Communication

Indium-Catalyzed Cycloisomerization of 1,6-Cyclohexenylalkynes

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1. Introduction

Indium was discovered in 1863 by Reich and Richter of the Freiberg School of Mines in Germany [1]. It is a fairly rare metal, its presence in the earth’s crust is estimated at about 0.05 parts per million. Indium comes mainly from by-products of zinc mining (95%), and to a lesser extent, from tin, lead and copper ores. Used from the 1950s in the preparation of semiconductors, it is then used in the form of indium phosphate in the development of light-emitting diodes (LEDs). In the 21st century, its application in the form of indium oxide in high-tech industries such as liquid crystal displays (LCDs) has led to a sustained growth in world demand for indium. Its use in organic synthesis in the form of salts (halides or acid derivatives) has been growing for three decades and the pronounced Lewis acid character of indium has pushed organic chemists to study its reactivity with an additional financial interest since its price is attractive compared to other noble salts [2–6]. The first examples of indium-catalyzed intramolecular hydroarylation reactions of alkynes were reported by Fürstner’s group from ɑ-alkyne biaryl derivatives leading to halophenanthrene derivatives in yields ranging from 59% to 95% (Scheme 1, (1)) [7]. Chatani’s group studied in 2006 the rearrangement of 1,6-enynes in the presence of indium trichloride as catalyst leading to the formation of 1-vinylcyclo-alkene derivatives (1,3-diene) or 1-allylcyclo-alkene derivatives (diene-1,4) depending on the substitution of the alkynyl moiety. The exo process was favored for non-substituted alkynes whereas the endo pathway was generally observed for substituted alkynes. Then, the presence of electron-withdrawing groups on the aryl substituted alkyne increased the ratio of the exo isomer. DFT calculations were performed on stability of intermediates and corroborated the intervention of InCl3.

Keywords: indium; cycloisomerization reaction; 1,6-enzyme; catalysis; atom economy

[Abstract and main text follow]
trichloride in alkyne activation for carbocyclization reactions by describing an efficient synthesis of exo-methylene α-disubstituted cyclopentane derivatives [14–16] and following our continuous work on gold catalysis [17–21], we wondered if we could promote cycloisomerization processes on cyclohexenylalkynes [22] in the presence of indium salts. These bicyclic derivatives are key building blocks and represent privileged scaffolds for biologically active molecules and natural products [23–28]. We wish therefore to describe our results in the presence of InCl₃ catalyst and a critical comparison with our previous results with gold complexes.

2. Results

At the outset of our study, we prepared several functionalized 1,6-enynes, starting from ethyl 4-cyclohexanone-carboxylate according to a straightforward three-step route implying a triflate formation, a Suzuki–Miyaura coupling and a propargylation (Scheme 2). We prepared non-substituted alkynes 1a–d as well as substituted ones such as Me-substituted 1e, and Ar-substituted 1f–1p, the latter being obtained via classical Sonogashira cross-coupling reactions on 1a [22].

Based on our gold-catalyzed experience, we have recently studied the cycloisomerization reactions of the known ethyl 4-oxocyclohexane carboxylate 1a and showed that the use of gold catalysts allowed the formation of bicyclo[3.2.1]oct-2-ene 2a as well as the isomerized 3a in various ratio depending on the gold catalyst (Table 1, entries 1–3) [22]. The reaction allowed the formation of 2a in 81% conversion after 1 h with 2 mol % catalyst, but 3a was observed in high ratio (Entry 1). In toluene, the reaction was similar and led to 2a:3a in 53:47 ratio (Entry 2). The use of a NHC-type gold catalyst IPrAuNTf₂ gave selectively the desired cycloisomerized adduct 2a in 90% yield with a lower catalyst loading (Entry 3). Disappointingly, the same reaction conditions in the presence of commercially available InCl₃ salt did not promote the cyclization (Entry 4). Increasing the temperature and the catalyst loading to 5 mol %, according to Chatani’s work [8], was very positive as the desired adduct 2a was isolated in 90% yield and in an excellent 99:1 ratio (Entry 5). Noteworthy that no conversion was observed at room temperature in the presence of

![Scheme 1](image-url)
5 mol % indium. When the reaction was conducted in DCE at 40 °C, a lower yield was observed, because of some degradation (Entry 6). Moreover the isomerization process was competitive and the 3a:2a ratio increased to 15:85.

