ORGANIC LETTERS

2004
Vol. 6, No. 26
5015−5017

Platinum(IV) Oxide Catalyzed H−D Exchange Reactions in Arylsilanes

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Received November 3, 2004

ABSTRACT

$$Ar_nR_{4-n}Si \xrightarrow[D_2O,\ 250\ °C,\ 4\ MPa]{PtO_2\ 5\ mol\%} R_{4-n}Si(Ar\text{-}d)_n$$

Arylsilanes were regioselectively labeled with deuterium by treatment with platinum(IV) oxide and deuterium oxide under hydrothermal conditions. Arylsilanols were also labeled with regioselectively under the same conditions.

The H−D exchange reaction in organic compounds is an important method for preparing labeled compounds. These compounds are important for biological research and have also been studied as substrates for structural analyses by NMR or neutron scattering.[1] Recently, they have also been recognized as new materials for use in optical communication.[2] The H−D exchange reaction with deuterium oxide has been performed in various ways.[3] For example, the base-catalyzed H−D exchange reaction with supercritical or subcritical deuterium oxide has been applied to phenol and aniline derivatives,[4] and an acid-catalyzed version has been applied to alkenes.[5] In addition, a transition-metal-catalyzed exchange reaction with deuterium oxide has also been studied, since Garnett and Shilov developed a homogeneous platinum salt catalyzed H−D exchange reaction.[1c,3,6,7] We previously demonstrated that H−D exchange reactions could be effectively performed in alkanes and alkenes with Pd/C catalyst in hydrothermal deuterium oxide,[8a,b] and reactions in polystyrene samples could also be performed with PtO_2 catalyst in hydrothermal deuterium oxide.[8c] In these H−D exchange reactions, in hydrothermal or supercritical deuterium oxide, an important problem is functional group tolerance. The acid- and base-catalyzed reactions offer conditions that may be too severe for many functional groups to survive. Although transition metal catalyzed reactions may improve this situation,[1c] there is little information available on this subject.

If arylsilane compounds, which are useful reagents for the coupling reaction with halides,[9] can be subjected to the H−D exchange reactions, the deuterated products should be important reagents for the preparation of deuterium-containing aromatic compounds. Acid- and base-catalyzed reactions in hydrothermal or supercritical deuterium oxide do not seem to be promising, since the protiodesilylation of organosilanes in supercritical water has been shown to proceed effectively, even without the addition of a base or acid.[10] We examined

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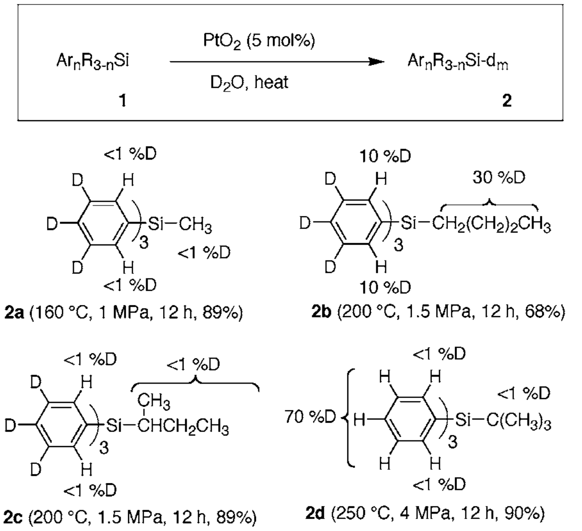
10.1021/ol047738w CCC: $27.50

the platinum(IV) oxide catalyzed H−D exchange reaction of arylsilanes in hydrothermal deuterium oxide.

The substrate (**1a**−**d** in Scheme 1, 1.0 mmol), PtO_2 (0.05 mmol), and deuterium oxide (2.0 g) were pulverized and mixed completely by a ball mill machine (planetary ball mill, P-5, Fritsch, using an 80-mL stainless steel vessel and five stainless balls (ϕ 20 mm)).[8c] The resulting mixture was heated with deuterium oxide (10 g) at 160−250 °C for 12 h in a 30-mL Teflon-lined stainless autoclave that has been described previously.[8a] After heating, the mixture was extracted with ether. The products were analyzed by ^{1}H NMR, ^{2}H NMR, ^{13}C NMR, and mass spectroscopy. The deuterium atom contribution was determined both by ^{1}H NMR and ^{2}H NMR using an internal standard. The results are shown in Scheme 1.

