Selective Formation of Internal Olefinic Trimer of α-Methylstyrenes with HI Gas and Ketones

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Supporting Information

ABSTRACT: Reaction of α-methylstyrene in the presence of HI gas and methyl p-tolyl ketone selectively resulted in an internal olefinic trimer. We revealed that the ketones with the stabilization of the protonated state were efficient to give the corresponding trimers, whereas the other ketones gave the usual indane compound. From the investigation for the mechanistic path, we found that the trimer is a kinetic product and that indane is a thermodynamic product.

■ INTRODUCTION

Control of the reaction of α-methylstyrenes under acidic conditions has attractive features for the formation of polymers and oligomers. α-Methylstyrene dimer (4-methyl-2,4-diphenylpent-1-ene) is utilized as a molecular weight modifier. 1 α-Methylstyrene homopolymer is known to be difficult to form because of its low ceiling temperature.2,3 However, it succeeded in the reaction with HI/I2 as an initiator in liquid SO2 because dormant (C−I-bonded compound) is activated by I2 to form cationic species.4 The indane was obtained as a major product from the reaction of α-methylstyrene with trifluoroacetic acid,5 whereas other acids6−8 resulted mainly in three compounds: 2,4-diphenyl-4-methyl-1-pentene, 2,4-diphenyl-4-methyl-2-pentene, and 1,1,3-trimethyl-3-phenylnindane. Other conditions with acidic ionic liquids,9,10 molecular sieves,11 acidic ion-exchange resins, and clays8 also resulted in indane as a main product.

We have been interested in the application of HI gas for organic synthesis, and we reported the α-alkylated ketone formation with two ketones12 and the indane formation via styrene derivatives.13 We attempted the reaction of the combination of ketone and styrene derivatives to find the unique selective formation of indane (1) and internal olefinic trimer (2), which was rarely obtained in the acidic conditions. Herein, we report the formation of 2 with HI under solvent-free conditions. This reaction showed the complete selectivity with or without methyl p-tolyl ketone (Scheme 1). In addition, we also revealed that 2 is a kinetic product and 1 is a thermodynamic (equilibrium controlled) product.

■ RESULTS AND DISCUSSION

We examined the reaction of α-methylstyrene in the presence of 0.2 equiv molar amounts of methyl p-tolyl ketone because

![Scheme 1. Reaction of α-Methylstyrene Derivatives and HI with or without Methyl p-Tolyl Ketone](image)
Table 1. Reaction of α-Methylstyrene and HI Gas in the Presence of Methyl p-Tolyl Ketone$^*$

| entry | equiv of HI$^{10}$ | equiv of ketone$^b$ | 1a [major/minor]$^c$ | 2a | 3 | 4 |
|-------|-----------------|-------------------|----------------|---|---|---|
| 1     | 1.0             | 0.20              | 51             | 0 | 0 | 0 |
| 2     | 0.80            | 0.20              | 45             | 0 | 0 | 0 |
| 3     | 0.60            | 0.20              | 10             | 34  | 76:23 | 12 | 16 |
| 4     | 0.40            | 0.20              | 0              | 61  | 76:23 | 8 | 16 |
| 5     | 0.20            | 0.20              | 0              | 68  | 68:32 | 7 | 21 |
| 6     | 0.10            | 0.20              | 0              | 65  | 71:29 | 4 | 18 |
| 7     | 0.050           | 0.20              | 0              | 49  | 62:38 | 13 | 33 |
| 8     | 0.20            | 1.0               | 0              | 49  | 64:36 | trace | 27 |
| 9     | 0.20            | 0.50              | 0              | 56  | 64:36 | 4 | 24 |
| 10    | 0.20            | 0.40              | 0              | 70  | 69:31 | 7 | 21 |
| 11    | 0.20            | 0.10              | 0              | 63  | 72:28 | 5 | 16 |
| 12    | 0.20            | 0.050             | 66             | 9 | 70:30 | 3 | 7 |
| 13    | 0.20            | 0.0               | 61             | 0 | 0 | 0 |

$^a$Reaction conditions: α-methylstyrene (5.0 mmol) at 25 °C for 1 d in no solvent. $^b$On the basis of the amount of α-methylstyrene. $^c$Determined by the integration of $^1$H NMR using p-chlorobenzaldehyde as an internal standard.

