Accepted Manuscript

Selective reaction of benzyl alcohols with HI gas: Iodination, reduction, and indane ring formations

Shoji Matsumoto, Masafumi Naito, Takehisa Oseki, Motohiro Akazome, Yasuhiko Otani

PII: S0040-4020(17)31145-6

DOI: 10.1016/j.tet.2017.11.009

Reference: TET 29089

To appear in: *Tetrahedron*

Received Date: 29 August 2017

Revised Date: 31 October 2017

Accepted Date: 3 November 2017

Please cite this article as: Matsumoto S, Naito M, Oseki T, Akazome M, Otani Y, Selective reaction of benzyl alcohols with HI gas: Iodination, reduction, and indane ring formations, *Tetrahedron* (2017), doi: 10.1016/j.tet.2017.11.009.

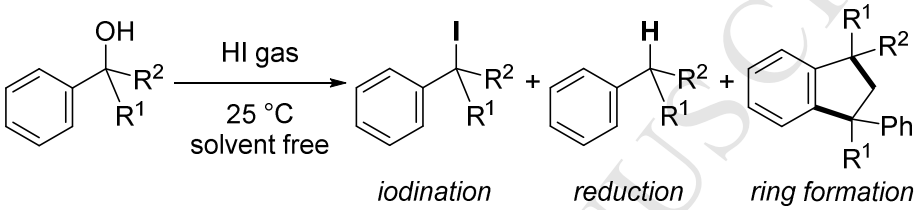
Graphical Abstract

To create your abstract, type over the instructions in the template box below.
Fonts or abstract dimensions should not be changed or altered.

Selective reaction of benzyl alcohols with HI gas: Iodination, reduction, and indane ring formations

Leave this area blank for abstract info.

Shoji Matsumoto[a,*], Masafumi Naito[a], Takehisa Oseki[a], Motohiro Akazome[a], and Yasuhiko Otani[b]
[a] *Department of Applied Chemistry and Biotechnology, Graduate School of Engineering, Chiba University, 1-33 Yayoicho, Inageku, Chiba 263-8522, Japan*
[b] *GODO SHIGEN CO., LTD., 1365 Nanaido, Chosei-mura, Chosei-gun, Chiba 299-4333, Japan*



Tetrahedron
journal homepage: www.elsevier.com

Selective reaction of benzyl alcohols with HI gas: Iodination, reduction, and indane ring formations

Shoji Matsumoto[a,*], Masafumi Naito[a], Takehisa Oseki[a], Motohiro Akazome[a], and Yasuhiko Otani[b]

[a] *Department of Applied Chemistry and Biotechnology, Graduate School of Engineering, Chiba University, 1-33 Yayoicho, Inageku, Chiba 263-8522, Japan*
[b] *GODO SHIGEN CO., LTD., 1365 Nanaido, Chosei-mura, Chosei-gun, Chiba 299-4333, Japan*

ARTICLE INFO

Article history:
Received
Received in revised form
Accepted
Available online

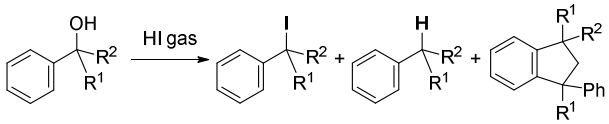
Keywords:
Hydrogen iodide
Iodination
Reduction
Ring formation
Solvent-free reaction

ABSTRACT

Reactions of benzyl alcohols with HI in solvent-free conditions were examined. Three types of reactions (iodination, reduction, and ring formation) occurred depending on the degree of crowding around the benzyl position and the benzylic stabilization of substrates. Results also showed that the ring formation to give indanes proceeded efficiently when HI was used, and that compounds with electron-rich aromatic rings gave indane derivatives in good yields.

1. Introduction

Hydrogen iodide (HI) is commercially available as a 55–57 wt% aqueous solution for use as a synthetic reagent, and is used as an acid,[1] a reducing agent,[2] a nucleophile,[3] and so on.[4] Recently, we explored the utilization of HI gas in reaction with acetophenones to form α-alkylated acetophenones under solvent-free conditions.[5] Related to that reaction mechanism, we were interested in the reactivity of benzyl alcohols toward HI. In this manuscript, we described the reaction of benzyl alcohols with HI gas; three types of reactions, i.e., iodination, reduction, and ring formation, occurred at ambient temperature under solvent-free conditions (Scheme 1). The formation of indane rings due to the reaction of styrene derivatives with Brønsted acids has been reported, although oligomerization occured in some cases as a side reaction.[6] Selective formations of indanes have been achieved with styrene by using Lewis acids,[7] transition metals,[8] and ionic liquids.[9] Benzyl alcohols can produce indanes through dimerization.[10] Stavber and co-workers reported that the reaction of 2-phenyl-2-propanol in the presence of I_2 at 70 °C gave indane products under solvent-free conditions.[11] Hence, we also investigated the scope and limitations of indane ring formation under ambient conditions.



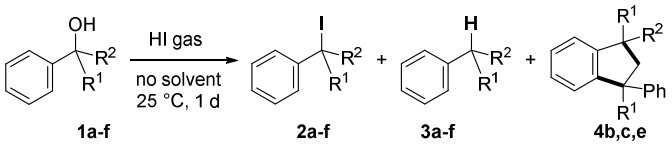
Scheme 1. Three types of reactions of benzyl alcohols with HI.

