Pentaphenylcyclopentadiene, mp 250°C (Ref.[2] 248—250°C); ^{1}H NMR (C_6D_6, 400 MHz), δ: 5.23 (s, 1 H, CH); 7.40—6.85 (m, 25 H, arom.).

1,2,5-Triphenyl-3,4(1,8-naphthylene)cyclopentadiene, mp 234°C. Mass spectrum, *m/z* (70 eV, direct inlet): $[M]^+$ 418. ^{1}H NMR (C_6D_6, 400 MHz), δ: 5.62 (s, 1 H, CH); 6.75—7.40 (m, 21 H, arom.).

Found (%): C, 94.65; H, 5.35. $C_{33}H_{22}$. Calculated (%): C, 94.70; H, 5.30.

References

1. L. D. Field, M. Ho. Kanthy, C. M. Lindall, A. F. Masters, and A. G. Webb, *Aust. J. Chem.*, 1990, **98**, 281.
2. C. Janiak, H. Schuman, C. Stader, B. Wrackmeyer, and J. J. Zuckerman, *Chem. Ber.*, 1988, **121**, 1745.
3. J. W. Chambers, A. J. Bashar, S. G. Bott, J. L. Atwood, and M. D. Rausch, *Organometallics*, 1986, **5**, 1635.
4. W. Dithley, I. Horst, and W. Schommer, *J. Prakt. Chem.*, 1935, **143**, 189.
5. P. W. Reeves, and B. L. Williamson, *Synth. Commun.*, 1987, **17**, 1721.
6. A. B. Sigalov, E. S. Petrov, L. F. Rybakova, and I. P. Beletskaya, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1983, 2615 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1983, **32**, 2351 (Engl. Transl.)].
7. A. B. Sigalov, E. S. Petrov, L. F. Rybakova, and I. P. Beletskaya, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1986, 2143 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1986, **35**, 1955 (Engl. Transl.)].
8. A. B. Sigalov, E. S. Petrov, and I. P. Beletskaya, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1984, 2386 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1984, **33**, 2181 (Engl. Transl.)].
9. Z. Hou, H. Taniguchi, and Y. Fujivara, *Chem. Lett.*, 1987, 305.
10. T. Imamoto, T. Kusumoto, Y. Tawarayama, Y. Sugiura, T. Mita, Y. Hatanaka, and M. Yokoyama, *J. Org. Chem.*, 1984, **49**, 3904.
11. V. S. Abramov, and P. G. Mal'skii, *Zh. Obshch. Khim.*, 1939, **9**, 1533 [*J. Gen. Chem.*, 1939, **9** (Engl. Transl.)].
12. C. F. H. Allen, and Van Allan, *J. Org. Chem.*, 1952, **17**, 845.

Received July 29, 1992

$PdCl_2$-catalyzed hydrogenolysis of a C—O bond in monoaryl sulfates by sodium phosphinate in an aqueous alkaline medium

*D. V. Davydov and I. P. Beletskaya**

M. V. Lomonosov Moscow State University,
Leninskie Gory, 119899 Moscow, Russian Federation.
Fax: +7 (095) 939 1854

The hydrogenolysis of the C—O bond in monoaryl sulfates by the action of an excess of NaH_2PO_2 in the presence of catalytic amounts of $PdCl_2$ and KOH is studied. The reaction proceeds chemoselectively with complete ester conversion to the corresponding arenes.

Key words: hydrogenolysis, monoaryl sulfates, palladium, catalysis.

The removal of OH groups from aromatic compounds is widely employed in synthetic organic chemistry for various purposes, including modification of natural substrates.[1—4] According to modern catalytic methods, phenols are first converted into such derivatives as esters of perfluorosulfonic acids,[5—10] urethanes,[11,12] tetrazoles,[13] dialkyl phosphates,[14] etc. On the one hand, the hydrogenolysis of such derivatives necessitates the use of anhydrous organic solvents and, on the other hand, a portion of the molecule, whose introduction required expensive reagents, is lost. It seemed attractive, therefore, to use derivatives of inorganic acids for the deoxygenation of phenols and to abandon organic solvents.

The hydrogenolysis of monoaryl sulfates in water in the presence of a Raney alloy has been described.[15] The main drawback of this method is the use of large amounts of the Raney alloy, which produces the problem of utilizing the wastes containing Ni and Al. A method for the hydrogenolysis of an Ar—X bond, where X is Br or

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 3, pp. 605—606, March, 1993.

1066-5285/93/4203-0573 $12.50

I, by the action of $NaBH_4$ in the presence of catalytic amounts of $PdCl_2$ in an aqueous alkaline medium for water-soluble halogen derivatives of aromatic acids, phenols, amines, and heterocycles was suggested by us.[16] An increase in the reaction temperature leads to the rapid decomposition of $NaBH_4$, whereas the activity of Pd is maintained for 4—6 h. Thus, there is the possibility of using more stable hydrogen sources. The aim of the present research was to investigate the hydrogenolysis of monoaryl sulfates under similar conditions by the action of NaH_2PO_2, which is more thermally stable in the presence of Pd than $NaBH_4$.