Next, we examined various ketones as an additive in this reaction (Table 2). Unique selectivity was observed by using methyl tolyl ketone isomers. When $o$- and $p$-isomers were added, 2a was obtained as a major product (entries 1 and 3). Contrarily, 1a was formed in the presence of methyl $m$-tolyl ketone (entry 2). The addition of acetonaphene and benzophenone was ineffective in producing 2a (entries 4 and 5), but fluorenone was efficient for 2a (entry 6). When $p$-methoxyphenyl methyl ketone was used, a lower yield of 2a was observed with 3 as a main product (entry 7). HI was well-known as a cleavage reagent of the methoxy group. Thus, dissociation of HI occurred to interrupt the formation of a trimer. When we treated with $p$-chlorophenyl methyl ketone, 2a was still formed as a major product (entry 8). An aliphatic ketone such as an acetone was insufficient to result in 2a (entry 9). We found that benzamide was capable of forming 2a, but that they gave a lower yield than that of methyl $p$-tolyl ketone (entry 10). In the case of addition of amines, higher $pK_{BH}^+$ of conjugated acid in dimethyl sulfoxide (9.0, 3.6, and 2.5 for trimethylamine, aniline, $N,N$-dimethylaniline, respectively) gave a higher yield of 2a (entries 11–13). However, the formation of 1a or the recovery of α-methylstyrene were also observed. No formation of 1a and 2a was found in the case of phosphine and sulfur oxides (entries 14 and 15). An aqueous solution of HI, which means H$_2$O as an additive, gave 2a in 52% yield with the concomitant with 1a (23%) (entry 16). This result was a clear contrast in the case of using gaseous HI (entry 13 in Table 1). From those results, one possibility that arose as a reason for occurring selectively was the difference of the basicity of the additive. The acidity of the conjugated acid of ketones was reviewed by Freiberg. The $pK_{BH}^+$ values for methyl $p$-tolyl ketone, acetonaphene, benzophenone, $p$-methoxyphenyl methyl ketone, $p$-chlorophenyl methyl ketone, and acetone were $-4.02, -4.32, -4.95, -3.31, -4.85$, and $-2.85$, respectively, even though $pK_{BH}^+$ value was determined by fitting into the Bunnett–Olsen equation in aqueous sulfuric acid. We could not find any relation between $pK_{BH}^+$ value and the selectivity in our investigation. Therefore, we suspected that the stabilization of the protonated complex of the carbonyl moiety would be affected to produce 2a.

Table 2. Reaction of α-Methylstyrene and HI Gas with Additives$^d$

| entry | R$^1$ | R$^2$ | 1a [major/minor]$^e$ | 2a | 3 | 4 |
|-------|------|------|----------------|---|---|---|
| 1     | Me   | H    | 0              | 68 | [68:32] | 7 | 21 |
| 2     | Me   | H    | 70             | 0 | 0 | 0 |
| 3     | Me   | H    | trace          | 63 | [74:26] | 6 | 17 |
| 4     | Ph   | H    | 72             | 0 | 0 | 0 |
| 5     | Ph   | H    | 67             | 0 | 0 | 0 |
| 6$^f$ | Me   | Cl   | 53             | [73:27] | 5 | 17 |
| 7     | Me   | Me   | 34             | [58:42] | 39 | 18 |
| 8     | ClC$_6$H$_4$ | Me | Trace | 48 | [79:21] | 3 | 10 |
| 9     | Me   | Me   | 66             | 0 | 0 | 0 |
| 10$^g$ | 0    | 27   | [67:33] | 23 | 14 |
| 11$^g$ | 45   | 33   | [72:28] | 4 | 12 |
| 12$^g$ | 0    | 9    | [52:48] | 8 | 4 |
| 13$^g$ | 0    | 0    | 4 | 0 |
| 14$^g$ | 0    | 0    | 30 | 0 |
| 15$^g$ | 0    | 0    | trace | 0 |
| 16$^g$ | 23   | 52   | [76:24] | 4 | 10 |

