

Synthesis of Deuterium Labeled Isobutane : Isobutane-2-d₁, Isobutane-1-d₉ and Isobutane-d₁₀

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SUMMARY

2-Methylpropane-2-d₁ (isobutane-2-d₁), 2-(methyl-d₃)-propane-1,1,1,3,3,3-d₆ (nonadeuterated isobutane) and 2-methylpropane-d₁₀ (perdeuterated isobutane) were synthesized by using a combination of classical organic chemistry and recently developed H/D exchange processes on solid acids. Isobutane-2-d₁ was synthesized from t-butyl chloride by Grignard synthesis with an overall yield of 27.0% (chemical purity : 99.9% and isotopic purity : 96.0%). Isobutane-1-d₉ was prepared by H/D exchange of 2-methylpropane (isobutane) with a D₂O exchanged zeolite. The deuteriated product was obtained with an overall yield of 80.0% (chemical purity : 99.9% and isotopic purity : 98.7%). Perdeuteriated isobutane was prepared by reacting isobutane-2-d₁ with 98.0% deuteriated sulfuric acid and was obtained in a total yield of 98.0% (chemical purity : 99.8% and isotopic purity : 97.9%).

Key Words : 2-methylpropane, deuterium, isobutane-2-d, isobutane-1-d₉, isobutane-d₁₀

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INTRODUCTION

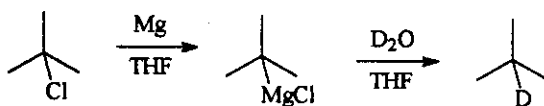
International environmental laws require the petroleum industry to replace lead derivatives in gasoline by oxygenated compounds, which work as octane boosters (1). Isobutane is a key product in the alkylation processes leading to the synthesis of gasoline additives such as methyl t-butyl ether (MTBE) or isooctane (2,2,4 trimethylpentane). In this way many research groups are still working on acid catalyzed alkylation processes and synthesis of environmentally friendly gasoline additives using isobutane as starting material (2). An important goal is to understand the mechanism of alkane reactions on acidic material such as zeolites by comparison with superacid catalyzed alkane activation. One of the best tools for mechanistic investigation is to follow the reactions using labeled starting materials. This methodology can give information about reaction rates, isotope effects and regioselectivity.

In this paper we describe the synthesis of three different isobutane isotopologues: 2-methylpropane-2- d_1 , methyl- d_3 -propane-1,1,1,3,3,3- d_6 and 2-methylpropane- d_{10} with fair to good overall yields, high chemical and isotopic purities and relatively low synthetic costs.

RESULTS AND DISCUSSION

2-Methylpropane-2- d_1

2-Methylpropane-2- d_1 was prepared from t-butyl-chloride by a Grignard type reaction. The Grignard reagent was prepared by reaction of t-butyl-chloride with solid Mg. Because of the low boiling point of ethyl ether, THF was used as reaction solvent. D_2O was then added to the reaction mixture and 2-methylpropane-2- d_1 was formed (Scheme 1):



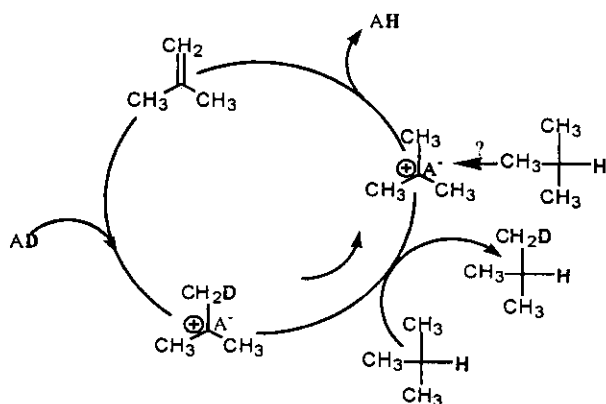
Scheme 1: Synthesis of 2-methylpropane-2- d_1 using a Grignard reagent

In order to remove isobutene formed by the competing elimination reaction, the obtained gaseous mixture, containing 2-methylpropane-2-d₁, was purified by reacting with Br₂ followed by distillation.