Results and Discussion

Monoaryl sulfates were prepared by a standard method according to the following scheme[15]:

$$2\mathrm{PhNMe_2} + \mathrm{HSO_3Cl} \xrightarrow[-\mathrm{PhNMe_2}\cdot\mathrm{HCl}]{} \mathrm{PhNMe_2}\cdot\mathrm{SO_3} \xrightarrow{\mathrm{ArOH}}$$

$$[\mathrm{PhNHMe_2}]^+[\mathrm{OSO_3Ar}]^- \xrightarrow[\mathrm{H_2O}]{\mathrm{KOH}} [\mathrm{ArOSO_2O}]^-\mathrm{K}^+ \qquad (1)$$

The hydrogenolysis reaction was studied without isolation of esters, since the last step in their preparation was carried out in water. The hydrogenolysis conditions were optimized with a standard set of phenols by varying the reaction temperature and the amounts of the catalyst and the reducing agent. Complete conversion of the esters prepared could be achieved at 60—70°C with 5 moles of NaH_2PO_2 per mole of the phenol and 5 % $PdCl_2$ after 6 h.

Hydrogenolysis proceeds according to the scheme:

$$\mathrm{ArOSO_3K} + \mathrm{NaH_2PO_2} \xrightarrow[60\text{—}70^\circ\mathrm{C}]{5\%\ \mathrm{PdCl_2},\ \mathrm{KOH},\ \mathrm{H_2O},\ \mathrm{N_2}} \mathrm{ArH} \qquad (2)$$

The results obtained are summarized in Table 1. It can be seen that under the conditions found the monoaryl sulfates are converted completely into the respective arenes in preparative yields.

Hence, the method suggested has definite advantages over conventional procedures with respect to ease of operation.

Experimental

Phenols, dimethylaniline, and chlorosulfonic acid of chemically pure grade were purified by known methods. A solution of $PdCl_2$ (1 *M*) in conc. HCl was used as a catalyst. Analytically pure $NaH_2PO_2 \cdot H_2O$ was used in the studies. The reaction mixtures were analyzed on a Chrom-5 chromatograph equipped with a flame-ionization detector and nitrogen as a carrier gas at a flow rate of 60 mL min^{-1}; a glass column (3 m × 3 mm) was packed with 4 % OV-17 on Chromosorb W treated with dimethyldichlorosilane.

Table 1. Deoxygenation of phenols

Original phenols	Product	Yield (%)
4-Phenylphenol	Diphenyl	95
4-Phenoxyphenol	Diphenyl oxide	94
4-Methoxyphenol	Anisole	93
n-Cresol	Toluene	73
α-Naphtol	Naphthalene	89
β-Naphtol	Naphthalene	88
Thymol	Cumene	83

Note. Yields were determined by GLC.

The products were identified and the yields were determined by means of GLC by comparing the retention times of the products and authentic compounds with the use of an internal standard.

Catalytic hydrogenolysis. General procedure. In a flask equipped with a magnetic stirrer was placed potassium monoaryl sulfate prepared from the phenol (1 mmol) in the presence of KOH (3 mmol) in water (20 mL), and $PdCl_2$ (5 %) was added under nitrogen. The mixture was heated to 60—70°C and stirred for 4—6 h, NaH_2PO_2 (5 mmol) being added portionwise at about 1-h intervals to complete cessation of hydrogen evolution. The reaction mixture was cooled and acidified with HCl, and the products were extracted with ether. The extract was dried with sodium sulfate and analyzed following the addition of a standard. The maximum product yields are achieved by adding the $PdCl_2$ solution to the reaction system first and in the absence of palladium black from previous experiments on the vessel and stirrer surfaces (the residual black must be removed with aqua regia).