$^d$Reaction conditions: α-methylstyrene (5.0 mmol), HI (1.0 mmol, 0.20 equiv), and additives (1.0 mmol, 0.20 equiv) at 25 °C for 1 d in no solvent. $^e$Determined by the integration of $^1$H NMR using p-chlorobenzaldehyde as an internal standard. $^f$Fluorenone was used. $^g$Benzamide was used as an additive. $^h$Triethylamine was used as an additive. $^i$Aniline was used as an additive and the recovery of α-methylstyrene (12%) was observed. $^j$NN-Dimethylaniline was used as an additive and the recovery of α-methylstyrene (51%) was observed. $^k$DMSO was used as an additive and the recovery of α-methylstyrene (57%) was observed. $^l$Triphenylphosphine oxide was used as an additive and the recovery of α-methylstyrene (66%) was observed. $^m$57 wt % aqueous HI (0.02 equiv) was used instead of HI gas.
group on α- and p-position stabilized the positive charge on carbon at the carbonyl group by an inductive effect and hyperconjugation. Chlorine atoms also stabilized its positive charge by a mesomeric effect. Furthermore, we examined the reaction with or without methyl p-tolyl ketone in the presence of various acids (Table 3). There was no reaction in the case of a solution of HCl.

From those investigations, we proposed the reaction mechanism depicted as Scheme 2. At first, the protonation to α-methylstyrene occurs to produce benzyl cation A. Moreover, the addition of another α-methylstyrene forms a dimer cation B. In the case of an internal nucleophilic attack by benzene ring, 1a is obtained through intermediate C (path a). When the counter anion $\text{I}^-$ acts as a base, dimer olefins 3 and 4 are formed (path b and c). Hofmann elimination proceeds to give less-substituted olefin 3 because of the bulkiness of a base (path c).¹⁴ Cation A can be reacted toward less hindered olefin 3 to give the trimer cation D. After deprotonation with $\text{I}^-$, 2a is obtained. When methyl p-tolyl ketone exists in this system, the protonation with HI would be competitive with 2a and ketone. As a result, the reaction conditions with ketone situate under kinetic control to produce 2a as a major product. In the absence of methyl p-tolyl ketone, the equilibrium condition is achieved to result in the thermodynamic product 1a as major product. Complex formation with methyl p-tolyl ketone and HI would be also affected for the formation of A. However, the protonation to bulkier olefin in 2a is more difficult than in α-methylstyrene. The kinetic and thermodynamic products were supported by density functional theory (DFT) calculations (see Supporting Information). The preference of the protonation between 2a and methyl p-tolyl ketone was also

Table 3. Reaction of α-Methylstyrene with/without Methyl p-Tolyl Ketone in the Presence of Various Acids

| entry | acid (0.20 equiv.) | ketone | 1a [major/minor] | 2a [major/minor] | 3 | 4 |
|-------|-------------------|--------|-----------------|-----------------|---|---|
| 1     | conc. (37 wt %aq) HCl | ×      | 0               | 0               | 0 | 0 |
| 2     | conc. (37 wt %aq) HCl | ○      | 0               | 0               | 0 | 0 |
| 3     | 47 wt %aq HBr      | ×      | 0               | 0               | 9 | 0 |
| 4     | 47 wt %aq HBr      | ○      | 0               | 0               | 10| 0 |
| 5     | conc. (96 wt %aq) H2SO4 | ×      | 84              | 0               | 0 | 0 |
| 6     | conc. (96 wt %aq) H2SO4 | ○      | 65              | 12 [78:22]      | 0 | trace |
| 7     | 60 wt %aq HClO3    | ×      | 0               | 16 [74:26]      | 18| 31|
| 8     | 60 wt %aq HClO3    | ○      | 14              | 10 [63:37]      | 11| 36|
| 9     | p-TsOH-H2O         | ×      | 0               | 0               | 54| 0 |
| 10    | p-TsOH-H2O         | ○      | 0               | 0               | 14| 0 |
| 11    | TfOH               | ×      | 58              | 0               | 0 | 0 |
| 12    | TfOH               | ○      | 97              | 0               | 0 | 0 |
| 13    | MeOH               | ×      | 89              | 0               | 0 | 0 |
| 14    | MeOH               | ○      | 13              | 36 [58:42]      | 8 | 30 |

