Organic LETTERS

Letter

Cite This: Org. Lett. XXXX, XXX, XXX−XXX

pubs.acs.org/OrgLett

Stainless Steel-Mediated Hydrogen Generation from Alkanes and Diethyl Ether and Its Application for Arene Reduction

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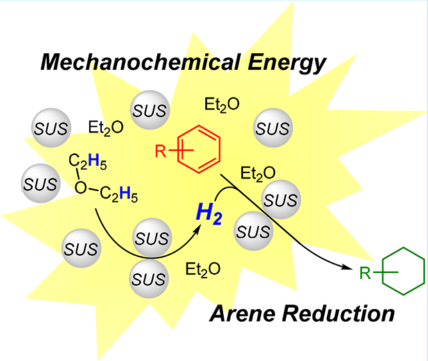
Supporting Information

ABSTRACT: Hydrogen gas can be generated from simple alkanes (e.g., *n*-pentane, *n*-hexane, etc.) and diethyl ether (Et_2O) by mechanochemical energy using a planetary ball mill (SUS304, Fritsch Pulverisette 7), and the use of stainless steel balls and vessel is an important factor to generate the hydrogen. The reduction of organic compounds was also accomplished using the in-situ-generated hydrogen. While the use of pentane as the hydrogen source facilitated the reduction of the olefin moieties, the arene reduction could proceed using Et_2O. Within the components (Fe, Cr, Ni, etc.) of the stainless steel, Cr was the metal factor for the hydrogen generation from the alkanes and Et_2O, and Ni metal played the role of the hydrogenation catalyst.



Hydrogen technology is becoming of increasing importance as an alternative manner to avoid global climate changes, which are mainly based on the emission of carbon dioxide (CO_2) derived from the combustion of fossil fuels.[1] Because industrial hydrogen production methods using fossil fuels such as methane (CH_4) as its raw materials emit substantial quantities of CO_2 as a byproduct, it is quite important to spur the development of new CO_2-free practical technologies for hydrogen production resulting in the coproduction of elemental carbon.[2] The transition-metal-catalyzed CO_2-free hydrogen generation consisting of dehydrogenation and C−C bonds cleavage reactions (decomposition) of alkanes is an useful strategy to produce H_2 gas.[2,3] Although such alkane-decomposition techniques have been the subject of active investigations in the past two decades, industrial practical hydrogen production (hydrogen recovery) processes have still not been developed. On the other hand, the reduction of organic compounds is a fundamental reaction in organic chemistry. In particular, the catalytic hydrogenation of resonance-stabilized arenes[4,5] is an important method for accessing the corresponding cyclohexane derivatives, which are utilized as functional materials and are expected to be used for hydrogen storage as liquid organic hydrogen carrier (LOHC) systems in the energy field.[6] However, the use of large amounts of industrially produced flammable H_2 gas under high pressure and temperature is constantly required.[4] From the point of view of safety, easy handling, and the reduction of environmental burdens, the development of a CO_2-free direct arene hydrogenation (hydrogen transfer) method from a LOHC is extremely attractive. We have previously developed a heterogeneous noble metal-catalyzed arene hydrogenation reaction using isopropanol as the CO_2-free hydrogen source.[5] Meanwhile, we have also recently accomplished a stainless-steel (SUS304) and mechanochemical energy-mediated quantitative hydrogen generation reaction from water (water splitting),[7a] and the in-situ-generated hydrogen could be utilized as a reductant of the coexisting reducible functional groups (alkyne, alkene, aromatic halides, nitro group, azide, ketone, etc.) in a planetary ball milling vessel.[7b] We now report the stainless-steel (SUS304) and mechanochemical energy-mediated CO_2-free hydrogenation reaction of alkenes, alkynes, and ketones using alkanes and diethyl ether (Et_2O) to generate the appropriate quantities of H_2 gas; the process is accompanied by the formation of gaseous molecular hydrocarbons such as CH_4, generated by C−C bond cleavage of the parent alkanes and Et_2O. It is noteworthy that the hydrogenation of resonance-stabilized aromatic nuclei could also be achieved by using Et_2O as the hydrogen source to give the cyclohexane derivatives without the use of any noble-metal catalysts.