Scheme 1



2a (160 °C, 1 MPa, 12 h, 89%) **2b** (200 °C, 1.5 MPa, 12 h, 68%)

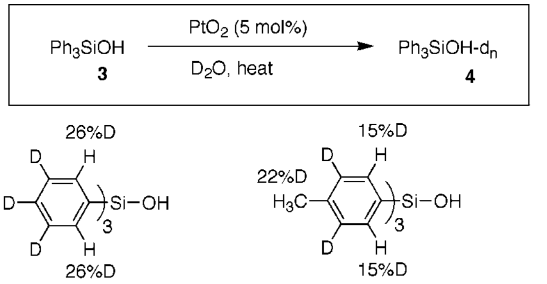
2c (200 °C, 1.5 MPa, 12 h, 89%) **2d** (250 °C, 4 MPa, 12 h, 90%)

In parentheses (reaction temperature, internal pressure, reaction time, yield)

In these cases, the H−D exchange reaction was observed mainly on aromatic rings. The regioselectivities at the *meta*- and *para*-positions in the exchange reactions in Scheme 1 can be explained by steric hindrance. In all cases, the exchange reaction at the *ortho*-position was suppressed because of steric hindrance. The bulkiness around the Si may be indispensable for this transformation, since the formation of a highly coordinated silicate with OD^- anion from hydrothermal deuterium oxide should cause protiodesilylation.[10] For example, after trimethyphenylsilane was treated with PtO_2 in 180 °C water for 12 h, protiodesilylation of the Ph−Si bond was the major reaction.

For the transition-metal-catalyzed coupling of organosilane compounds,[9b] we tried to use a deuterated arylsilanol. To obtain the silanol, triphenylsilanol was treated with the above H−D exchange conditions. As shown in Scheme 2, the phenyl groups in the silanol deuterated with PtO_2 catalyst in deuterium oxide under hydrothermal conditions. The H−D exchange reactions at the *meta*- and *para*-positions were complete, and partial exchange at the *ortho*-position was also observed (**4a** in Scheme 2). The H−D exchange in tris(*o*-tolyl)silanol did not complete because of steric hindrance (**4b** in Scheme 2).

Scheme 2

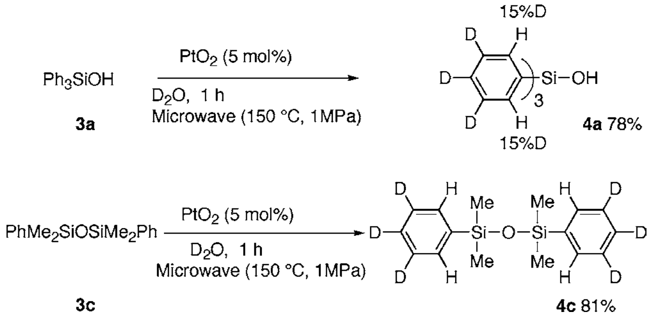


4a (160 °C, 1,5 MPa, 12 h,82%) **4b** (160 °C, 1,5 MPa, 12 h,44%)

In parentheses (reaction temperature, internal pressure, reaction time, yield)

Microwave irradiation of the reaction in a sealed vial made it easy to achieve hydrothermal conditions.[11,12] To a 10-mL vial (sealed by a septum) was added a mixture of triphenylsilanol (**3**, 2.0 mmol), PtO_2 (0.1 mmol), and deuterium oxide (1.0 g), which had all been pulverized and mixed completely as described above, and deuterium oxide (3.0 mL). The vial was irradiated with microwaves (100 W) and kept at 150 °C and 1.0 MPa for 1 h. Arylsilanes and arylsilanols were deuterated as shown in Schemes 2 and 3. Siloxane **3c** was also converted to the labeled compound **4c**.

Scheme 3



As shown in Scheme 4, deuterated triphenylsilanol was treated with iodobenzene and silver(I) oxide in the presence of palladium catalyst.[9b] Half-deuterated biphenyl **5** was obtained in an excellent yield.