¹⁴Reaction conditions: α-methylstyrene (5.0 mmol) and acid (1.0 mmol, 0.20 equiv.) at 25 °C for 1 d in no solvent. Determined by the integration of $^1$H NMR using p-chlorobenzaldehyde as an internal standard.
supported from the DFT calculation because the complex of methyl p-tolyl ketone with HI was more stable with the value of 5.030 kcal/mol than that of 2a, whose value was larger than the value in the case of \( \alpha \)-methylstyrene (3.846 kcal/mol) (Figure 1).

Finally, we examined the scope and limitation for the formation of 2 (Table 4). \( p \)-Methyl and \( p \)-chloro-\( \alpha \)-methylstyrene gave 2 in each 41% yield with no formation of 1 (entries 1 and 3). However, indane formation occurred when a strong electron-donating substituent was introduced at para position, as in \( p \)-methoxy-\( \alpha \)-methylstyrene (entry 2). Indane compound (1e) was obtained in 66% by \( C-C \) bond formation at the naphthalene 3 position in the case of 2-(propen-2-yl)napththalene (entry 4). Thus, the compounds with an electron-rich aromatic ring produced indane rings. It was caused because of the electron-rich aromatics accelerating intramolecular cyclization reaction (path a) of intermediate cation B in Scheme 2 or that the reverse reaction to

Table 4. Reaction of \( \alpha \)-Methylstyrene Derivatives with HI in the Presence of Methyl p-Tolyl Ketone

| entry | Ar       | R   | products and yields (%) [major/minor] |
|-------|----------|-----|-------------------------------------|
| 1     | \( p \)-MeC\(_6\)H\(_4\) | H   | 1\(_b\), 0                           |
| 2     | \( p \)-MeOC\(_6\)H\(_4\) | H   | 1\(_c\), 31                          |
| 3     | \( p \)-ClC\(_6\)H\(_4\) | H   | 1\(_d\), 0                           |
| 4     | 2-naphthyl | H   | 1\(_e\), 66                          |
| 5     | 1-naphthyl | H   |                                    |
| 6     | 2-thienyl | H   |                                    |
| 7     | Ph        | Ph  |                                    |

*Reaction conditions: \( \alpha \)-methylstyrene derivative (2.5 mmol), HI (0.5 mmol, 0.20 equiv), and methyl \( p \)-tolyl ketone (0.5 mmol, 0.20 equiv) at 25 °C for 1 d in no solvent. *Determined by the integration of \( ^1H \) NMR using \( p \)-chlorobenzaldehyde as an internal standard. *Complex mixtures. *Recovery of the starting material (40%).
intermediate cation D from 2 could not be inhibited by the ketone because of the large stability of D. In the case of 1-(propen-2-yl)naphthalene, the complex mixture was obtained (entry 5). Unfortunately, the reaction of m- and o-oriented methyl-α-methylylstanes resulted in products with the possibility of isomers of 2 about 25 wt % amount, but the mixture was too complicated to determine the products. The compound with aromatic rings containing heteroatom, such as thienyl group, gave the complex mixture (entry 6). In addition, the compound with phenyl rings on aliphatic chain of α-methylstyrene did not undergo the reaction (entry 7). The less steric hindrance around the cationic carbon would also necessitate the formation of the products.