Liquid alkanes as a part of the LOHCs are easily available and inexpensive, because of their production from fossil fuels, in most cases, and their frequent use as solvents in synthetic organic chemistry. First, the reactivity of alkanes in the hydrogen generation was investigated (see Table 1). Pentane (n-C_5H_{12}, 15 mmol) could be smoothly transformed to H_2 (0.93 mmol), along with the generation of CH_4 (2.36 mmol) and trace amounts of ethane and propane by the mechanochemical reaction using a planetary ball milling device equipped with stainless steel (SUS304) balls and a vessel at a 800 rpm rotation speed for 1 h (entry 1 in Table 1).[8] Hexane (n-C_6H_{14}) and heptane (n-C_7H_{16}) could also serve as hydrogen

Received: March 21, 2018

DOI: 10.1021/acs.orglett.8b00931

Table 1. Hydrogen Generation Activity of Alkanes under Ball Milling Conditions[a]

$$\underset{(15\ \text{mmol})}{\text{alkane}} \xrightarrow[\text{800 rpm, 1 h}]{\text{SUS304 balls}} \text{analysis of gas component}$$

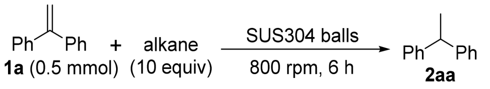
entry	alkane	Generated Gas[b] (mmol)	
		H_2	CH_4
1	n-C_5H_{12}	0.93	2.36
2	n-C_6H_{14}	1.06	0.84
3	n-C_7H_{16}	2.05	0.62
4	n-$C_{10}H_{22}$	not detected	not detected

[a]The reaction was carried out using a Fritsch Pulverisette 7 Premium Line 7 Ball Mill (PLP-7) that was equipped with a 80 mL SUS304 vessel and 100 SUS304 balls (diameter: ca. 5 mm). Alkanes were purchased from commercial sources and used without further purification. [b]The total quantity of the generated gas and the proportion of hydrogen, methane, etc., including nitrogen and oxygen contaminated from the air during operation are described in the Supporting Information. Trace amounts of ethane and propane were also detected by the GC analysis.

sources (entries 2 and 3 in Table 1), while no hydrogen generation was observed using decane (n-$C_{10}H_{22}$) as a substrate (entry 4 in Table 1).

The in-situ-generated H_2 in a SUS304 ball milling vessel could be utilized for the reduction of olefin (see Table 2). 1,1-Diphenylethane (**2aa**) as a hydrogenated product was produced by the rotation (800 rpm) of a mixture of 1,1-diphenylethene (**1a**; 0.5 mmol), 10 equiv of n-C_5H_{12} and 5 mm diameter SUS304 balls (50 pieces) in a 12 mL SUS304 vessel for 6 h in 24% yield, together with 60% of unchanged **1a** (Table 2, entry 1). n-C_6H_{14} was the apparent hydrogen source in this instance (Table 2, entry 2), since n-C_7H_{16} and n-$C_{10}H_{22}$ were ineffective as reaction solvents (Table 2, entries 3 and 4). The hydrogenation activity was not correlated with the in-situ-generated H_2 amount (compare Tables 1 and 2). The cyclic alkanes, such as c-C_5H_{12} and c-C_6H_{14}, possessed similar hydrogenation activities, in comparison to n-C_5H_{12} and n-C_6H_{14}. The use of n-C_5H_{12} (20 equiv) for a longer rotation time (24 h) completed the reduction of **1a** to give **2aa** in moderate yield (Table 2, entry 7).[8] A 1.0 mol scale reaction of **1a** using the same vessel (12 mL) and number of balls (50 pieces) lowered the reactivity (Table 2, entry 8), which indicated that the internal capacity of the vessel and the ball number might need to be increased for scaleup.