![Scheme 2. Structures of prepared 1,6-enynes.](image)

**Table 1. Au and In-catalyzed cycloisomerization reaction of ethyl 4-oxocyclohexane carboxylate.**

| Entry | [M] (x mol %) | Solvent | T (°C) | t (h) | 2a:3a Ratio (%) | Yield (%) |
|-------|---------------|---------|--------|-------|-----------------|-----------|
| 1     | (PPh₃)AuNTf₂ (2) | DCM     | rt     | 1     | 45:55           | 60 (81)   |
| 2     | (PPh₃)AuNTf₂ (2) | toluene | rt     | 0.5   | 53:47           | 50 (100)  |
| 3     | IPrAuNTf₂ (1)   | toluene | rt     | 0.75  | 99:1            | 90 (100)  |
| 4     | InCl₃ (1)       | toluene | rt     | 2     | /               | / (0)     |
| 5     | InCl₃ (5)       | toluene | 40     | 1     | 99:1            | 90 (96)   |
| 6     | InCl₃ (5)       | DCE     | 40     | 0.33  | 85:15           | 60 (100)  |
| 7     | Bi(OTf)₃ (5)    | toluene | 40     | 1     | 80:20           | 35 (40)   |

1 Determined on ¹H NMR of crude mixture. ² Isolated yield.

Comparatively, the use of another similar Lewis acid such as bismuth [29] led to the desired bicyclo[3.2.1]oct-2-ene but in a lower yield and selectivity compared to the results with indium (Entry 7 versus entry 5). We anticipated that Bi(OTf)₃ would promote the isomerization of the exo-double bond, which was demonstrated by submitting 2a to 5 mol % of Bi(OTf)₃. Indeed when bismuth triflate was added to the exo derivative 2a, the isomerization of the double bond was observed very quickly, in 30 min. The ratio of exo derivative 2a to exo isomerized derivative 2b is 40/60 and was observed similarly in both solvents, DCE and toluene (Entries 6, 7) [30]. The isomerization of the exo-double bond may therefore be explained by a Brønsted acid catalyzed process (TiOH or HCl) as already observed in the literature for other polycyclic structures [31–33]. The origin of such acids would come from partial hydrolysis of the catalyst InCl₃ and Bi(OTf)₃ in the presence of traces of water.

We selected the optimized conditions employing InCl₃ in toluene at 40 °C, and studied the scope and limitations with a wide range of functionalized enynes (Scheme 3). In the case of propargyl enyne derivatives 1a–d, complete conversions were observed in 2 h.
up to 15 h with temperatures of 40 °C and 80 °C. The cycloisomerization reaction was particularly efficient with the derivatives possessing the 4-methoxy-phenyl 1a, the phenyl 1b and the 4-n-propylphenyl 1c groups (75–90% yields). Excellent 5-endo isomer selectivity was also observed. With the chlorinated derivative 1d, the reaction led to the products 2d and 3d in a lower yield of 60% at 50 °C and a 65:35 mixture of the 5-endo isomer and its 5-exo isomerized counterpart. A higher temperature (80 °C) resulted in a worse yield of 42%, due to degradation. The isomerization of the double bond was also observed in a higher proportion.

\[ \text{Scheme 3. In-catalyzed cycloisomerization of ethyl 4-oxocyclohexane carboxylate derivatives 1a–d.} \]

In the case of substituted alkynes 1e–p (Scheme 4), the reactions were more sluggish and we had to increase the temperature to 110 °C and the catalyst loading to 7 mol %. The reaction outcomes allowed the formation of 2 isomers, 2 and 4, resulting from 5-endo and 6-endo cyclization processes respectively. In most cases, the 5-endo derivative was determined as the major isomer, but the competition with the formation of the 6-exo adduct could be important in some cases. The cycloisomerization reaction of the methyl-substituted enyne 1e led to the 5-endo derivative 4e as the major adduct in 87% isolated yield (Scheme 4, (1)). The endo/exo ratio was still high for 4-MeO- and 4-F-functionalized derivatives 4g and 4i respectively, but slowly decreased for phenyl, 4-Cl- as well as 3-F- or 2-F-functionalized adducts (Scheme 4, (2)). In the case of enynes bearing electron-withdrawing groups such as 1l–n, the preference towards a cyclization mode was reduced and the endo/exo ratios were closed to 50:50. The reactions were nevertheless very efficient as the mixture of endo/exo isomers were isolated in good to excellent yields (89–99%). In contrast, for the heterocyclic derivatives 1o–p, the yields were much lower, 44% for the 2-thiophenyl derivative 4p and only 5% for the 2-furanyl 4o (Scheme 4, (3)). Additional tests were performed, decreasing the reaction temperature to 40 °C and 80 °C but without significant improvement. Degradation products, which could not be identified were isolated at 110 °C in the case of the 2-thiophenyl.
Scheme 4. In-catalyzed cycloisomerization of substituted derivatives 1e–p (Ar = 4-MeOC₆H₄).

