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Regiodivergent Synthesis of Functionalized Indene Derivatives via Pt-Catalyzed Rautenstrauch Reaction of Propargyl Carbonates

Jinbo Zhao and Daniel A. Clark*

*1-014 Center for Science and Technology, Department of Chemistry,
Syracuse University, Syracuse, New York 13244, United States*

daclar01@syr.edu

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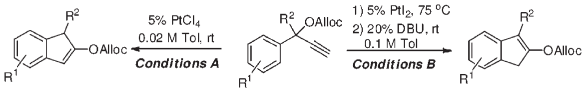
ABSTRACT



A regiodivergent synthesis of functionalized indene derivatives from a Pt-catalyzed Rautenstrauch reaction of propargyl carbonate is described. A one-pot Rautenstrauch/Tsuji–Trost reaction delivering 2-indanones was realized efficiently using this methodology.

Indene is a privileged structural motif in natural product,[1] pharmaceutical,[2] and materials chemistry[3] and has found use as a ligand for transition metal complexes.[4] Despite numerous reports on the synthesis of indenes,[5] methods for the selective syntheses of heteroatom functionalized indene derivatives, especially 2-indanones, are still lacking.[6,7] The goal of this study was to ascertain a selective method to access both regioisomers of 2-substituted indenes using Rautenstrauch methodology.

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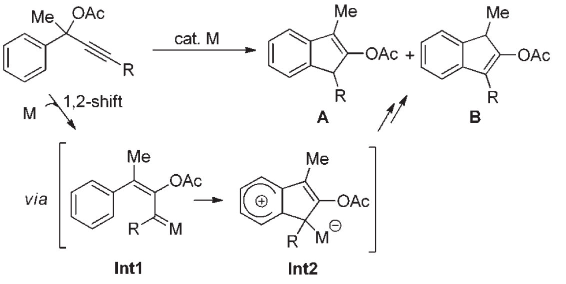
The Rautenstrauch reaction has recently garnered increased attention because it provides straightforward access to cyclopentanones from readily available 1,4-enynes.[8] Functionalized indenes were later found to be readily accessed using this reaction when an aryl group was used in place of the alkene moiety.[9] The aryl group participated in the pentannulation process, presumably through an electrophilic metalation of the carbenoid species **Int1** generated through a 1,2-acyloxy shift[10,11] induced by a transition metal (Scheme 1). Recently, Sarpong has reported a regioselective synthesis of functionalized indenes using ester-activated propargyl acetates.[9b] However, the use of terminal propargyl acetate derivatives, as reported by Ohe and coworkers, provided a mixture of regioisomers with poor selectivities. The product ratios reported by Ohe typically favor of the 1-methyl-1*H*-indene **B** (Scheme 1).[9c] They attributed this regioselectivity issue to the nonselective proton shift steps after protonation of **Int2** in the catalytic cycle. This unsolved challenge of regioselectivity has limited the application of this reaction in organic synthesis.[12] Herein, we report an efficient solution to this problem: the use of a propargyl carbonate allows a highly regioselective synthesis of 1-alkyl-1*H*-indenes, while its regioisomer 3-alkyl-1*H*-indenes may be accessed by a Pt-catalyzed Rautenstrauch reaction/catalytic isomerization sequence.

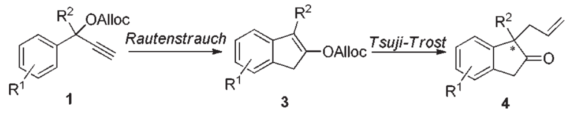
Our interest in this field stems from our intention to synthesize enantioenriched 2-indanone derivatives. We envisoned that allyl propargyl carbonates **1** would undergo a regioselective Rautenstrauch reaction to form 3-alkyl-1*H*-indene **3**,[13] which bears the requisite functionality for a Tsuji–Trost reaction to afford 2-indanone **4** with an all-carbon quarternary stereocenter (Scheme 2).