Table 2. Hydrogenation of Olefin Using Alkane as a Hydrogen Source[a]

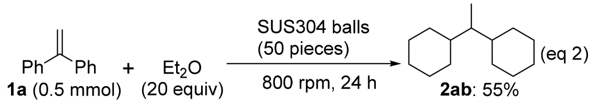


entry	alkane	Yield (%)	
		recovered **1**	**2aa**
1	n-C_5H_{12}	60	24
2	n-C_6H_{14}	92	6
3[b]	n-C_7H_{16}	no reaction	
4[b]	n-$C_{10}H_{22}$	no reaction	
5	c-C_5H_{10}	76	10
6	c-C_6H_{12}	85	6
7[c]	n-C_5H_{12}	0	55
8[c,d]	n-C_5H_{12}	68	16

[a]The reaction was carried out using a Fritsch Pulverisette 7 Classic Line Ball Mill (PL-7) that was equipped with a 12 mL SUS304 vessel and 50 SUS304 balls (diameter: ca. 5 mm). Alkanes were purchased from commercial sources and used without further purification. [b]The use of distilled n-C_7H_{16} or n-$C_{10}H_{22}$ resulted in no reaction. [c]20 equiv of n-C_5H_{12} were used, and the reaction was carried out for 24 h. [d]1.0 mol of **1a** was used using a Fritsch Pulverisette 7 Classic Line Ball Mill (PL-7) equipped a 12 mL SUS304 vessel and 50 SUS304 balls (diameter: ca. 5 mm).

Et_2O also proved to be an efficient hydrogen source under the same reaction conditions, as shown in Table 1, and 3.01 mmol H_2 gas and 0.84 mmol CH_4 were produced from 15 mmol Et_2O in 1 h (eq 1). Intriguingly, and contrary to our expectations, the hydrogenation of **1a** could be accomplished at 800 rpm in the presence of 20 equiv of Et_2O as a hydrogen source to generate 1,1-dicyclohexylethane (**2ab**). Here, hydrogenation of the olefin moiety, as well as the aromatic nuclei, occurred (eq 2).

$$\underset{(15\ \text{mmol})}{Et_2O} \xrightarrow[\text{800 rpm, 1 h}]{\text{SUS304 balls (100 pieces)}} \begin{array}{l} H_2\ (3.01\ \text{mmol}) \\ CH_4\ (0.84\ \text{mmol}) \\ \text{etc.} \end{array} \qquad \text{(eq 1)}$$

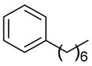
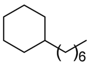
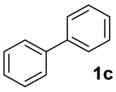
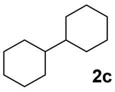
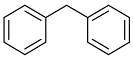
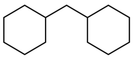
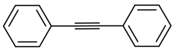
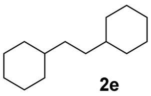
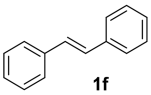
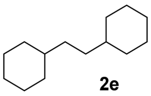
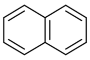
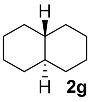
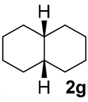
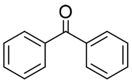
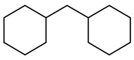
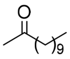
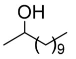
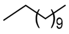
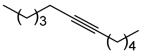
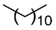


Via this protocol, a wide variety of arene derivatives were mechanochemically hydrogenated in the presence of Et_2O as a hydrogen source (see Table 3). The detailed optimization using n-heptylbenzene (**1b**, 0.5 mmol) as a simple arene substrate has been described in the Supporting Information (Table S2). The aromatic nucleus of **1b** was thoroughly hydrogenated to produce **2b** in 67% yield (Table 3, entry 1). Biphenyl (**1c**) and diphenylmethane (**1d**) bearing two aromatic rings within the molecule were also hydrogenated to the corresponding biscyclohexane derivatives (**2c** and **2d**) in moderate yields (Table 3, entries 2 and 3). Diphenylacetylene (**1e**) and stilbene (**1f**) were transformed to 1,2-dicyclohexylethane (**2e**) with complete hydrogenation of the aromatic nuclei as well as the alkyne and alkene moieties (Table 3, entries 4 and 5). Naphthalene (**1g**) was also entirely hydrogenated to give bicyclo[4,4,0]decane (decaline, **2ga** and **2gb**) as a mixture of *cis* and *trans* isomers (Table 3, entry 6). Benzophenone (**1h**) also efficiently underwent arene hydrogenation to give dicyclohexylmethane (**2d**), along with hydrogenolysis of the ketone function (Table 3, entry 7). 2-Dodecanone (**1i**) as an aliphatic ketone was less reactive, and 2-dodecanol (**2i**) as a secondary alcohol was obtained in 32% yield in association with the recovery of the unchanged starting material (61%, **1i**). Meanwhile, the aliphatic alkyne functionalities of **1j** and **1l** were efficiently hydrogenated to the corresponding alkanes (**2j** and **2l**) in good yields (Table 3, entries 9 and 10).