2. Results and discussion

First, we examined the reactivities of primary, secondary, and tertiary benzyl alcohols with HI gas; their substituents were fixed with methyl and phenyl groups (Table 1). Unique selectivity was observed. Compounds with less crowding around the benzyl position, such as **1a** and **1b** gave iodination products **2a** and **2b** (entries 1–3). The use of more than one equivalent of HI led to the efficient generation of **2a**. Even with one equivalent of HI, **2b** was obtained in good yield (80%) from secondary alcohol **1b**, whose benzyl cation would be stabilized efficiently. When tertiary alcohol **1c** was treated with HI gas, a cyclized product, indane **4c**, was obtained in 62% yield (entry 4). With secondary alcohol **1d**, which contains a second phenyl ring, a complex mixture was obtained. However, we were able to find reduction product **3d**, which was produced in 14% yield (entry 5). In the case of tertiary alcohol **1e**, a mixture of reduction product **3e** and indane **4e** was obtained; iodination product **2e** was not found (entry 6). When this reaction was conducted with

* Corresponding author. Tel.: +0-000-000-0000; fax: +0-000-000-0000; e-mail: author@university.edu

Table 1. Reaction of various benzyl alcohols with HI gas



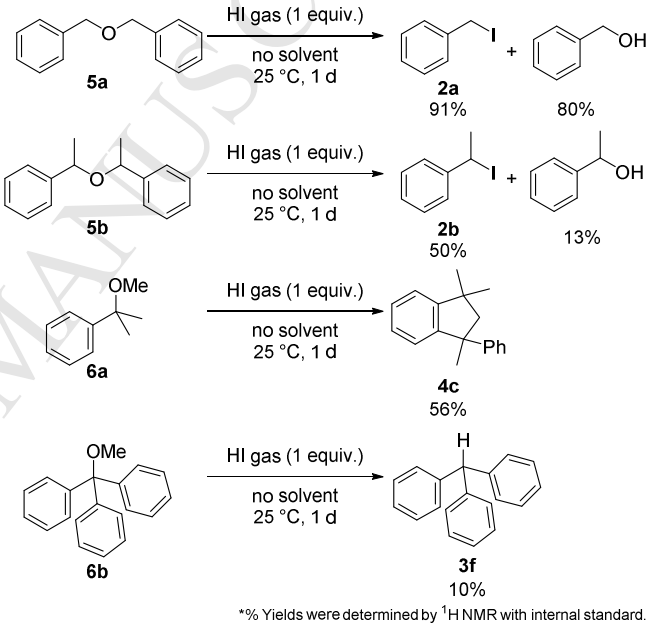
entry	compound	R^1	R^2	equiv. of HI	% yield[a]		
					2 [iodination]	**3** [reduction]	**4** [ring formation][b]
1	**1a**	H	H	1	42	0	–
2				1.5	77	0	–
3	**1b**	Me	H	1	80	0	0
4	**1c**	Me	Me	1	0	0	62
5	**1d**	Ph	H	1	0	14	–
6	**1e**	Ph	Me	1	0	46	53
7	**1f**	Ph	Ph	1	0	24	–
8				2	0	64	–

[a] Yield was determined by integration of ^{1}H NMR peaks using *p*-chlorobenzaldehyde as an internal standard.

[b] Yield was estimated as the formation of one molecule of **4** from two molecules of **1**.

triphenylmethanol (**1f**), reduction product **3f** was obtained (entry 7). The yield of **3f** was increased when two equivalents of HI were used (entry 8). The reduction of triphenylmethanol derivatives with aqueous HI has been reported in the literature[12] and required refluxing conditions. When HI gas is used, the reaction can proceed at ambient temperatures.

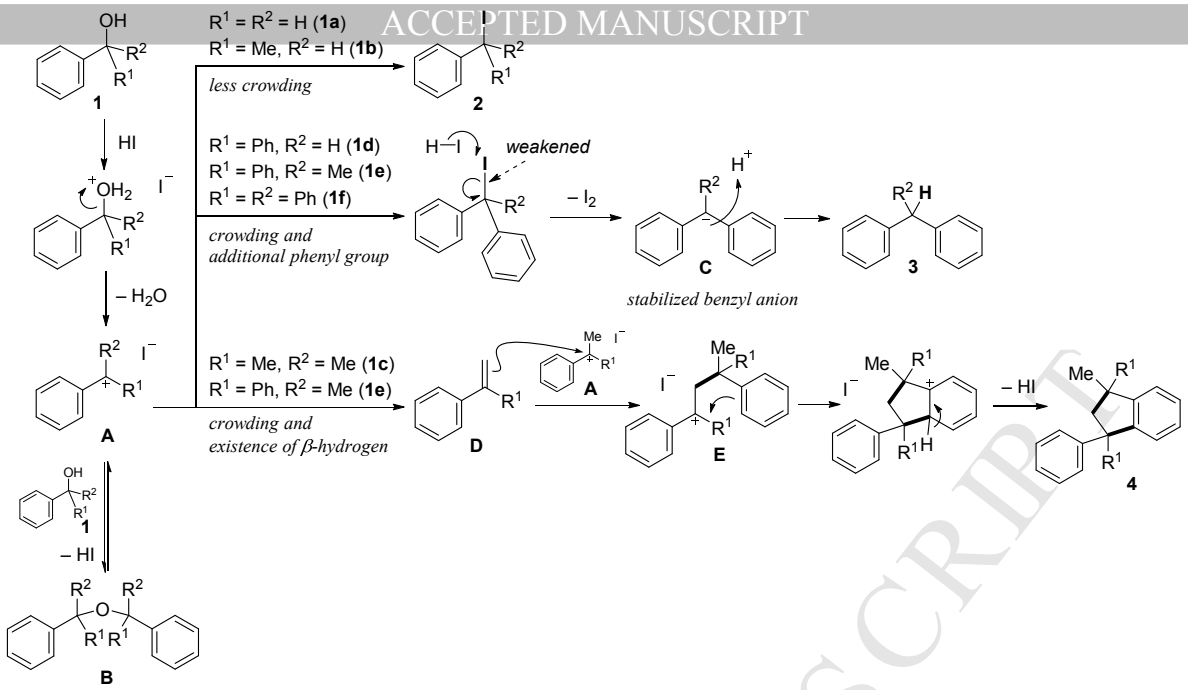
Under those conditions, the formation of ethers as side products is plausible. However, the corresponding ethers could not be found in crude ^{1}H NMR spectra. This may because the products can be formed from the ethers under the reaction conditions. To test this hypothesis, we examined the reaction of the ethers under the same conditions (Scheme 2). The results showed that the corresponding products could be obtained from the ethers. The reaction of dibenzyl ether (**5a**), the ethereal form of **1a**, gave iodination product **2a** in 91% yield, along with the leaving alcohol (80%). Ether **5b** gave iodination product **2b** in 50% yield with 13% of the corresponding alcohol. Unfortunately, we could not prepare the corresponding ethers of **1c** and **1f**. Hence, we attempted to the reactions of their methyl ethers (**6a** and **6b**, respectively). These reactions also produced **4c** and **3f**. Therefore, the ethers are also possible reaction intermediates.



