

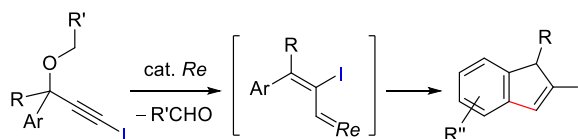
Rhenium-Catalyzed Cyclization via 1,2-Iodine and 1,5-Hydrogen Migration for the Synthesis of 2-Iodo-1*H*-indenes

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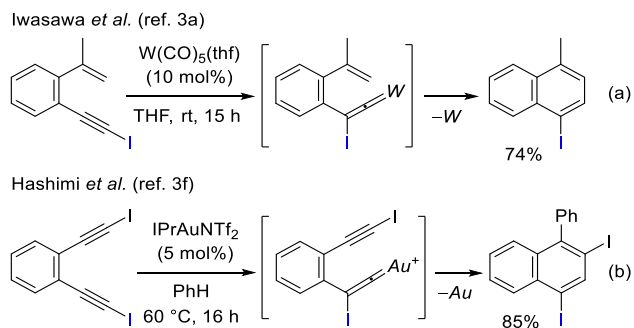
Supporting Information



ABSTRACT: A rhenium complex catalyzed the formation of 2-iodo-1*H*-indene derivatives through iodine and hydrogen migration of 3-iodopropargyl ethers. The reaction proceeded *via* generation of 1-iodoalkenylrhenium carbene species by sequential 1,2-iodine and 1,5-hydrogen shifts with readily available precursors under neutral conditions. Insight into the reaction mechanism and the reactivity of the generated alkenylcarbene species were also investigated.

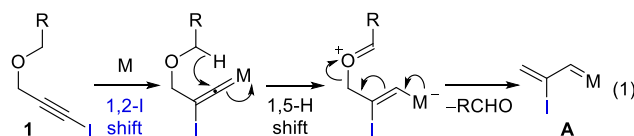
Transition metal-catalyzed 1,2-H shift of terminal acetylenes is a powerful and operationally simple method to provide synthetically useful vinylidene species atom-efficiently.¹ Reactivity of the resulting vinylidene species is influenced by substituents adjacent to the generated carbene carbon centers. Therefore, vinylidene formation from alkynes with functional groups, such as SiR₃, GeR₃, SnR₃, SR, SeR, or a halogen group, at the terminus *via* their 1,2-shift is an efficient and straightforward approach to reactive and functionalized vinylidene species.^{2,3} Among the functional groups, the iodo group is an important coupling partner, and the precursors, iodoalkynes, are attractive class of alkynes having unique reactivity.⁴ Since the seminal report by Iwasawa describing tungsten-catalyzed cycloisomerization leading to 1-iodonaphthalenes *via* generation of iodovinylidene species,^{3a,5} 1,2-I shifts have been used in several unique transformations by Fürstner and Hashimi *et al.* (Scheme 1).^{3b-g} However, most of the iodoalkynes used in the previous studies were derived from arylacetylenes,^{3a-d,f,g} and the activity of catalysts other than tungsten, ruthenium, and gold complexes is unknown.

Recently, we have reported rhenium-catalyzed *anti*-Markovnikov addition reaction of carbon nucleophiles to terminal alkynes, which involves the formation of rhenium vinylidene species generated *via* a 1,2-H shift of the terminal proton of acetylene.^{6,7} We envisioned that rhenium complexes may also serve as promoters for the generation of halogen-substituted vinylidene species *via* 1,2-halogen shift of haloalkynes.⁸ To investigate the catalytic generation of iodovinylidene species *via* 1,2-I shift of 1-iodo-2-alkylalkynes derived from aliphatic acetylenes, a propargyl ether **1** was selected as a precursor in this work. Since the resulting vinylidene species possesses an electrophilic carbene center attached with electron-withdrawing iodo substituents, further conversion into 1-iodoalkenyl carbene species **A** was hypothesized to occur *via*



Scheme 1. Generation of iodovinylidene species *via* 1,2-I shift of iodoalkyne

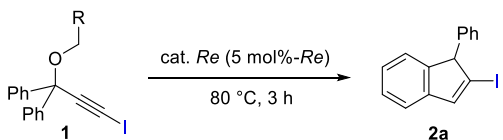
sequential 1,5-H shift followed by elimination of an aldehyde (Eq 1).⁹ Although an alkenyl carbene species is widely used for the construction of various heterocycles by cycloadditions and annulations,^{9d,10} those that possess an iodo group at the alkenyl or carbene carbon are rare.