Mechanochemical energy could be effectively applied to various reactions,[9] and the metallic component of the ball mill system sometimes facilitated the desired reaction.[10] The present SUS304 and mechanochemical energy-mediated hydrogen generation from alkanes and Et_2O in a SUS304 ball milling vessel never proceeded when using ZrO_2 balls (diameter 5 mm) and a vessel (20 mL, Table 4, entry 1). Stainless steel (SUS304) is composed of Fe, Cr, and Ni as the main components (Fe, 69%; Cr, 18%−20%; Ni, 8%−10%). Therefore, the metal efficiencies to promote the H_2 gas generation using Et_2O (3.75 mmol) under the stated ball milling conditions were next investigated via the addition of zerovalent

Table 3. Scope of Substrates[a]

$$\underset{(0.5\ \mathrm{mmol})}{\text{substrate}} + \underset{(20\ \mathrm{equiv})}{Et_2O} \xrightarrow[\text{800 rpm, 24 h}]{\text{SUS304 balls}} \text{product}$$

entry	substrate	product	yield (%)
1	 **1b**	 **2b**	67
2	 **1c**	 **2c**	56
3	 **1d**	 **2d**	61
4	 **1e**	 **2e**	48
5	 **1f**	 **2e**	49
6	 **1g**	 **2ga**  **2gb**	27 (30:70)
7	 **1h**	 **2d**	43
8	 **1i**	 **2i**	32 (61)[b]
9	 **1j**	 **2j**	86
10	 **1l**	 **2l**	64

[a] The reaction was carried out using a Fritsch Pulverisette 7 Classic Line Ball Mill (PL-7) equipped with a 12 mL SUS304 vessel and 50 SUS304 balls (diameter: ca. 5 mm). Et_2O was purchased from commercial sources and used without further purification. [b] Recovery of the substrate.

Table 4. Essential Metal To Generate Hydrogen and Methane[a]

$$\underset{(3.75\ \mathrm{mmol})}{Et_2O} \xrightarrow[\text{800 rpm, 0.5 h}]{ZrO_2\text{ balls, additive (0.5 equiv)}} \text{analysis of gas component}$$

		Generated Gas (mmol)	
entry	additive	H_2	CH_4
1		not detected	not detected
2	Fe	not detected	not detected
3	Cr	0.52	0.075
4	Ni	not detected	not detected

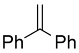
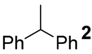
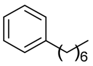
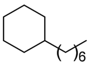
[a] The reaction was carried out using a Fritsch Pulverisette 7 Premium Line 7 Ball Mill (PLP-7) that was equipped with a 20 mL ZrO_2 vessel and 25 ZrO_2 balls (diameter: ca. 5 mm). Et_2O was purchased from commercial sources and used without further purification.

Fe, Cr, or Ni powder (0.5 equiv) in the ZrO_2 vessel (20 mL) with ZrO_2 balls (25 pieces). As a result, significant amounts of generated hydrogen could be observed in the presence of Cr powder (Table 4, entry 3), while the addition of Fe or Ni powder proved totally ineffective (Table 4, entries 2 and 4).