Scheme 2. Reaction of ethers with HI gas.

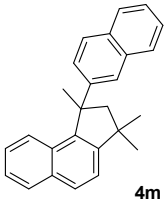
According to those results, the preferred reaction can be predicted based on the stabilization of the intermediate and the crowding at the benzyl position. The proposed reaction mechanism is depicted in Scheme 3. First, alcohol **1** is protonated by HI to generate an oxonium ion. After elimination of H_2O, benzyl cation **A** is formed. Intermediate **A** can produce ether **B** by reacting with **1**. However, ether **B** can generate **A** under acidic conditions. With less crowded benzyl cations such as those of **1a** and **1b**, iodide counter ion can attach easily to the cation to give iodination product **2**. When an additional substituent is attached to the benzyl cation, there are two possible paths. One path is the formation of reduction product **3**. The additional phenyl group at the benzyl position in **1d**, **1e**, and **1f** weakens the C–I bond even though the C–I bond was formed because of the static interaction. The C–I bond (2.285 Å) of triphenylmethyl iodide (CCDC Refcode: TEWWEX)[13] is longer than the typical C–I bond distance (2.162 Å).[14] Therefore, iodide can be removed by HI to form a benzyl anion (**C**). Furthermore, reduction product **3** is obtained via the protonation of **C**. The formation of **3** in greater than 50% yield in the presence of two equivalents of HI is reasonable (Table 1, entry 8). The formation of reduction product **3** through homolytic cleavage of the C–I bond in the iodinated compound is also plausible. However, Kahr and co-workers reported that triphenylmethyl iodide is stable under these conditions (reacted at 25 °C). The other path from cation **A** is taken when the temperature is below 80 °C.[13] Consequently, the radical path via homolytic cleavage can be excluded from our reaction when there is an additional substituent, since the cyclization reaction occurs. When there is a β-hydrogen at the cationic carbon as with **1c** and **1e**, an elimination reaction occurs to give styrene derivative **D**. Carbon–carbon bond formation occurs between intermediate **D** and cation **A** to give tertiary cation **E**. Intramolecular nucleophilic attack by the phenyl ring and elimination of HI produce cyclization product **4**.

We also investigated indane ring formation, which involves selective carbon–carbon bond formation. The results are presented in Table 2. According to the reaction mechanism in Scheme 3, a catalytic amount of HI is sufficient to advance the reaction. However, the use of one molar equivalent of HI gave indane **4c** efficiently in 62% yield (entries 1–3). It is reasonable that H_2O generated as a side product would decrease the acidity of HI. This reaction could be conducted in $CHCl_3$ (entry 4). However, the formation of **4c** was inhibited strongly when



Scheme 3. Plausible reaction mechanism and requirements of **2**, **3**, and **4** formation.

aqueous HI was used (entry 5). The results suggest that it is important to conduct the reaction under anhydrous conditions. The use of other acids such as HCl and $MeSO_3H$ gave unsatisfactory results (entries 6 and 7). Therefore, efficient indane formation requires the HI. The presence of a methyl group, which is an electron-donating substituent, on the phenyl ring increased the yield (entries 8–10). In contrast, lower yields were obtained with compounds with chloro- and trifluoromethyl groups, which are electron-withdrawing substituents (entries 11 and 12), which destabilize benzyl cation intermediate **A** in Scheme 1. Substrates with naphthyl groups reacted efficiently to give the corresponding indanes (entries 13 and 14). In paticular, the 2-naphthyl substrate gave a single isomer **4m** in 79% yield (entry 14) although reactions also occurred at the 1 and 3 positions of the naphthalene ring. The use of heteroaromatics gave no indane product and led to either a complex mixture (Ar = 2-thienyl group) or no reaction (Ar = pyridyl group). Substrates with longer alkyl groups gave undesirable results. For example, a complex mixture was obtained in the reaction of 3-phenylpentan-3-ol. Furthermore, an elimination reaction occurred and no indane ring was formed when diisopropylphenylmethanol was treated with HI (eq. 1). We also examined the reaction of a styrene with HI because the styrene is formed in the proposed reaction mechanism. When α-methylstyrene was treated with HI gas, corresponding indane **4c** was obtained. However, the yield was not as high as that of the reaction with alcohol **1c** (eq. 2). We were unable to explain the differences between those reactions, but the gradual production of styrene derivatives prevent polymerization.



In conclusion, three types of reaction occurred between benzyl alcohols and HI. The product selectivity depended on the degree of crowding and the benzylic stabilization. These reactions were conducted under solvent-free conditions at ambient temperature. Furthermore, the indane ring formation, which involves a reaction between two molecules, proceeded efficiently even under solvent-free conditions.