The present study began with treatment of benzyl propargyl ether **1a** with a catalytic amount of a transition metal complex in 1,4-dioxane (0.10 M) at 80 °C. 2-Iodo-1*H*-indene **2a** was formed with the use of several rhenium catalysts, such as ReBr(CO)₅, ReI(CO)₅, and [ReBr(CO)₃(thf)]₂ (Table 1, entries 1-3). In contrast, other metal complexes, including W(CO)₅(thf), AuCl, and IPrAuNTh₂, which were effective for the generation of iodovinylidene species *via* 1,2-I shift in a previous study,³ did not provide **2a** even at higher temperatures due to

competitive decomposition of **1a**.¹¹ Although a higher temperature (120 °C) is required, **2a** was also obtained, albeit in low yield using $\text{Re}_2(\text{CO})_{10}$ as a catalyst (entry 4). The proper choice of solvents was crucial, and formation of **2a** was observed in ethereal solvents, such as THF, CPME, $n\text{Bu}_2\text{O}$, and DME (entries 5-6).¹² Substituents on the oxygen atom slightly affected reaction efficiency, and precursors **1aa**, **1ab**, **1ac**, and **1ad** containing methoxymethoxy, propoxy, or benzyloxy groups with electron-donating and -withdrawing functional groups were converted to **2a** in lower yields compared to those with **1a** (entries 7-10).^{13,14}

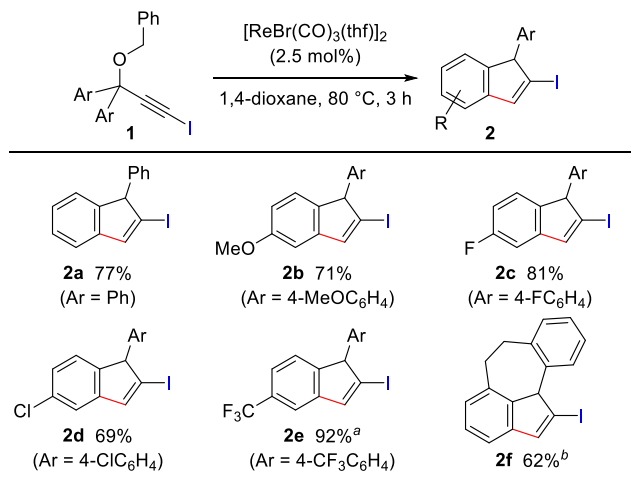
Table 1. Optimization of reaction conditions



entry	cat. Re	solvent	R	Substrate	Yield / %
1	$\text{ReBr}(\text{CO})_5$	dioxane	Ph	1a	71
2	$\text{ReI}(\text{CO})_5$	dioxane	Ph	1a	70
3	$[\text{ReBr}(\text{CO})_3(\text{thf})_2]$	dioxane	Ph	1a	78 (77)
4 ^a	$\text{Re}_2(\text{CO})_{10}$	dioxane	Ph	1a	22
5	$[\text{ReBr}(\text{CO})_3(\text{thf})_2]$	THF	Ph	1a	32
6	$[\text{ReBr}(\text{CO})_3(\text{thf})_2]$	$\text{ClCH}_2\text{CH}_2\text{Cl}$	Ph	1a	7
7	$[\text{ReBr}(\text{CO})_3(\text{thf})_2]$	dioxane	OMe	1aa	63
8	$[\text{ReBr}(\text{CO})_3(\text{thf})_2]$	dioxane	Et	1ab	68
9	$[\text{ReBr}(\text{CO})_3(\text{thf})_2]$	dioxane	4-MeOC ₆ H ₄	1ac	71
10	$[\text{ReBr}(\text{CO})_3(\text{thf})_2]$	dioxane	4-BrC ₆ H ₄	1ad	74

^a 120 °C for 18 h.