References

1. J. I. DeGraw, J. C. Christinsen, V. H. Brown, and M. J. Cory, *J. Heterocycl. Chem.*, 1974, **11**, 363.
2. S. Sakai, A. Kubo, T. Hamamoto, M. Wakabayashi, K. Takahashi, J. Haginiva, and Y. Ohtani, *Tetrahedron Lett.*, 1969, **19**, 1489.
3. C. F. Barfknecht, R. V. Smith, and V. D. Reif, *Can. J. Chem.*, 1970, **48**, 2138.
4. H. C. Beyerman, E. Buurman, T. S. Lie, and L. Maat, *Rec'. Trav. Chim. Pays-Bas,* 1976, **95**, 43.
5. L. R. Subramanian, A. G. Martinez, A. H. Fernandez, and R. M. Alvarez, *Synthesis,* 1984, **143**, №6, 481.
6. S. Cacci, P. Gp Giattini, E. Morrera, and G. Ortar, *Tetrahedron Lett.,* 1986, **27**, 5541.
7. Q. Y. Chen and Y. B. He, *Synthesis,* 1988, 896.
8. B. J. Hassey, R. A. W. Johnstone, and I. D. Entwistle, *Tetrahedron,* 1982, **38**, 3775.
9. G. A. Peterson, F. A. Kunng, J. S. McCallum, and W. D. Wulf, *Tetrahedron Lett.*, 1987, **28**, 1380.
10. E. Vowinkel and H. J. Baese, *Chem. Ber.*, 1974, **107**, 1213.
11. E. Vowinkel and C. Wolff, *Chem. Ber.*, 1974, **107**, 907.
12. J. D. Weaver, E. J. Eisenbraun, and L. E. Harris, *Chem. Ind.* (London), 1973, 187.
13. W. J. Musliner and J. W. Gates, *J. Am. Chem. Soc.*, 1966, **88**, 4271.
14. T. Shono, Y. Matsumoto, K. Tsubata, and Y. Sugihara, *J. Org. Chem.*, 1979, **44**, 4508.

15. W. Lonsky, H. Traitler, and K. Kratzl, *J. Chem. Soc., Perkin Trans. 1*, 1975, 169.

16. D. V. Davydov and I. P. Beletskaya, *Metalloorg. Khim.*, 1983, **6**, 11. [*J. Organomet. Chem. USSR*, 1983, **6** (Engl. Transl.)].

Received June 29, 1992

$PdCl_2$-catalyzed hydrogenolysis of an Ar—Cl bond by sodium phosphinate in an aqueous alkaline medium

D. V. Davydov and I. P. Beletskaya*

M. V. Lomonosov Moscow State University,
Leninskie Gory, 119899 Moscow, Russian Federation.
Fax: +7 (095) 939 1854

The hydrogenolysis of the Ar—Cl bond in chlorinated benzoic acids, anilines, and nitrogen-containing heterocycles by the action of NaH_2PO_2 in the presence of catalytic amounts of $PdCl_2$ and NaOH in an aqueous medium was studied. Under these conditions aryl chlorides were quantitatively converted into the corresponding arenes. Chloropyridines, such as 2-chloropyridine and 3,5-dichloropicolinic acid, did not undergo hydrogenolysis even in the presence of an equivalent amount of NaI. A distinct *ortho* effect was observed for *ortho*-substituted substrates.

Key words: hydrogenolysis, palladium, catalysis, aryl chlorides.

The hydrogenolysis of a C—X bond, where X = Hal, particularly in aromatic compounds, is of great importance in synthetic organic chemistry.[1] Blocking of a definite position of an aromatic ring followed by dehalogenation is widely used in syntheses of carbo- and heterocycles.[2—5] The partial dehalogenation of polyhalides[6] and the specific deuteration of an arene[7] deserve special studies. The hydrogenolysis of an Ar—Cl bond presents special difficulties.[1]

We have shown that water-soluble aryl iodides and aryl bromides, unlike aryl chlorides, readily undergo hydrogenolysis by $NaBH_4$ in the presence of "ligand-free" palladium in an aqueous alkaline medium. For aryl chlorides[8] the extent of conversion of the substrates does not exceed 30 %. The reason for the low reactivity of aryl chlorides is the low rate of their oxidative addition to zero-valent palladium. The attempts to carry out the hydrogenolysis of chloroarenes at high temperatures failed due to the rapid decomposition of $NaBH_4$ under the conditions employed.

There are a few controversial reports on the hydrogenolysis of aryl chlorides in alkaline aqueous-organic media by NaH_2PO_2 in the presence of Pd/C as a catalyst. For example, it was stated that chlorine cannot be eliminated from *p*-chlorocinnamic acid under the conditions mentioned.[9] In contrast, this substrate, as well as chlorobenzene, were reported to be reduced to the corresponding arenes in preparative yields.[10]

Since sodium dihydrogen phosphinate is far more thermally stable in the presence of Pd than $NaBH_4$, the process can be accelerated without an appreciable drop in the extent of conversion of certain substrates. The aim of the present research was a systematic study of the hydrogenolysis of the Ar—Cl bond in water-soluble substrates in the presence of $PdCl_2$ with NaH_2PO_2 as a hydrogen source.

Results and Discussion

p-Chlorobenzoic acid with an electron-acceptor substituent was chosen as the test compound for optimization of the hydrogenolysis conditions. The chlorine atom could easily be eliminated from this molecule by heating the reaction mixture to 50°C (Table 1). The reaction of aryl chlorides with strong electron-donor groups proceeds in a similar way as shown below:

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 3, pp. 607—609, March, 1993.

1066-5285/93/4203-0575$12.50