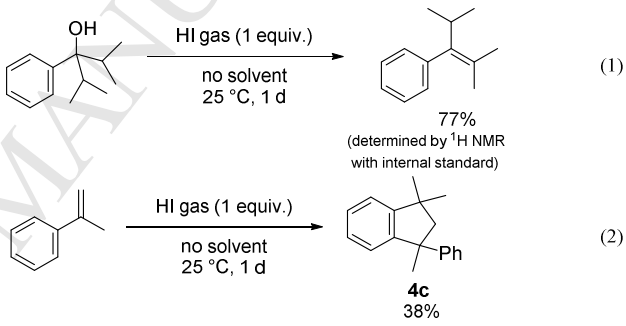
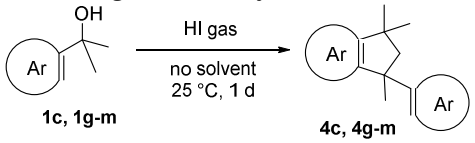


Table 2. Indane ring formation by reaction of **1** with HI gas[a]



entry	compound	Ar	equiv. of HI	% yield
1	**1c**	Ph	1	62
2			2	44
3			0.5	33
4[b]			1	64
5[c]			1	complex mixture
6			–[d]	0
7			–[e]	trace
8	**1g**	4-MeC_6H_4	1	84
9	**1h**	3-MeC_6H_4	1	64[f]
10	**1i**	2-MeC_6H_4	1	64
11	**1j**	4-ClC_6H_4	1	49
12	**1k**	4-$CF_3C_6H_4$	1	complex mixture
13	**1l**	1-naphthyl	1	78
14	**1m**	2-naphthyl	1	79[g]

[a] Reaction conditions: substrate (1.0 mmol), 25 °C, 1 d. Yield was determined by integration of ^{1}H NMR peaks using *p*-chlorobenzaldehyde as an internal standard.
[b] Reacted in $CHCl_3$ (3.3 M).
[c] 55 wt% aqueous HI was used instead of HI gas.
[d] Conc. HCl (1 equiv.) was used as the acid.
[e] $MeSO_3H$ (1 equiv.) was used as the acid.
[f] Obtained as regioisomers (68 : 32, determend from ^{1}H NMR analysis).
[g] Obtained as a single isomer **(4m)**.

3. Experimental section

General: Melting points were determined with Yanaco MP-J3 and values were uncorrected. ^{1}H and ^{13}C NMR measurements were performed on a Varian MURCURY plus (300 MHz) spectrometer and a Bruker AVANCE III-400M (400 MHz) spectrometer. Chemical shifts (δ) of ^{1}H NMR were expressed in parts per million downfield from tetramethylsilane in $CDCl_3$ (δ = 0) as an internal standard. Multiplicities are indicated as s (singlet), d (doublet), t (triplet), sept (septet), m (multiplet), and coupling constants (J) are reported in hertz units. Chemical shifts (δ) of ^{13}C NMR are expressed in parts per million downfield or upfield from $CDCl_3$ (δ = 77.0) as an internal standard. Infrared spectra (IR) spectra were recorded on a JASCO FT/IR-460 plus spectrometer. Mass spectra were carried out on a THERMO Scientific Exactive in Center for Analytical Instrumentation, Chiba University. Analytical thin-layer chromatography (TLC) was performed on glass plates that had been pre-coated with silica gel (0.25 mm layer thickness). Column chromatography was performed on 70–230 mesh silica gel. Anhydrous THF was distilled from sodium benzophenone ketyl immediately prior to use. Anhydrous $CHCl_3$ was distilled from $CaCl_2$ after washing with aq. NaOH, and was stored with MS 4Å. Other chemical materials were used as obtained commercially.

3.1 Preparation of the Reactant

2-(4-Tolyl)propan-2-ol (1g): To a suspension of Mg (turnings) (0.293 g, 12.1 atom) in anhydrous Et_2O (17.5 mL) was dropwise added MeI (1.90 g, 13.4 mmol) at 0 ºC. The suspension was stirred for 1.5 h at room temperature until Mg was disappeared. To the solution was dropwise added 4-methylacetophenone (1.36 g, 10.1 mmol) at 0 ºC, and the mixture was stirred for 12 h at room temperature. To the reaction mixture was added H_2O (25 mL) and saturated aqueous NH_4Cl (25 mL). After being extracted with EtOAc (30 mL × 3), the organic layer was dried with $MgSO_4$. After the concentration, 2-(4-tolyl)proan-2-ol (1.44 g, 9.55 mmol) was obtained in 94% yield as colorless oil: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.57 (s, 6H), 1.72 (s, 1H), 2.34 (s, 3H), 7.15 (d, J = 8.0 Hz, 2H), 7.38 (d, J = 8.2 Hz, 2H).[15]

2-(3-Tolyl)propan-2-ol (1h): The titled compound was prepared in 80% yield (1.251 g, 8.32 mmol) according to the similar procedure mentioned in 2-(4-tolyl)propan-2-ol with Mg (0.254 g, 10.4 atom), MeI (1.651 g, 11.6 mmol), and 3-methylacetophenone (1.451 g, 10.8 mmol) as yellowish oil: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.57 (s, 6H), 1.79 (s, 1H), 2.37 (s, 3H), 7.06 (d, J = 7.0 Hz, 1H), 7.20-7.32 (m, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.6, 31.7, 72.5, 121.4, 125.1, 127.4, 128.1, 137.8, 149.0. HRMS (ESI): Calcd. for $C_{10}H_{14}NaO$ ($[M+Na]^+$) 173.0937, found 173.0936.

2-(2-Tolyl)propan-2-ol (1i): To Mg (turnings) (0.271 g, 11.2 atom) was dropwise added a solution of 2-bromotoluene (1.773 g, 10.4 mmol) in anhydrous THF (25 mL) at 0 ºC. The suspension was stirred for 3 h at refluxing conditions. To the solution was dropwise added acetone (2.0 mL, 27.3 mmol) at 0 ºC, and the mixture was stirred for 12 h at 40 ºC. To the reaction mixture was added H_2O (25 mL) and saturated aqueous NH_4Cl (25 mL). After being extracted with EtOAc (30 mL × 3), the organic layer was dried with $MgSO_4$. After the concentration, the residue was subject to column chromatography on SiO_2 (hexane : $CHCl_3$ = 5 : 1) to give 2-(2-tolyl)propan-2-ol (0.826 g, 5.50 mmol, 53%) as colorless cubic crystals: mp 36-38 ºC [lit.:[16] 38-39 ºC]; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.66 (s, 6H), 1.70 (s, 1H), 2.60 (s, 3H), 7.13-7.16 (m, 3H), 7.45 (m, 1H).[17]