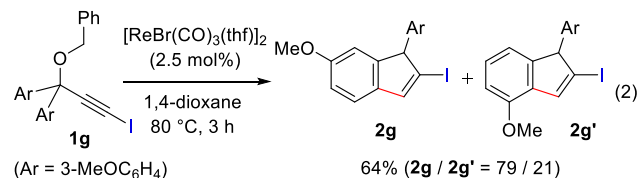
Under the optimized reaction conditions listed in entry 3 of Table 1, the scope and functional group tolerance were investigated briefly with several benzyl propargyl ethers **1** (Figure 1). Functional groups such as methoxy, fluoro, and chloro groups were tolerated to provide the corresponding 2-iodo-1H-indene derivatives **2b**, **2c**, and **2d**, respectively, in good yields. Higher reaction temperatures were necessary for complete conversion of trifluoromethyl group substituted



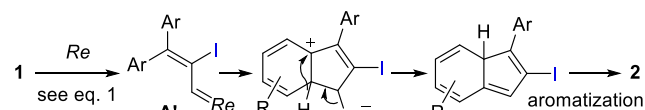
^aAt 100 °C. Mixture with double bond isomer **2e'** in the ratio of 69 : 31 (see ESI for the structure of **2e'**). ^bAt 65 °C.

Figure 1. Rhenium-catalyzed synthesis of 2-iodo-1H-indene derivatives **2**

precursor **1e** leading to **2e**. In this case, transposition of the double bond to yield **2e'** occurred competitively due to the presence of an acidic benzylic proton in the structure of **2e**.¹⁵ The reaction could be applicable to benzyl propargyl ether **1f** derived from dibenzosuberone, and indene fused tetracycle **2f** was formed in moderate yield. Precursor **1g**, which contained a *meta*-methoxyphenyl group, reacted preferentially at the less sterically hindered position to afford **2g** along with its regioisomer **2g'** as a minor product (Eq 2).



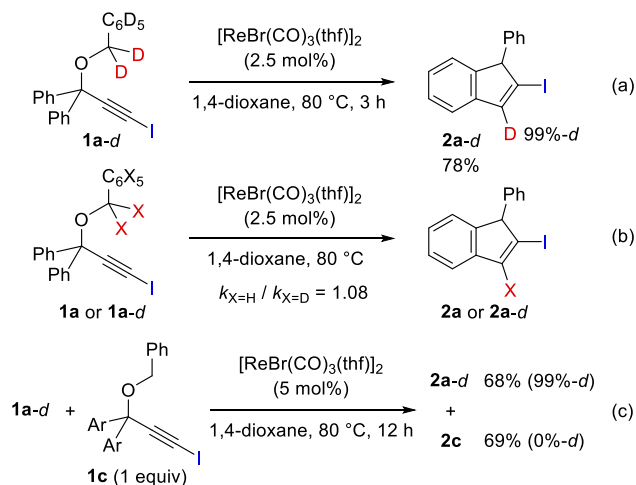
A proposed mechanism for the formation of 2-iodo-1H-indenes **2** in the current reaction is shown in Scheme 2. First, alkenyl carbene species **A'** was generated *via* sequential 1,2-I and 1,5-H shifts, followed by elimination of benzaldehyde, as shown in Eq 1. A deuterium-labelling experiment using **1a-d** confirmed that a 1,5-shift of the deuterium atom from the benzylic position of **1a** onto the alkenyl carbon of **2a** (Scheme 3a). Furthermore, a parallel reaction of **1a** and **1a-d** in a separate flask provided a KIE value of 1.08, which suggested that the hydrogen shift of **1** was not involved in the rate-determining step (Scheme 3b). Due to the relatively fast this 1,5-H shift, direct insertion of a vinylidene species into the benzylic C–H bond^{3g} leading to 3-iodo-2,5-dihydrofuran derivatives did not occur. A crossover experiment using **1a-d** and **1c** in the same flask provided **2a-d** and **2c**, and no exchange of the deuterium label was observed (Scheme 3c). Thus, the current 1,5-H shift occurred through an intramolecular process. Because cyclization of **1e**, which contained electron-withdrawing trifluoromethyl groups, required higher temperatures, the carbenoid carbon of **A'** possessed electrophilic character. Thus, nucleophilic attack of the aryl group on the carbene carbon, followed by subsequent elimination of rhenium species and aromatization, is most plausible for formation of the indene skeletons (Scheme 2).¹⁶ As an alternate pathway, however, direct insertion of the carbenoid carbon of **A'** into a nearby aromatic C–H bond followed by transposition of double bond would also afford **2**.



