the palladium species, maybe from $Pd(PPh_3)_n$ to metallic palladium. The observed effect on the selectivity obviously depends on the catalyst concentration.

In conclusion, tetrakis(triphenylphosphine)palladium, $Pd(PPh_3)_4$, is an efficient catalyst for the selective dechlorination of 2,3-dichloronitrobenzene into 3-chloronitrobenzene. During the reaction the selectivity is over 90% in a very reproducible manner and the reaction can be stopped at the maximum selectivity.

This is the first reported example of both chemoselective (versus the nitro group) and regioselective (versus chlorine in the *meta* position) dechlorination of a polychloronitrobenzene. $Pd(PPh_3)_4$ is also a catalyst for the one-pot transformation of 2,3-dichloronitrobenzene into 3-chloroaniline (selectivity >60%). This is the first example of the regioselective dechlorination–hydrogenation sequence of polychloronitrobenzenes.

Further investigations are in progress directed to improve the catalyst stability during the reaction in order to allow much lower catalyst concentrations to be used.

Acknowledgements

The authors gratefully thank the Centre National de la Recherche Scientifique and the Société National des Poudres et Explosifs for financial support.

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