2-(4-Chlorophenyl)propan-2-ol (1j): The titled compound was prepared in 65% yield (1.116 g, 6.54 mmol) according to the similar procedure mentioned in 2-(4-tolyl)propan-2-ol with Mg (0.254 g, 10.5 atom), MeI (2.080 g, 14.7 mmol), and 4-chloroacetophenone (1.557 g, 10.1 mmol) as colorless solid: mp 43-45 ºC [lit.:[18] 43.3 ºC]; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.57 (s, 6H), 1.74 (s, 1H), 7.30 (d, J = 8.8 Hz, 2H), 7.42 (d, J = 8.8 Hz, 2H).[19]

2-(4-(Trifluoromethyl)phenyl)propan-2-ol (1k): The titled compound was prepared in 41% yield (1.04 g, 4.92 mmol) according to the similar procedure mentioned in 2-(2-tolyl)propan-2-ol with Mg (0.291 g, 12.0 atom), 4-(trifluoromethyl)bromobenzene (2.755 g, 12.2 mmol), and acetone (1.0 mL, 13.6 mmol) as pale yellow solid: 37-38 ºC [lit.:[20] 40.5-41.5 ºC]; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.60 (s, 6H), 1.78 (s, 1H), 7.60 (s, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 31.8, 72.5, 124.2 (q, $J_{C\text{-}F}$ = 270.1 Hz), 124.8, 125.2 (q, $J_{C\text{-}C\text{-}C\text{-}F}$ = 3.9 Hz), 128.9 (q, $J_{C\text{-}C\text{-}F}$ = 31.9 Hz), 153.0.[21]

2-(Naphthalen-1-yl)propan-2-ol (1l): The titled compound was prepared in 39% yield (0.732 g, 3.93 mmol) according to the similar procedure mentioned in 2-(4-tolyl)propan-2-ol with Mg (0.265 g, 10.9 atom), MeI (1.553 g, 10.9 mmol), and 1-acetylnaphthalene (1.730 g, 10.2 mmol) as colorless solid: mp 78 ºC; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.85 (s, 6H), 1.99 (s, 1H), 7.39 (t, J = 7.5 Hz, 1H), 7.45 (dt, J = 1.5 and 6.8 Hz, 1H), 7.50 (dt, J = 1.8 and 6.8 Hz, 1H), 7.57 (dd, J = 1.1 and 7.3 Hz, 1H), 7.76 (d, J = 8.1 Hz, 1H), 7.85 (dd, J = 2.2 and 9.6 Hz, 1H), 8.81 (d, J = 8.4 Hz, 1H).[22]

2-(Naphthalen-2-yl)propan-2-ol (1m): The titled compound was prepared in 64% yield (1.227 g, 6.59 mmol) according to the similar procedure mentioned in 2-(4-tolyl)propan-2-ol with Mg (0.278 g, 11.4 atom), MeI (1.716 g, 12.1 mmol), and 2-acetylnaphthalene (1.744 g, 10.3 mmol) as colorless solid: mp 55-56 ºC; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.68 (s, 6H), 1.87 (s, 1H), 7.42-7.49 (m, 2H), 7.60 (dd, J = 1.9 and 8.7 Hz, 1H), 7.81-7.85 (m, 3H), 7.93 (d, J = 1.8 Hz, 1H).[23]

Bis(1-phenylethyl) ether (5b):[24] To a solution of 1-phenylethanol (**1b**) (0.362 g, 2.97 mmol) in $MeNO_2$ (3 mL) was added TfOH (14 μL, 016 mmol) at room temperature, and the mixture was stirred for 2 h at that temperature. After removal of $MeNO_2$ in vacuo, to the reaction mixture was added saturated aqueous $NaHCO_3$ (5 mL). After being extracted with hexane (10 mL × 3), the organic layer was dried with $MgSO_4$. After the concentration, the residue was subject to column chromatography on SiO_2 (hexane : EtOAc = 5 : 1) to give bis(1-phenylethyl) ether (diastereomer ratio = 73 : 27) (0.2425 g, 1.07 mmol, 72%) as colorless oil: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.38 (d, J = 6.6 Hz, 4.38H), 1.47 (d, J = 6.4 Hz, 1.62H), 4.25 (q, J = 6.5 Hz, 1.46H), 4.53 (q, J = 6.4 Hz, 0.54H), 7.26-7.39 (m, 10H).

2-Phenyl-2-methoxypropane (6a): To a solution of 2-phenyl-2-propanol (**1c**) (1.413 g, 10.4 mmol) in THF (20 mL) was added NaH (60 wt% oil dispersion) (1.422 g, 35.6 mmol) and MeI (4.755 g, 33.5 mmol) at room temperature, and the mixture was stirred for 15 h at that temperature. To the reaction mixture was added H_2O (30 mL). After being extracted with EtOAc (30 mL × 3), the organic layer was dried with $MgSO_4$. After the concentration, the residue was subject to column chromatography on SiO_2 (hexane : EtOAc = 9 : 1) to give 2-phenyl-2-methoxypropane (0.850 g, 5.66 mmol, 54%) as colorless oil: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.53 (s, 6H), 3.07 (s, 3H), 7.25 (t, J = 7.1 Hz, 1H), 7.35 (t, J = 7.8 Hz, 2H), 7.42 (d, J = 8.2 Hz, 2H).[25]

Triphenylmethyl methyl ether (6b): The titled compound was prepared in 71% yield (0.589 g, 2.15 mmol) according to the similar procedure mentioned in 2-phenyl-2-methoxypropane with triphenylmethanol (0.786 g, 3.01 mmol), NaH (60 wt% oil dispersion) (0.147 g, 3.67 mmol) and MeI (0.28 mL, 4.50 mmol) as colorless solid: mp = 78-79 ºC [lit.:[26] 82.6-82.9 ºC]: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.06 (s, 3H), 7.23 (t, J = 7.3 Hz, 3H), 7.30 (t, J = 7.7 Hz, 6H), 7.44 (d, J = 7.1 Hz, 6H).[27]