Methyl-d₃-propane-1,1,1,3,3,3-d₆

Alkanes are known to react on acidic zeolites (protonic form) with the formation of adsorbed carbenium ions as intermediates (2). At high temperatures (> 200°C) they can undergo H/D exchange, isomerization and cracking. However at moderate temperatures (100°C-200°C) we have recently shown that for isoalkanes only a regiospecific H/D exchange takes place (4). The exchange mechanism, based on the Markovnikov rule, is similar to that proposed by Otvos and Stevenson (5) in concentrated sulfuric acid (98%) and can be illustrated by the catalytic cycle (Scheme 2).

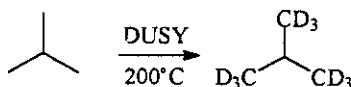
The first step is the formation of a carbenium ion from the alkane that can transfer a proton to the catalyst to form an alkene. The former can be protonated/deuterated by the acidic sites of the catalyst to give a new carbenium ion containing a deuterium atom in the primary position. This cycle can be repeated leading to an isotopic enrichment of the carbenium ion. The last step is a hydride transfer from an incoming alkane to the carbenium ion giving a



Scheme 2 : Catalytic H/D exchange cycle of isobutane on deuteriated zeolite.

deuterium containing isobutane molecule. In this mechanism it is important to note that only the primary hydrogens of isobutane are exchanged by deuterons and that no deuterium will be found in the tertiary position.

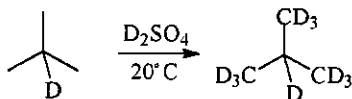
Whilst, in sulfuric acid the initial activation step of the alkane is known to be the oxidation of the alkane as shown by the formation of SO_2 (6), on zeolite this step is still a matter of debate. The advantage of using D_2O exchanged zeolite instead of sulfuric acid is the fact that the zeolite can be easily regenerated whereas in sulfuric acid the build-up of oligomeric material will lead to a loss of selectivity in the deuteration of the isoalkane (6) and the acid must be discarded before reaching that stage. On the other hand, the drawback of using the zeolite is the small number of exchangeable protons per gram of catalyst (of the order of 10^3 equivalent g^{-1}) by comparison with sulfuric acid $\sim 10^2$ equivalent/g. For this reason USY-zeolite was used in preference to other analogous material because of the larger number of acid sites (2.9 mmol H^+ /g of catalyst).



Scheme 3 : Synthesis of methyl-d₃-propane-1,1,1,3,3,3-d₆

2-Methylpropane-d₁₀

For 2-methylpropane-d₁₀, the Grignard method was first used for the synthesis of 2-methylpropane-2-d₁ and then we tried D_2SO_4 for exchanging the primary hydrogens. This helped us to show that a better yield was obtained with D_2SO_4 by comparison with D_2O -exchanged zeolite.



Scheme 4 : Synthesis of 2-methylpropane-d₁₀

EXPERIMENTAL

Materials

The reagents were used as received from the suppliers. Isobutane (purity: 99.95%) was purchased from AIR PRODUCTS, t-butyl-chloride (purity: 99%), D₂SO₄ (98wt%, 99.5 atom%D) from ALDRICH CHEMICALS, Br₂ (99.8%) and Na₂S₂O₃·5H₂O (99.5%) from ACROS. THF (99.7%) and magnesium for Grignard were purchased from PROLABO, and D₂O (99.90%) from SDS. HUSY is the protonic form of an ammonium exchanged zeolite (Area: 566m²/g, Si/Al (chemical analysis) = 2.6, Na₂O = 0.3wt%), and was obtained from PETROBRAS (Brazil).

Apparatus

Gas Chromatography: Reaction products were separated by gas chromatography (GC 8000, CARLO ERBA INSTRUMENTS) equipped with a capillary column DB 624, G&W Scientific (30 m, diam. = 0.25 mm, film thickness = 1.4 μm). The oven temperature was maintained at 35°C. The detector and injector temperature was maintained at 150°C.