Furthermore, the role of the metal components of SUS304 that influenced the hydrogenation were also investigated under atmospheric H_2 conditions (Table 5). 1,1-Diphenylethene (**1a**) was never hydrogenated by ball milling (800 rpm for 3 h) in a ZrO_2 vessel (20 mL) in the presence of ZrO_2 balls (25 pieces) (Table 5, entry 1). While the addition of Fe or Cr powder (1 equiv) was ineffective for the hydrogenation (Table 5, entries 2 and 3), 1 equiv of Ni powder as an additive did facilitate the hydrogenation of the olefin function of **1a** to the alkane product (**2aa**) (Table 5, entry 4). While the arene hydrogenation of **1b** never proceeded without an additive or the addition of Fe, Cr, or Ni powder (1 equiv) (Table 5, entry 5), it could proceed in the presence of Ni powder under pressurized H_2 conditions (5 atm) using 75 ZrO_2 balls. Therefore, the progression of the mechanochemically mediated arene hydrogenation requires the appropriate internal pressure of the SUS304 ball milling vessel. Since the internal temperature of the SUS304 ball milling vessel under 800 rpm rotation conditions reaches ∼60 °C,[7a] the use of several organic solvents with low boiling points, such as *n*-pentane (boiling point (bp) = 36.1 °C), *c*-pentane (bp = 49 °C), and diethyl ether (bp = 34.6 °C), indicated a good progression of the hydrogenation (see Table 2 and eq 2). Therefore, *n*-heptane (bp = 98.3 °C) as a higher-boiling-point solvent may be inefficient, as shown in entry 3 in Table 2. These results indicate that Cr metal is an absolutely essential metal for the H_2 generation, and the hydrogenation is thoroughly catalyzed by Ni metal. However, both reactions were much more effectively facilitated by stainless steel 304 as an alloy of Fe, Cr, and Ni, in comparison to the independent use of Cr or Ni. Actually, a small amout of SUS304 alloy was collisionally eroded from balls in the mixture as a fine powder during the arene reduction in the presence of Et_2O (eq 2), although the precise role of each metal is still under investigation.[11]

Table 5. Essential Metals for Hydrogenation[a]

$$\underset{(0.5\ \mathrm{mmol})}{\text{substrate}} \xrightarrow[\text{800 rpm, 3 h}]{H_2,\ ZrO_2\text{ balls (25 pieces)},\ \text{additive (1 equiv)}} \text{product}$$

entry	substrate	additive	product	yield (%)
1	 **1a**	none	no reaction	
2	**1a**	Fe	 **2aa**	1 (54)[b]
3	**1a**	Cr	**2aa**	5 (62)[b]
4	**1a**	Ni	**2aa**	63
5	 **1b**	none, Fe, Cr or Ni	no reaction	
6[c]	**1b**	Ni	 **2b**	38 (23)[b]

[a] The reaction was carried out using a Fritsch Pulverisette 7 Premium Line 7 Ball Mill (PLP-7) equipped a 20 mL ZrO_2 vessel and 25 ZrO_2 balls (diameter: ca. 5 mm). [b] Recovery of the substrate. [c] The reaction was carried out under H_2 (5 atm) using 75 ZrO_2 balls.

In conclusion, hydrogen transfer utilizing alkanes and Et_2O as hydrogen sources has been accomplished under mechanochemical (ball milling) conditions using SUS304 balls and an SUS304 vessel. The in-situ-generated hydrogen could be used to hydrogenate a variety of reducible functionalities on the organic compounds. In particular, Et_2O was applicable as a pseudo-reductant for the hydrogenation of aromatic nuclei to produce the materially useful cycloalkane derivatives. The present reaction is an innovative hydrogenation method for the direct (one-pot) utilization of hydrogen atoms on LOHC molecules and it can also be expected to contribute to the further application of alkanes and ethers as clean energy processes without CO_2 production for the next generation.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.8b00931.

Synthetic procedures and spectroscopic data for the products (PDF)

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Author Contributions

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This study was partially supported by a Grant-in-Aid for Scientific Research (B) (No. 16H05075), the Canon Foundation, Koshiyama Science Technology Foundation and ESPEC Foundation for Global Environment Research and Technology (Charitable Trust) (ESPEC Prize for the Encouragement of Environmental Studies). We are grateful for the kind assistance provided by Fritsch Japan Co, Ltd., relevant to the Fritsch Pulverisette 7 Premium Line 7 Ball Mill (PLP-7).

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DOI: 10.1021/acs.orglett.8b00931