2,4-Dimethyl-3-phenylpentan-3-ol:[28] To a suspension of Mg (turnings) (0.4862 g, 0.02 atom) in THF (2.5 mL) was dropwise added a solution of 2-bromopropane (2.540 g, 20.7 mmol) in anhydrous THF (25 mL) at 0 ºC. After being stirred for 3 h, $ZnCl_2$ (0.147 g, 1.08 mmol) was added to the solution at 0 ºC, and the solution was stirred for 40 min at that temperature. To the mixture was dropwise added a solution of isobutylophenone (1.487 g, 10.0 mmol) in THF (10 mL) at 0 ºC, and the mixture was stirred for 16 h at room temperature. To the reaction mixture was added saturated aqueous NH_4Cl (25 mL). After being extracted with EtOAc (30 mL × 3), the organic layer was dried with $MgSO_4$. After the concentration, the residue was subjected to column chromatography on SiO_2 (*n*-hexane : EtOAc = 20 : 1) to give 2,4-dimethyl-3-phenylpentan-3-ol (0.330 g, 1.72 mmol) in 17% yield as colorless oil: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.77 (d, J = 6.8 Hz, 6H), 0.85 (d, J = 6.8 Hz, 6H), 1.49 (s, 1H), 2.31 (sept, J = 6.8 Hz, 1H), 7.22 (tt, J = 2.5 and 7.0 Hz, 1H), 7.31 (diffused t, J = 7.9 Hz, 2H), 7.38 (diffused d, J = 7.2 Hz, 2H).

3.2 Handling the apparatus for HI collection

[Caution!: HI is corrosive in the case to contact with moisture. The experiment should be conducted into fume hood.] To pick up anhydrous HI, the stainless tube of the apparatus for HI collection was dehydrated by heating with heating gun in vacuo with vacuum pump. The apparatus was filled with argon gas and was made depression. This cycle was repeated in several times. After filled with argon gas, the vacuum pump was exchanged to the line for HI collection. Argon gas was flowed through the apparatus for 10 min (the flow was controlled by the control valve for argon). And the following operation was done at the same time: closing the control valve of argon and opening the valve of HI cylinder. After 5 min to flow HI gas (the flow was controlled by the control valve for HI gas), it was picked up through rubber septum with a syringe attached with disposable needle. The apparatus was worked off as follows. The valve of HI cylinder was closed and the control valve of argon was opened. After continuing argon flow until the neutralization of the evolved gas (checked by pH paper), the valve of argon cylinder was closed. The line for HI collection was exchanged to the vacuum pump, and the apparatus was made depression for 30 min. During the reduced pressure, the stainless tube was heated with heating gun. The vacuum pump was stopped, and the apparatus was filled with argon with an application of pressure (4~5 MPa). The depression and the filling of argon was repeated in three times to completely exclude HI gas.

3.3 Procedure for the Reaction of Benzyl Alcohols with HI gas

In a round bottom flask fitted with three-way cock with septum was placed benzyl alcohol analogue (1.0-1.5 mmol). The flask was filled with nitrogen after reducing pressure. After slight decompression to ease to the gas introduction, HI gas (0.5-2.0 equiv.) was brought in the vessel with syringe through the septum (the weight of HI gas was calculated the change of the weight of the equipment before and after the introduction of HI gas). And nitrogen gas was introduced into vessel to release deference of pressure against atmosphere. The mixture stood at 25 ºC for 2 d. After reducing pressure to release HI gas, to the reaction mixture was added saturated $Na_2S_2O_3$ (20 mL) and brine (15 mL). After being extracted with $CHCl_3$ or Et_2O (15 mL × 3), the organic layer was dried with $MgSO_4$. After the concentration, *ca*. 10.0 mg of the residue was combined with *p*-chlorobenzaldehyde (*ca.* 10.0 mg) as an internal standard. And the mixture was measured with ^{1}H NMR to determine the yield by the integration of methyl, methylene or methine peak of the product and formyl peak of *p*-chlorobenzaldehyde (9.98 ppm). Furthermore, the reaction mixture included in *p*-chlorobenzaldehyde was subject to column chromatography on SiO_2 to give the product.

Iodinated products, (iodomethyl)benzene (**2a**),[29] (1-iodoethyl)benzene (**2b**),[30] and reduction products, diphenylmethane (**3d**),[31] 1,1-diphenylethane (**3e**),[32] triphenylmethane (**3f**),[33] were assigned by the corresponding proton peaks at benzylic positions compared with the chemical shift reported in the literatures.

1,1,3-Trimethyl-3-phenyl-2,3-dihydro-1*H*-indene (4c): Colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.04 (s, 3H), 1.35 (s, 3H), 1.69 (s, 3H), 2.19 (d, J = 13.0 Hz, 1H) 2.42 (d, J = 13.0 Hz, 1H), 7.11-7.29 (m, 9H).[34]

1-Methyl-1,3,3-triphenyl-2,3-dihydro-1*H*-indene (4e): colorless solid; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.54 (s, 3H), 3.09 (d, J = 13.5 Hz, 1H), 3.39 (d, J = 13.5 Hz, 1H), 7.00-7.29 (m, 19H).[34]

1,1,3,5-Tetramethyl-3-(4-tolyl)-2,3-dihydro-1*H*-indene (4g): Colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.04 (s, 3H), 1.32 (s, 3H), 1.66 (s, 3H), 2.16 (d, J = 13.0 Hz, 1H), 2.30 (s, 3H), 2.35 (s, 3H), 2.37 (d, J = 13.0 Hz, 1H), 6.90 (s, 1H), 7.03-7.09 (m, 6H).[34]