Scheme 1. Regioselectivity Issue in Transition-Metal-Catalyzed Pentannulation of Propargyl Esters



a) R = CO_2Et, **A/B** = 80/20~92/8 (Sarpong, **2005**) M = [Pt]
b) R = H, **A/B** = 17/83~74/26 (Ohe, K. et al, **2007**)
M = [Pt], [Au], [Ru]

Scheme 2. Tandem Rautenstrauch/Tsuji–Trost Reactions for the Synthesis of 2-Indanones



To this end, allyl carbonate **1a** was synthesized using standard conditions from the commercially available alcohol and allylchloroformate. We explored a variety of metal salts that are known to work well in the Rautenstrauch reaction (Table 1). Under the original Rautenstrauch conditions, almost no conversion was observed (entry 1, Table 1).[8] While $AuCl_3$ led to complete conversion, the yield of the products was low (entry 2, Table 1). AuCl(PPh_3) did not effect good conversion; the addition of silver salts to form the corresponding cationic gold(I) species led to complete decomposition of the starting material regardless of solvent (entries 4–6, Table 1). The reactions catalyzed by Pt(II) and Pt(IV) gave the best results, giving excellent yields in toluene. Other catalysts such as ruthenium, copper, and rhodium complexes were ineffective.[14]

The reaction catalyzed by $PtCl_4$ afforded isomer **2a** highly selectively, albeit in moderate yield (entry 11, Table 1). Lowering the reaction temperature to 0 °C led exclusively to product **2a** (entry 12, Table 1). A scrutiny of the crude reaction mixture revealed a byproduct, which appeared to be an unidentified decarboxylative dimerization product.[15] To minimize potential bimolecular processes, the effect of concentration was examined. Thus, the yield of **2a** greatly improved to 91% (86% isolated yield) when the reaction concentration was decreased from 0.1 to 0.02 M (entries 11 and 13, Table 1). Of note, even under these dilute conditions, the reaction was complete in <5 min.

We reasoned that 3-methyl-1*H*-indene **3a** should be the thermodynamic product since it bears a tetrasubstituted double bond in the cyclopentene moiety. Thus, **2a** might be isomerized to **3a** in the presence of a suitable base. The tautomeric rearrangement of simple alkyl-substituted indene ring systems studied by Weidler lended support to this proposal.[16] In accordance with this hypothesis, **2a** underwent smooth isomerization to **3a**. On the basis of the ease of use and overall yield, 20 mol % of DBU was selected as a base for the isomerization process.[14] We observed cleaner

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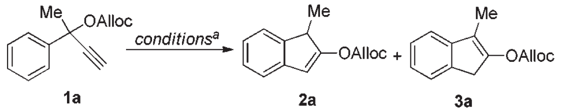
Table 1. Reaction Optimization



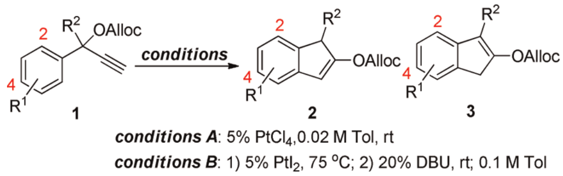
entry	catalyst	solvent (temp/°C)	yield[b]/% (**2a**/**3a**)[b]
1[c]	$PdCl_2(CH_3CN)_2$	MeCN (60)	0 (–)
2	$AuCl_3$	Tol (80)	~16 (~32/68)
3	$AuCl(PPh_3)$	DCM (25–40)	– (–)
4	$AuCl(PPh_3)/AgSbF_6$	CH_3NO_2 (25)	– (–)
5	$AuCl(PPh_3)/AgSbF_6$	DCM (25)	– (–)
6	$AuCl(PPh_3)/AgSbF_6$	Tol (80)	<5 (–)
7	$PtCl_2(PPh_3)_2$	Tol (110)	>27 (70/30)
8[d]	$PtCl_2(PPh_3)_2$/2PhIO	Tol (100)	63 (84/16)
9	$PtCl_2$	Tol (80)	70 (83/17)
10	PtI_2	Tol (60)	74 (42/58)
11	$PtCl_4$	Tol (25)	53 (96/4)
12	$PtCl_4$	Tol (0)	45 (>99/1)
13[e]	$PtCl_4$	Tol (25)	91 (94/6)

[a] Reaction conditions: **1a** (0.20 mmol), catalyst (5 mol % metal), and solvent (2 mL) unless otherwise specified. [b] On the basis of ^1H NMR of crude reaction mixture with mesitylene as internal standard. [c] Concentration: 0.7 M. [d] 10 mol % [Pt], 20 mol % PhIO, 0.2 M. [e] Concentration: 0.02 M, isolated yield: 86%.

pentannulation reactions of propargyl carbonates with PtI_2 compared to $PtCl_2$ for the synthesis of the thermodynamic product **3**. Although no further optimization was done on catalyst loading, it was found that the loadings of PtI_2 and DBU could be reduced to 1 and 10 mol %, respectively, on a 1 mmol scale using **1a**, with the reaction affording product **3a** in 84% yield.