The selectivity towards “5-exo” and “6-endo” cyclized product was then compared between the indium and gold catalytic systems. In the case of 1e, 1f, 1g as well as for the F-substituted enynes 1i–k or the heterocyclic adducts 1o–p, similar results were observed having endo:exo ratio equal or very similar. A significant difference in percentage was observed in the case of the 3-NO₂-substituted derivative as the use of IPrAuNTf₂ allowed the formation of 4n in 70% selectivity (2n:4n = 30:70). As 2n and 4n were easily separated, the interest of indium salt was thus to allow the formation of the exo derivative in a better ratio. The case of 1l and 1m also showed significant difference in selectivity. According to the same trend, the percentage of the exo isomers were significantly increased with indium catalyst, as 2l and 2m were isolated in a 85:15 (2l:4l) and 65:35 (2m:4m) respectively in the presence of gold.

These unexpected results on the selectivity induced by In or Au prompted us to perform DFT calculations with the Gaussian 16 suite of programs (Revision A.03) [34] on the intermediates related to endo and exo isomer and we chose the 3-NO₂ adduct for this study. Mechanistically [35–37], the π activation of the alkyne, would lead to intermediate B and then the nucleophilic addition of alkynyl group would proceed according to a 5-exo or 6-endo pathway (Scheme 5). The resulting vinyl metal intermediates C and D would then give 2n or 4n by protodemetallation. The difference between indium and gold may be evaluated by considering the stability of intermediates C and D.

Following the seminal work from Gandon [9] and Yu [38–40] with indium and gallium salts, In and Au intermediates C and D were optimized with the dispersion corrected B3LYP-D3 exchange-correlation functional [41–45] and the results are collected in Table 2. The effective-core potential of Hay and Wadt with a double-ξ valence basis set (LANL2DZ) was used to describe In and Au [46] and the other atoms were described by the 6–31g(d,p) basis set. We used the PCM implicit solvation model to take into account the solvation...
effects of toluene. Computing vibrational frequencies and summing electronic and thermal free energies led to the reported Gibbs free energies. Indium was considered as InCl₃ or InCl₂ as previously advocated [9,35–37].

![Mechanistic rationale diagram]

Scheme 5. Mechanistic rationale.

Table 2. DFT calculations.

| Entry | Experimental endo:exo Ratio (%) | [M]   | endo | exo  | Theoretical endo:exo Ratio (%) |
|-------|---------------------------------|-------|------|------|-------------------------------|
| 1     | 54:46                           | InCl₃ | ![DFT Diagram](#) | ![DFT Diagram](#) | 43:57                         |
| 2     | 54:46                           | InCl₂ | ![DFT Diagram](#) | ![DFT Diagram](#) | 96:4                          |
| 3     | 70:30                           | IPrAu | ![DFT Diagram](#) | ![DFT Diagram](#) | 99:1                          |

In the case of the InCl₃ intermediate, the theoretical stability of the exo vinylmetal intermediate (entry 1) was found to be slightly higher than the endo one. It was in good
agreement with the experimental analysis of the reactivity of In. The reaction of In led to an endo:exo mixture in a 54:46 ratio (Scheme 4, (2)). The InCl$_2$ intermediates did not allow any relevant correlation with the experimental results (Table 2, entry 2). We also analyzed the stability of the vinyl gold complexes, and the exo intermediate was also found to be the more stable one (Table 2, entry 3), in a higher ratio, experimentally and theoretically. This difference between indium and gold could be explained considering the higher Lewis acid properties of gold compared to indium, inducing a higher polarization of the triple bond.

We verified this statement on our substrate by comparing the partial charges (using the MKUFF method for Au and in alkyne complexes, see Supporting Information) between B-In and B-Au intermediates. In the case of π-gold complex, the polarization of alkynyl carbons was found to be 0.175 and −0.305 (0.48 difference), whereas the carbons were found to be charged −0.209 and −0.056 (0.153 difference), which therefore explains the difference in selectivity. Therefore the experimental values were in agreements with the theoretical data.

In conclusion, we have extended the methodology of the indium-catalyzed reactions by studying the cycloisomerization of cyclohexenylalkynes leading to functionalized bicyclo[3.2.1]oct-2-ene and bicyclo[3.3.1]nonadiene. The scope and limitations study showed that the cyclizations occurred according to an exo process in the case of non-substituted alkynes whereas the endo isomers were generally obtained for substituted alkynes. The presence of electron-donating and electron-withdrawing groups on the aryl substituted alkylene influenced the cyclization outcome, increasing the ratio of the exo isomer for electron-deficient groups. DFT calculations confirmed the prevalence of InCl$_3$-based intermediates and showed good correlations with the experimental data. This methodology is therefore complementary to the one developed in the presence of gold. Further studies will focus on potential asymmetric versions of this atom economical process and on the applications of such skeletons.

Supplementary Materials: Supplementary materials present the synthesis of bicyclic adducts 2, 3 and 4, as well as the DFT calculations. The following are available online at https://www.mdpi.com/article/10.3390/catal11050546/s1.

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