1,3,3,5-Tetramethyl-1-(3-tolyl)-2,3-dihydro-1*H*-indene and 1,1,3,4-Tetramethyl-3-(3-tolyl)-2,3-dihydro-1*H*-indene (4h): Colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.03 (s, 0.96H), 1.20 (s, 2.04H), 1.33 (s, 0.96H), 1.34 (s, 2.04H), 1.65 (s, 0.96H), 1.76 (s, 2.04H), 1.89 (s, 2.04H), 2.15 (d, J = 13.3 Hz, 0.68H), 2.16 (d, J = 13.0 Hz, 0.32H), 2.28 (d, J = 13.3 Hz, 0.68H), 2.30 (s, 2.04H+0.96H), 2.39 (s, 0.96H), 2.40 (d, J = 12.9 Hz, 0.32H), 6.91-7.22 (m, 7H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 19.2, 21.5, 21.7, 27.5, 29.7, 30.4, 30.6, 31.1, 31.2, 31.6, 42.6, 42.7, 50.3, 51.3, 59.4, 61.3, 120.2, 123.1, 123.5, 123.8, 124.8, 126.1, 126.2, 127.0, 127.3, 127.4, 127.5, 127.8, 127.9, 129.4, 134.7, 136.7, 137.4, 137.5, 146.0, 147.0, 150.7, 151.1, 152.3, 152.7. HRMS (ESI): Calcd. for $C_{20}H_{23}$ ([M-H]$^-$) 263.1794, found 263.1796.

1,3,3,4-Tetramethyl-1-(2-tolyl)-2,3-dihydro-1*H*-indene (4i): Colorless thin plate crystals; mp 64-65 ºC; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.22 (s, 3H), 1.48 (s, 3H), 1.74 (s, 3H), 2.11 (d, J = 13.2 Hz, 1H) ,2.17 (s, 3H), 2.43 (s, 3H), 2.53 (d, J = 13.2 Hz, 1H), 6.83 (d, J = 7.5 Hz, 1H), 7.00-7.11 (m, 6H).[35]

5-Chloro-3-(4-chlorophenyl)-1,1,3-trimethyl-2,3-dihydro-1*H*-indene (4j):[34] Colorless solid; mp 69-71 ºC; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.03 (s, 3H), 1.32 (s, 3H), 1.65 (s, 3H), 2.19 (d, J = 13.2 Hz, 1H), 2.36 (d, J = 13.2 Hz, 1H), 7.03 (d, J = 2.0 Hz, 1H), 7.07-7.13 (m, 3H), 7.19-7.27 (m, 3H).

1,1,3-Trimethyl-3-(naphthalen-2-yl)-2,3-dihydro-1*H*-cyclopenta[*a*]naphthalene (4l):[36] Colorless solid; mp 193-194 ºC; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.50 (s, 3H), 1.62 (s, 3H), 1.94 (d, J = 14.8 Hz, 1H), 2.01 (s, 3H), 3.04 (d, J = 14.6 Hz, 1H), 6.80-6.89 (m, 2H), 7.13-7.26 (m, 3H), 7.52-7.88 (m, 10H).

1,3,3-Trimethyl-1-(naphthalen-2-yl)-2,3-dihydro-1*H*-cyclopenta[*a*]naphthalene (4m): Colorless solid; mp 116-117

ºC [lit.:[37] 118-120 ºC, 122-124 ºC (after recyrst.)]; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.40 (s, 3H), 1.45 (s, 3H), 2.08 (s, 3H), 2.36 (d, J = 13.5 Hz, 1H), 2.47 (d, J = 13.5 Hz, 1H), 7.09 (t, J = 7.0 Hz, 1H), 7.21 (dd, J = 1.9 and 8.6 Hz, 1H), 7.29 (t, J = 7.0 Hz, 1H), 7.35-7.48 (m, 4H), 7.65 (d, J = 8.7 Hz, 1H), 7.75-7.85 (m, 5H).[35]

(2,4-Dimethylpent-2-en-3-yl)benzene: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.87 (d, J = 6.9 Hz, 6H), 1.36 (s, 3H), 1.81 (s, 3H), 3.05 (sept, J = 6.9 Hz, 1H), 6.97 (diffused d, J = 8.2 Hz, 2H), 7.21-7.32 (m, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 19.3, 21.6, 22.4, 29.9, 125.6, 125.9, 127.5, 130.0, 140.8, 141.4. HRMS (ESI): Calcd. for $C_{13}H_{22}N$ ($[M+NH_4]^+$) 192.1747, found 192.1751.

Acknowledgments

This work was supported by a Leading Research Promotion Program “Soft Molecular Activation” from Chiba University, Japan.

Supplementary data

Supplementary data associated with this article can be found in the online version at