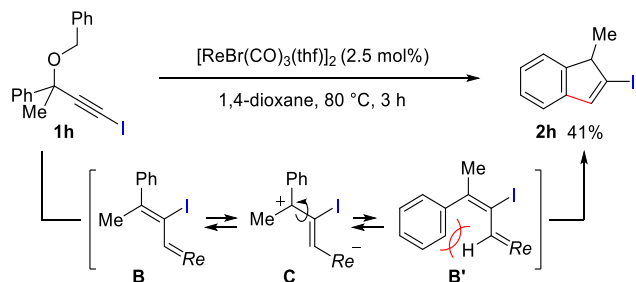
Scheme 2. Proposed reaction mechanism for formation of 2-iodo-1H-indenes **2**

The corresponding 2-iodo-1H-indene **2h** was also obtained from benzyl propargyl ether **1h** containing phenyl and methyl groups at the propargyl position. In this system, the alkenylcarbene intermediate **B**, having a carbene center situated anti to the phenyl group, was thought to be predominant to **B'** due to steric repulsion.¹⁷ However, formation of **2h** in moderate yield suggested that **B** could be interconverted to **B'** *via* zwitterionic intermediate **C** (Scheme 4).¹⁸

In contrast, iodoallene **3i** was obtained in 88% yield when benzyl propargyl ether **1i**, which did not possess aryl groups at the propargyl position, was used as a precursor (Scheme 5).¹⁹ The 1,5-H shift followed by elimination of benzaldehyde occurred very quickly, and products derived from vinylidene

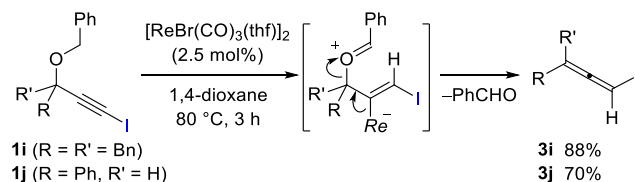


Scheme 3. Control experiments using deuterated substrate **1a-d** (Ar = 4-FC₆H₄)



Scheme 4. Interconversion of alkenylcarbene intermediate **B**

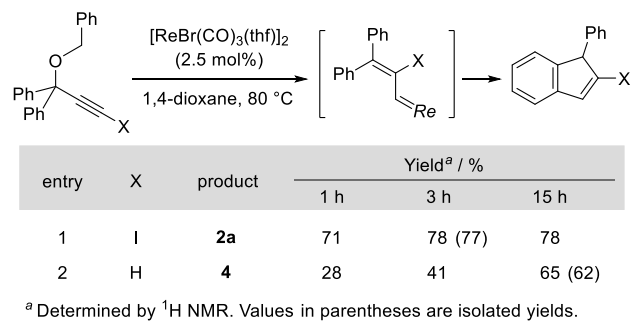
formation *via* a 1,2-I shift were not observed. The corresponding iodoallene **3j** was also obtained in the reaction of *sec*-propargyl ether **1j**. These results indicate that selectivity of these 1,*n*-shifts was influenced by the steric environment of the substituents at the propargyl positions. Although the expected vinylidene species was not generated, these transformations are also useful as a novel approach to iodoallenes, which are useful synthetic building blocks to introduce two consecutive allenyl double bonds into target molecules.