■ CONCLUSIONS

In summary, we revealed the selective formation of internal olefinic trimer (2) from α-methylstyrene by the combination of H1 gas and methyl p-tolyl ketone. The additive ketones with the stabilization of the protonated cation by the inductive, hyperconjugative, and mesomeric effects were efficient at producing 2 instead of indane (1). We also found that 2 is a kinetic product under these reaction conditions and that 1 is a thermodynamic product. From those investigations, the ketone would be affected by the inhibition to result in equilibrium conditions by the formation of the protonated ketone. This result would lead to a novel controlling method for polymeric and oligomeric compounds.

■ EXPERIMENTAL SECTION

General Information. Melting points were uncorrected. NMR spectra were recorded with 300 or 400 MHz spectrometer for 1H NMR and with 75 or 100 MHz spectrometer for 13C NMR. Chemical shifts (δ) of 1H NMR were expressed in parts per million downfield from tetramethylsilane in CDCl3 (δ = 0) as an internal standard. Multiplicities are indicated as s (singlet), d (doublet), t (triplet), quartet (qq), quint (quintet), m (multiplet), and coupling constants (J) are reported in hertz units. Chemical shifts (δ) of 13C NMR are expressed in parts per million relative to the residual solvent [CDCl3 (δ = 77.0)]. Analytical thin-layer chromatography was performed on glass plates precoated with silica gel (0.25 mm layer thickness). Column chromatography was used on 70–230 mesh silica gel. Recycling preparative gel permeation chromatography (GPC) was performed with YMC column (O-SIL-5-06-D 5–5, SIL 60A). Anhydrous tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl immediately prior to use. Other chemical materials were used as obtained commercially.