Mass Spectroscopy: The products were analyzed by mass spectrometry using a QMD 1000 spectrometer (CARLO ERBA INSTRUMENTS) with an ionization voltage of 70 eV and a source temperature of 150°C.

NMR: The alkanes were collected in a cold trap and analysed by (400 MHz) ¹H and (61 MHz) ²H NMR after addition of an adequate amount of a CFC₃ solution of a CDCl₃/CHCl₃ mixture used as internal standard for the H/D distribution measurement.

2-Methylpropane-2-d₁

A 50 ml solution of t-butyl-chloride (42.55g, 0.459 mole) dissolved in 200ml of freshly distilled and sodium/benzophenone dried THF was added to 12.7g of pre-activated Mg turnings (heated at 120°C for 90 min) in 20 ml of THF over a period of 5 hours with magnetic stirring.

On completion of the addition the mixture was stirred for a further 2 hours, warmed up to boiling for 15 minutes and then cooled in an ice bath in order to remove gaseous isobutane and isobutene which are eventually formed (see scheme 1). 10 ml of D₂O (0.553 mole) in 20 ml of dry THF were then added progressively, and the produced gases collected in a trap cooled at -196°C (liquid nitrogen) equipped with gas tight taps and connected on the top of the condenser by a polyethylene tube and a rubber cap. After addition of all the deuterium oxide, the reaction mixture was heated up to the boiling point to release all the dissolved gases. Then 1.7 g of Br₂ was added to the condensed gases in the cold trap, which was then placed in the refrigerator (4°C) for 1.5 hours. The crude 2-methyl-propane-2-d₁ was then distilled, and the gaseous product was bubbled through two traps containing an aqueous solution of Na₂S₂O₃ (5.3 g Na₂S₂O₃.5H₂O in 13 ml of solution), collected in a final trap (-196°C) and stored over 3 Å molecular sieves. 7.4 g (0.125 mole) of 2-methylpropane-2-d₁ was obtained (27% yield) with chemical and isotopic purities of 99.90% and 96%, respectively (based on GC and NMR analysis).

Methyl-d₃-propane-1,1,1,3,3,3-d₆

The catalytic reaction was run in an all glass, grease free, flow system (7). About 6 g of HUSY zeolite (2.9 mmol H⁺/g of catalyst) was heated at 500°C under nitrogen flow (38 mL.min⁻¹) for 1 hour. Deuteriation was then carried out at 200°C by passing 3 mol % D₂O in nitrogen (38 mL.min⁻¹) onto the catalyst for 1 hour followed by a nitrogen purge of 30 min. 50 ml of isobutane (2 mmol, 6% in the nitrogen) was passed at a total rate of 20 mL.min⁻¹ over the catalyst at 200°C. After reaction, isobutane was condensed in a cold trap and stored at -78°C for the next pass whilst the catalyst was flushed with N₂, reactivated at 500°C for 1 hour, and re-exchanged with D₂O at 200°C. After each pass isobutane was analyzed by GC-MS for deuterium content. This cycle was repeated 8 times exchanging the zeolite used every 2 passages to avoid secondary reactions. The nonadeuterated product was obtained with an overall yield of 80% (chemical purity based on GC analysis : 99.90% and isotopic purity based on NMR analysis : 98.70%).

2-Methylpropane-d₁₀

The catalytic reaction was also run in an all-glass grease free set-up with a recirculation pump. Isobutane (4.46 mmol) was bubbled at a rate of 4 ml/min through 2 ml (37.4 mmol) 98% D₂SO₄ (99.9%D), and recirculated at room temperature during 8 hours. Then wasted sulfuric acid was replaced by 1 ml of a fresh batch and the recirculation was carried out for an additional 20 hours. After this pass, a third pass (20 hours) with 1 ml of fresh deuteriated sulfuric acid was run under the same conditions. Isobutane was analyzed after each pass by GC-MS and by ¹H and ²H NMR after the three recirculations. At the end 98mL, (99.9%D) isobutane (98% yield) was recovered.

Acknowledgments

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