References and notes

1. (a) Olomola TO, Klein R, Kaye PT. *Synth. Commun.* 2012; 42: 251−257; (b) Kobayashi K, Hashimoto K, Hashimoto H, Kondo H, Konishi H. *Helv. Chim. Acta* 2011; 94: 1277−1282; (c) Matsumoto S, Mori T, Akazome M. *Synthesis* 2010: 3615−3622; (d) Kobayashi K, Shikata K, Fujii Y, Fukamachi S, Tanmatsu M, Konishi H. *Heterocycles* 2010; 81: 1459−1466; (e) Kobayashi K, Fujita S, Nakai D, Fukumoto S, Fukamachi S, Konishi H. *Helv. Chim. Acta* 2010; 93: 1274−1280; (f) Kobayashi K, Hashimoto H, Nagaoka T, Shirai Y, Konishi H. *Heterocycles* 2010; 81: 699−705.
2. (a) Ito Y, Ueda M, Takeda N, Miyata O. *Chem. Eur. J.* 2016; 22: 2616−2619; (b) Wu DD, Huang C-M, Wu Y-H, Fun H-K, Xu J-H, Zhang Y. *RSC Adv.* 2013; 3: 7529−7536; (c) Matsumoto S, Ogura K. *Tetrahedron Lett.* 2007; 48: 1117−1120; (d) Penso M, Mottadelli S, Albanese D. *Synth. Commun.* 1993; 23: 1385−1391; (e) Julia L, Riera J, Teixidó R. *J. Chem. Soc., Perkin Trans. 1* 1991: 1101−1105; (f) Hicks MG, Jones G, York DC. *J. Chem. Soc., Perkin Trans. 1* 1988: 69−75; (g) Hoeger CA, Johnston AD, Okamura WH. *J. Am. Chem. Soc.* 1987; 109: 4690−4698; (h) Parkam WE, Sayed YA. *Synthesis* 1976: 116−117.
3. (a) Zuo L, Yao S, Wang W, Duan W. *Tetrahedron Lett.* 2008; 49: 4054−4056; (b) Dol GC, Kamer PCJ, van Leeuwen PWNM. *Eur. J. Org. Chem.* 1998: 359−364.
4. Breton, G. W.; Kropp, P. J.; Harvey, R. G. In *Encyclopedia of Reagents for Organic Synthesis*; Paquett, E. A., Ed.; John Wiley & Sons: Chichester, 1995; Vol. 4, pp. 2728−2731.
5. Matsumoto S, Koitabashi S, Otani Y, Akazome M. *Tetrahedron Lett.* 2015; 56: 4320–4323.
6. (a) Tarlani A, Zarabadi MP, Muzart J, Lotfalipour E, Darkhosh F, Abedini M, Amini MM. *Catal. Commun.* 2011; 14: 89–91; (b) Wolovsky R, Maoz N. *J. Org. Chem.* 1973; 38: 4040; (c) Rosen MJ. *Org. Synth. Coll. Vol.* 1963; 4: 665.
7. (a) Ramulu BV. *Asian J. Org. Chem.* 2016; 5: 207–212; (b) Sun H-B, Li B, Hua R, Yin Y. *Eur. J. Org. Chem.* 2006: 4231–4236; (c) Peppe C, Lang ES, de Andrade FM, de Castro LB. *Synlett* 2004: 1723–1726.
8. (a) Miyake Y, Moriyama T, Tanabe Y, Onodera G, Nishibayashi Y. *Organometallics* 2011; 30: 5972–5977; (b) Nishiwaki N, Kamimura, R, Shono K, Kawakami T, Nakayama K, Nishino K, Nakayama T, Takahashi K, Nakamura A, Hosokawa T. *Tetrahedron Lett.* 2010; 51: 3590–3592.
9. Wang H, Cui P, Zou G, Yang F, Tang J. *Tetrahedron* 2006; 62: 3985–3988.
10. Howard F, Sawadjoon S, Samec JSM. *Tetrahedron Lett.* 2010; 51: 4208–4210.
11. Stavber G, Zupan M, Stavber S. *Tetrahedron Lett.* 2006; 47: 8463–8466.
12. (a) Julia L, Riera J, Teixidó R. *J. Chem. Soc., Perkin Trans. 1* 1991: 1101−1105; (b) Babbini DC, Iluc VM.; *Organometallics* 2015; 34: 3141−3151; (c) Chichibabin A. *Berichte der Deutschen Chemischen Gesellchaft* 1911; 44: 441−443.
13. Arkin CR, Cowans B, Kahr B. *Chem. Mater.* 1996; 8: 1500−1503.
14. Allen FH, Kennard O, Watson DG, Brammer L, Orpen AG, Taylor R. *J. Chem. Soc., Perkin Trans. 2* 1987: S1–S19.
15. Yamamoto Y, Hasegawa H, Yamataka H. *J. Org. Chem.* 2011; 76: 4652−4660.
16. Brown HC, Brady JD, Gravson M, Bonner WH. *J. Am. Chem. Soc.* 1957; 79: 4652−4660.
17. Too PC, Tnay YL, Chiba S. *Beilstein J. Org. Chem.* 2013; 9: 1217−1225.
18. Brown HC, Okamoto Y, Ham G. *J. Am. Chem. Soc.* 1957; 79: 1906−1909.
19. Miyoshi N, Matsuo T, Wada M. *Eur. J. Org. Chem.* 2005: 4253−4255.
20. Okamoto Y, Inukai T, Brown HC. *J. Am. Chem. Soc.* 1958; 80: 4969−4972.
21. Popielarz R, Arnold DR. *J. Am. Chem. Soc.* 1990; 112: 3068−3082.
22. Patschinski P, Zhang C, Zipse H. *J. Org. Chem.* 2014; 79: 8348−8357.
23. Baroudi A, Mauldin J, Alabugin, IV. *J. Am. Chem. Soc.* 2010; 132: 967−979.
24. Sanz R, Miguel D, Martínez A, Álvarez-Gutiérrez JM, Rodríguez F. *Org. Lett.* 2007; 9: 2027−2030.
25. Maslak P, Chapman Jr. WH. *J. Org. Chem.* 1990; 55: 6334−6347.
26. Norris JF, Young RC. *J. Am. Chem. Soc.* 1930; 52: 753−761.
27. Azzena T, Pisano L, Antonello S, Maran F. *J. Org. Chem.* 2009; 74: 8064−8070.
28. Hatano M, Suzuki S, Ishihara K. *J. Am. Chem. Soc.* 2006; 128: 9998−9999.
29. Ding R, He Y, Wang X, Xu J, Chen Y, Feng M, Qi C. *Molecules* 2011; 16: 5665−5673.
30. Lee JC, Park JY, Yoo ES. *Synth. Commun.* 2004; 34: 2095−2099.
31. Milstein D, Stille JK. *J. Am. Chem. Soc.* 1979; 101: 4992−4998.
32. Schoenebeck F, Murphy JA, Zhou S, Uenoyama Y, Miclo Y, Tuttle T. *J. Am. Chem. Soc.* 2007; 129: 13368−13369.
33. Prakash GKS, Panja C, Shakhmin A, Shah E, Mathew T, Olah GA. *J.Org. Chem.* 2009; 74: 8659−8668.
34. Sun H-B, Li B, Hua R, Yin Y. *Eur. J. Org. Chem.* 2006: 4231–4236.
35. Gopi A, Reddy K, Satyanarayana G. *J. Org. Chem.* 2016; 81: 12212–12222.
36. Reeves JT, Fandrick DR, Tan Z, Song JJ, Yee NK, Senanayake CH. *Tetrahedron Lett.* 2009; 50: 3077–3080.
37. Paquette LA, Phillips TR. *J. Org. Chem.* 1965; 30: 3883–3885.