Preparation of the Reactant. 1-Methyl-4-(propen-2-yl)benzene. To a suspension of methyltriphosphonophenium iodide (5.227 g, 12.9 mmol) in THF (100 mL) was added 1.64 M n-butyllithium in n-hexane (7.90 mL, 13.0 mmol) in the period of 30 min in ice bath. After being warmed to room temperature, the mixture was stirred for 1 h. To the mixture was added 4'-methylacetophenone (1.451 g, 10.8 mmol) in a period of 5 min. After being stirred for 28 h at that temperature, the reaction mixture was filtered. To the filtrate was added brine (50 mL). After the extraction with n-hexane (30 mL × 3), the organic layer was dried with MgSO4 and was concentrated. The residue was purified with column chromatography on SiO2 (n-hexane) to give 1-methyl-4-(propen-2-yl)benzene (0.724 g, 5.47 mmol, 51%) as a colorless oil: 1H NMR (CDCl3, 300 MHz): δ 2.14 (dd, J = 0.8 and 1.4 Hz, 3H), 2.34 (s, 3H), 5.03 (quint, J = 1.5 Hz, 1H), 5.33 (m, 1H), 7.13 (d, J = 7.9 Hz, 2H), 7.37 (d, J = 8.2 Hz, 2H).21 1-Methyl-3-(propen-2-yl)benzene. The titled compound was prepared in 89% yield (1.216 g, 9.20 mmol) according to the similar procedure mentioned in 1-methyl-4-(propen-2-yl)benzene with methyltriphosphonophenium iodide (4.853 g, 12.0 mmol), 1.55 M n-butyllithium in n-hexane (8.00 mL, 12.4 mmol), and 3'-methylacetophenone (1.582 g, 10.3 mmol) for 17 h as a colorless oil: 1H NMR (CDCl3, 400 MHz): δ 2.14 (dd, J = 0.8 and 1.4 Hz, 3H), 2.36 (s, 3H), 5.06 (quint, J = 1.5 Hz, 1H), 5.34–5.35 (m, 1H), 7.09 (d, J = 7.7 Hz, 1H), 7.22 (t, J = 7.3 Hz, 1H), 7.27 (d, J = 7.5 Hz, 1H), 7.28 (s, 1H).21 1-Methyl-2-(propen-2-yl)benzene. The titled compound was prepared in 71% yield (0.934 g, 7.06 mmol) according to the similar procedure mentioned in 1-methyl-4-(propen-2-yl)benzene with methyltriphosphonophenium iodide (4.850 g, 12.0 mmol), 1.55 M n-butyllithium in n-hexane (7.74 mL, 12.0 mmol), and 4'-methylacetophenone (1.505 g, 10.0 mmol) for 22 h as a white solid: mp 32–33 °C [lit.:22 33.5–34.5 °C], 1H NMR (CDCl3, 300 MHz): δ 2.13 (s, 3H), 3.82 (s, 3H), 4.99 (quint, J = 1.5 Hz, 1H), 5.29 (m, 1H), 6.86 (diffused d, J = 8.9 Hz, 2H), 7.42 (diffused d, J = 9.0 Hz, 2H).21 1-Methoxy-4-(propen-2-yl)benzene. The titled compound was prepared in 71% yield (1.044 g, 7.06 mmol) according to the similar procedure mentioned in 1-methyl-4-(propen-2-yl)benzene with methyltriphosphonophenium iodide (4.850 g, 12.0 mmol), 1.55 M n-butyllithium in n-hexane (7.74 mL, 12.0 mmol), and 4'-methoxyacetophenone (1.505 g, 10.0 mmol) for 22 h as a white solid: mp 51 °C [lit.:22 52 °C]. 1H NMR (CDCl3, 300 MHz): δ 7.18 (s, 1H), 7.28 (d, J = 7.7 Hz, 1H), 7.40 (d, J = 7.9 Hz, 1H).21 1-Chloro-4-(propen-2-yl)benzene. The titled compound was prepared in 66% yield (0.972 g, 6.37 mmol) according to the similar procedure mentioned in 1-methyl-4-(propen-2-yl)benzene with methyltriphosphonophenium iodide (4.701 g, 11.6 mmol), 1.62 M n-butyllithium in n-hexane (7.10 mL, 11.6 mmol), and 4'-chloroacetophenone (1.484 g, 9.60 mmol) for 20 h as a colorless oil: 1H NMR (CDCl3, 300 MHz): δ 2.13 (dd, J = 0.7 and 1.4 Hz, 3H), 5.09 (quint, J = 1.4 Hz, 1H), 5.34 (m, 1H), 7.29 (diffused d, J = 8.8 Hz, 2H), 7.39 (diffused d, J = 8.8 Hz, 2H).21 2-(Propen-2-yl)naphthalene. The titled compound was prepared in 84% yield (0.852 g, 5.06 mmol) according to the similar procedure mentioned in 1-methyl-4-(propen-2-yl)benzene with methyltriphosphonophenium iodide (2.749 g, 6.80 mmol), 1.64 M n-butyllithium in n-hexane (4.10 mL, 6.72 mmol), and 1-(naphthalen-2-yl)ethan-1-one (1.021 g, 6.00 mmol) for 24 h as a white solid: mp 51–52 °C [lit.:22 54–55.4 °C]. 1H NMR (CDCl3, 300 MHz): δ 2.27 (dd, J = 0.7 and 1.4 Hz, 3H), 5.20 (quint, J = 1.4 Hz, 1H), 5.53–5.54 (m, 1H), 7.42–7.49 (m, 2H), 7.68 (dd, J = 1.8 and 8.7 Hz, 1H), 7.78–7.85 (m, 4H).21 1-(Propen-2-yl)naphthalene. The titled compound was prepared in 78% yield (0.734 g, 4.73 mmol) according to the similar procedure mentioned in 1-methyl-4-(propen-2-yl)benzene with methyltriphosphonophenium iodide (2.916 g, 7.21 mmol), 1.55 M n-butyllithium in n-hexane (4.80 mL, 7.44 mmol), and 1-(naphthalen-1-yl)ethan-1-one (1.028 g, 7.44 mmol) for 17 h as a colorless oil: 1H NMR (CDCl3, 400 MHz): δ 2.21 (dd, J = 0.9 and 1.6 Hz, 3H), 5.06 (m, 1H), 5.40–5.41 (m, 1H), 7.31 (d, J = 7.0 Hz, 1H), 7.43 (dd, J = 7.1
and 8.0 Hz, 1H), 7.46–7.48 (m, 2H), 7.75 (d, J = 8.2 Hz, 1H), 7.83–7.86 (m, 1H), 8.04–8.07 (m, 1H).25