Scheme 5. Formation of iodoallenes **3** without 1,2-I shift

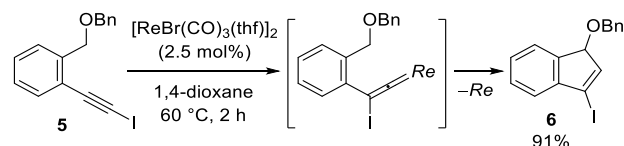
Impact of an iodo group at the alkyne terminal on the efficiency of the 1,2-shift was estimated by comparison of reactivity with the corresponding terminal alkyne (Table 2). Under the current optimized reaction conditions, iodoalkyne **1a** afforded the cyclization product **2a** more rapidly (entry 1) than the corresponding terminal alkyne (entry 2). A previous study on rhenium-catalyzed *anti*-Markovnikov addition to terminal alkynes revealed that vinylidene formation *via* 1,2-H shift was relatively slow and involved in the rate-determining step.⁶ These results suggest that 1,2-I shift leading to iodovinylidene species occurred much faster and did not involve in the rate-determining step. A crossover experiment using **1a-d** and a terminal alkyne having two 4-fluorophenyl

Table 2. Effect of terminal substituents of alkynes on 1,2-shifts



groups at the propargyl position also revealed that this 1,2-I shift occurred through an intramolecular process (see Eq S1 in SI).

The optimized rhenium catalyst, [ReBr(CO)₃(thf)]₂, was also effective for vinylidene formation from iodoalkynes derived from arylalkynes. For example, formation of 3-Iodo-1*H*-indene derivative **6** *via* insertion of C(sp³)-H bond into rhenium vinylidene species proceeded efficiently under the identical conditions (Scheme 6).^{3g}



Scheme 6. Rhenium-catalyzed cycloisomerization of iodoalkyne **5** derived from arylalketylene

In conclusion, 3-iodopropargyl ethers were found to be efficient 1-iodoalkenyl carbene generators when using rhenium catalysis under neutral conditions without additional phosphine or nitrogen-based ligands. Iodoalkynes derived from alkylalkynes were applicable as precursors, and the carbene intermediates generated were trapped efficiently through intramolecular cyclization for conversion into 2-iodo-1*H*-indene derivatives. The mechanistic study revealed that insights into the 1,2-I and 1,5-H shifts as well as the reactivity of the generated alkenylcarbene species. The current results provide novel insights into the reactivity of iodoalkynes, and offer new potential as readily available building blocks.

ASSOCIATED CONTENT

Supporting Information

Experimental procedures, spectroscopic data for all new compounds, and copies of ¹H and ¹³C NMR spectra. This material is available free of charge *via* the Internet at <http://pubs.acs.org>.

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- (11) **2a** was not obtained with the following catalysts (5 mol%-M) in dioxane at 100 °C: TaCl₅, Cr(CO)₅(thf), Mo(CO)₆, W(CO)₅(thf), WCl₆, Mn₂(CO)₁₀, MnBr(CO)₅, ReCl₅, Fe₂(CO)₉, [RuCl₂(CO)₃]₂, Ru₃(CO)₁₂, [Rh(OAc)₂]₂, [RhCl(cod)]₂, Ir₄(CO)₁₂, PtCl₂, AuCl, AuBr₃, IPrAuNTh₂, Au(PPh₃)SbF₆, and GaCl₃.
- (12) Effect of other solvents with 2.5 mol% of [ReBr(CO)₃(thf)]₂ at 80 °C for 3 h: Yield of **2a** was 12% in toluene, 9% in cyclohexane, 41% in Bu₂O, 63% in CPME, 43% in DME, 17% in AcOEt, 0% in MeCN or DMF. Effect of temperature with 2.5 mol% of [ReBr(CO)₃(thf)]₂ in 1,4-dioxane for 3 h: 68% at 70 °C, 58% at 90 °C. Additives, including amines, phosphines, and MS4A failed to improve the yield of **2a**.
- (13) Conversion of the corresponding bromoalkyne **1k** (see SI for the structure) instead of iodoalkyne **1a** did not occur at 80 °C. The desired 2-bromo-1*H*-indene was obtained at 120 °C but in less than 15% yield. For the generation of bromovinylidene species, see ref 2i.
- (14) Attempted synthesis of 2-iodo-1-phenyl-1*H*-inden-3-yl acetate from 1-iodopropargyl acetate **1ae** (see SI for the structure) via sequential 1,2-I and 1,3-acetoxy shifts followed by cyclization provided the complex mixture.
- (15) Transposition of the double bond of **2e** occurred even at 80 °C to afford a mixture of **2e** and **2e'** in the ratio of 67 / 32. See SI for the structure of **2e'**.
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