Several metal-catalyzed H−D exchange reactions in simple aromatic compounds other than arylsilanes in hydro-

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(11) Deuteration under microwave irradiation: (a) Fodor-Csorba, K.; Galli, G.; Holly, S.; Gács-Baitz, E. *Tetrahedron Lett*. **2002**, *43*, 3789. (b) Jones, J. R.; Lockley. W. J. S.; Lu. S.-Y.; Thompson, S. P. *Tetrahedron Lett*. **2001**, *42*, 331. (c) Yamamoto, M.; Oshima, K.; Matsubara, S. *Chem. Lett*. **2004**, *33*, 846.

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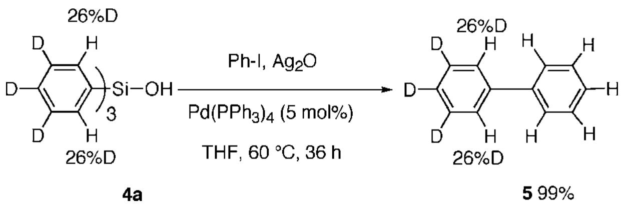
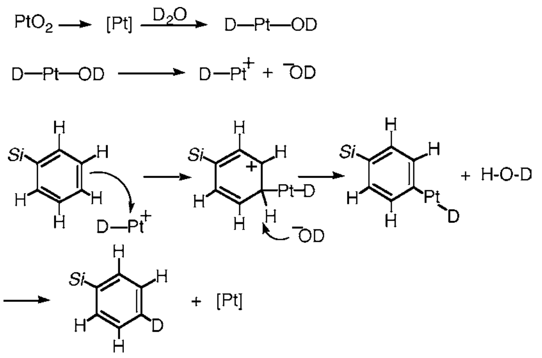
Scheme 4



thermal deuterium oxide or under microwave irradiation have been reported, but mechanistic studies have not been well discussed.[1c,6,13] We suppose that the reaction proceeds as shown in Scheme 5. Platinum(IV) oxide is reduced to metal in hydrothermal deuterium oxide and is inserted into deuterium oxide.[14,15] The resulting D-Pt-OD complex will give cationic platinum deuteride, which will interact with a benzene ring and undergo an H−D exchange reaction. We have no evidence for this proposed mechanism except for pyrolysis GC of the recovered platinum catalyst. After the H−D exchange reaction shown in Scheme 1, the platinum catalyst was recovered, washed with hexane and water, and dried in vacuo. Pyrolysis of the residue gave deuterium gas at 700 °C (Figure 1). This may show that platinum deuteride species was formed in situ.

Scheme 5



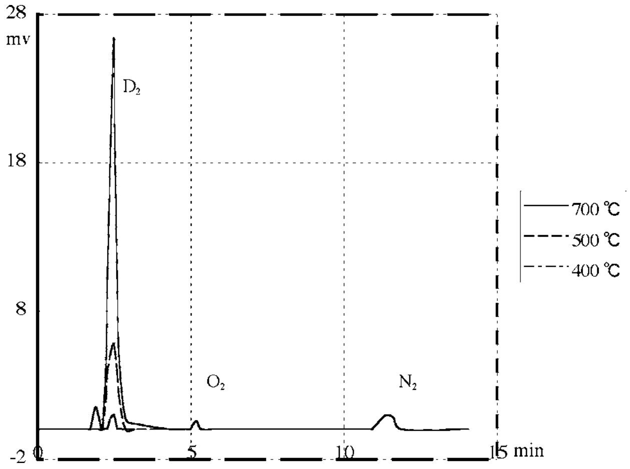


Figure 1. Pyrolysis GC of the recovered catalyst at 400, 500, and 700 °C.

Platinum(IV) oxide may be somewhat converted into deuteride species under hydrothermal conditions. Although its stability and reactivity are not clear, we suppose it is the reactive species for these H−D exchange reactions.

Acknowledgment. Pyrolysis GC was performed by Prof. Tsunehiro Tanaka (Kyoto University, Department of Molecular Engineering). We greatly appreciate his contribution. This work was supported financially by Kyoto University, International Innovation Centre. Financial support from Chugai Pharmaceutical Co., Ltd. and Takahashi Industrial and Economical Research Foundation are also acknowledged.

Supporting Information Available: Experimental details and spectral data of the compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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