2-(Propen-2-yl)thiophene. The titled compound was prepared in 52% yield (0.633 g, 5.22 mmol) according to the similar procedure mentioned in 1-methyl-4-(propen-2-yl)benzene with methylthiophenylphosphonium iodide (4.857 g, 12.0 mmol), 1.55 M n-butyllithium in n-hexane (7.80 mL, 12.1 mmol), and 1-(thiophen-2-yl)ethan-1-one (1.271 g, 10.0 mmol) for 17 h as a colorless oil: 1H NMR (CDCl3, 400 MHz): δ 2.15 (dd, J = 0.8 and 1.3 Hz, 3H), 4.95 (m, 1H), 5.38 (s, 1H), 6.98 (dd, J = 3.6 and 5.1 Hz, 1H), 7.03 (dd, J = 1.1 and 3.6 Hz, 1H), 7.17 (dd, J = 1.1 and 5.0 Hz, 1H).26

1,2,3-Triphenylpropane. A solution of bromobenzene (20.35 g, 13.0 mmol) in THF (50 mL) was added to Mg (turnings) (2.942 g, 12.1 atom) at 0 °C. The reaction mixture was added saturated aqueous NaHCO3 (25 g, 20.0 mmol), and the mixture was stirred for 68 h at that temperature. To the reaction mixture was added saturated aqueous NH4Cl (25 mL) and was extracted with EtOAc (30 mL × 3). The combined organic layer was dried with MgSO4 and was concentrated. The residual mixture was purified with column chromatography on SiO2 (CHCl3/n-hexane = 1:1) to give oil (4.273 g) included in 1,2,3-triphenylpropan-2-ol. The yield (91.8 mg, 0.234 mmol) with inseparable impurity for entry 1 in Table 3. Yellow oil; 1H NMR (CDCl3, 300 MHz): δ 0.86 (s, 4.20H), 1.16 (s, 4.20H), 1.43 (s, 1.04H), 1.77 (s, 0.99H), 5.58 (0.70H), 5.77 (0.30H), 6.61 (d, J = 8.1 Hz, 1.40H), 6.88–7.41 (m, 13.60H).15

Handling the Apparatus for HI Collection.13 [Caution!: HI is corrosive in the case to contact with moisture. The experiment should be conducted in fume hood.] To pick up anhydrous HI, the stainless tube of the apparatus was completely dehydrated in vacuo with a vacuum pump. The cycle of fill with argon and depression in the apparatus was repeated several times. After being filled with argon gas, the line for HI collection was attached with a buffer pot and saturated NaOH solution pot at the end of the line. Argon gas was flowed through the apparatus for 10 min. The control valve of argon was closed. At the same time, the valve of HI cylinder was opened. After over 5 min of HI gas flowing, it was picked up through rubber septum with a syringe attached with a disposable needle. The apparatus was worked off as follows. After the neutralization of the evolved gas under argon flow, the line for HI collection was exchanged to the vacuum pump for 30 min. During the reduced pressure, the stainless tube was heated with a heating gun for drying. The apparatus was filled with argon with an application of pressure (4–5 MPa). The depression and the filling of argon was repeated three times to completely exclude HI gas.

General Procedure for the Reaction of α-Methylstyrene with HI Gas in the Presence of Methyl p-Tolyl Ketone. In a round-bottom flask fitted with a three-way cock with septum was placed α-methylstyrene (0.598 g, 5.0 mmol) and methyl p-tolyl ketone (36.8 mg to 0.667 g, 0.25–5.0 mmol, 0.05–1.0 equiv). The flask was filled with nitrogen after reducing pressure. After slight decompression to ease the gas introduction, HI gas (32.0 mg to 0.637 g, 0.25–5.0 mmol, 0.05–1.0 equiv) was brought in the vessel with a syringe through the septum (the weight of HI gas was calculated with the change of the weight of the equipment before and after the introduction of HI gas). In addition, nitrogen gas was introduced into the vessel to release deference of pressure against the atmosphere. The mixture was stirred at 25 °C for 1 d under sealed conditions by using a three-way cock. After reducing the pressure to release HI gas, to the reaction mixture was added saturated Na2S2O3 (20 mL) and brine (15 mL). After being extracted with CHCl3 (15 mL × 3), the organic layer was dried with MgSO4. After the concentration, ca. 10.0 mg of the residue was combined with p-chlorobenzaldehyde (ca. 10.0 mg) as an internal standard. Moreover, the mixture was measured with 1H NMR to determine the yield by the integration of methine protons 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 SiO2 and preparative GPC to isolate the product.

Dimeric products, 4-methyl-2,4-diphenylpent-1-ene (3)29 and 4-methyl-2,4-diphenylpent-2-ene (4),30 were assigned by the corresponding proton peaks compared with the chemical shift reported in the literature.

2,6-Dimethyl-2,4,6-triphenyloct-3-ene (2a). Isolated as a mixture of geometric isomers (70:30) in 62% yield (0.368 g, 1.04 mmol) for entry 5 in Table 1. Colorless oil; 1H NMR (CDCl3, 300 MHz): δ 13.32 (s, 0.54H), 1.05 (s, 4.20H), 1.16 (s, 4.20H), 1.43 (s, 1.04H), 1.77 (s, 0.99H), 6.61 (d, J = 8.1 Hz, 1.40H), 6.88–7.41 (m, 13.60H).15

2,6-Dimethyl-2,4,6-tri(4-methylphenyl)oct-3-ene (2b). Isolated as a mixture of geometric isomers (91:9) in 28% yield (91.8 mg, 0.234 mmol) with inseparable impurity for entry 1 in Table 3. Yellow oil; 1H NMR (CDCl3, 300 MHz): δ 13.32 (s, 0.54H), 1.05 (s, 4.20H), 1.16 (s, 4.20H), 1.43 (s, 1.04H), 1.77 (s, 0.99H), 6.61 (d, J = 8.1 Hz, 1.40H), 6.88–7.41 (m, 13.60H).15

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1,1,3-Trimethyl-3-phenyl-2,3-dihydro-1H-indene (1a). Isolated in 56% yield (0.334 g, 1.41 mmol) for entry 13 in Table 1. Colorless oil; ^1H NMR (CDCl3, 300 MHz): δ 1.04 (s, 3H), 1.35 (s, 3H), 1.69 (s, 3H), 2.19 (d, J = 13.1 Hz, 1H) 2.42 (d, J = 13.0 Hz, 1H), 7.11 (m, 9H).31

1,1,3-Trimethyl-3-phenyl-2,3-dihydro-1H-indene (1a). Isolated in 19% yield (0.139 g, 0.469 mmol) for entry 2 in Table 3. Colorless oil; ^1H NMR (CDCl3, 400 MHz): δ 1.31 (s, 3H), 1.66 (s, 3H), 2.17 (d, J = 13.0 Hz, 1H), 2.36 (d, J = 12.9 Hz, 1H), 3.77 (s, 3H), 3.78 (s, 3H), 6.62 (d, J = 2.5 Hz, 1H), 6.78 (diffused d, J = 8.9 Hz, 2H), 6.84 (dd, J = 2.5 and 8.3 Hz, 1H), 7.09 (d, J = 8.4 Hz, 1H), 7.10 (diffused d, J = 8.9 Hz, 2H).3

ASSOCIATED CONTENT

Supporting Information

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Notes

The authors declare no competing financial interest.

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