With optimized conditions in hand, the substrate scope of this reaction was examined using substitution on the aryl group (R^1) and propargylic substitution (R^2, Table 2). Using Pt(IV) catalysis (*conditions A*), the reaction delivers kinetic products **2** in good to excellent yields with ≥95:5 regioselectivities, when R^1 is alkyl (entries 2 and 8, Table 2), halogen (entries 3 and 6, Table 2), or aryl (entry 4, Table 2). It is noted that in the presence of an *ortho*-methyl group, the reaction time was 1 h, and it afforded the corresponding product **2b** in 80% yield (entry 2, Table 2). However, the reaction of 3,5-dimethoxyl-substituted propargyl carbonate **1e** afforded a mixture of isomers **2e** and **3e** (entry 5, Table 2) in a ratio of 67/33 in 80% yield. The same reaction conducted at a lower temperature (0 °C) did not affect the selectivity. Similarly, the presence of a strong electron-withdrawing group such as *para*-trifluoromethyl gave diminished selectivity (79/21) and 37% yield (entry 7, Table 2). For substrates with electron-deficient aryl moieties, slow addition of substrate to the catalyst solution was used to reduce the undesired bimolecular byproduct (entries 3, 4, and 6, Table 2). Using Pt(II) (*conditions B*), all substrates underwent smooth cyclization and catalytic isomerization to exclusively afford the thermodynamic isomer **3**. Even substrates **1g**, which bears a CF_3 group, worked well under elevated temperature and delivered the product **3g** in good yield and excellent selectivity (entry 7, Table 2). The *ortho*-methyl-substituted substrate **1b** was the only substrate for which *conditions B* gave the thermodynamic product in slightly lower (92/8) selectivity; this was probably due to the $A^{1,3}$ strain of the two methyl groups in product **3b**. Under standard conditions, substrates with R^2 being linear alkyl (entries 9 and 11, Table 2), branched alkyl (entry 10, Table 2), and benzyl (entry 12, Table 2) groups all afforded both isomers in good yields and high regioselectivities.

Table 2. Substrate Scope Studies of Pt-Catalyzed Regioisomeric Synthesis of Functionlized Indenes[a]



conditions A: 5% $PtCl_4$,0.02 M Tol, rt
conditions B: 1) 5% PtI_2, 75 °C; 2) 20% DBU, rt; 0.1 M Tol

		conditions A		*conditions B*	
entry	R^1/R^2	yield[b]/%	**2**/**3**[c]	yield[b]/%	**2**/**3**[c]
1	H/Me (**1a**)	86 (**2a**)	96/4	76 (**3a**)	<1/99
2	2-Me/Me (**1b**)	80 (**2b**)	96/4	78 (**3b**)	8/92
3	4-Cl/Me (**1c**)	75[d] (**2c**)	95/5	63 (**3c**)	<1/99
4	4-Ph/Me (**1d**)	80[d] (**2d**)	94/6	63 (**3d**)	<1/99
5	3,5-di-MeO/Me (**1e**)	83[e] (**2e**/**3e**)	67/33	73 (**3e**)	<1/99
6	4-Br/Me (**1f**)	87[d] (**2f**)	95/5	85 (**3f**)	<1/99
7	4-CF_3/Me (**1g**)	37[e] (**2g**/**3g**)	79/21	72 (**3g**)	<1/99
8	4-*i*-Pr/Me (**1h**)	80 (**2h**)	95/5	82 (**3h**)	<1/99
9	H/Et (**1i**)	82 (**2i**)	94/6	84 (**3i**)	<1/99
10	H/*i*-Pr (**1j**)	91 (**2j**)	98/2	83 (**3j**)	<1/99
11	H/*n*-Bu (**1k**)	89 (**2k**)	97/3	76 (**3k**)	<1/99
12	H/Bn (**1l**)	78 (**2l**)	95/5	82 (**3l**)	<1/99

[a] Reaction scale: 0.2 mmol. [b] Isolated yields. [c] On the basis of ^1H NMR of crude reaction mixture. [d] Slow addition of substrate over 2 h. [e] ^1H NMR yield versus mesitylene as internal standard.

In order to clarify the unique regioselectivity in the $PtCl_4$-catalyzed conditions, several derivatives of the propargyl alcohol (**1m**–**1r**) were prepared and tested under both *conditions A* and *B*. The results in Table 3 show that esters (entries 1–3, Table 3) gave moderate selectivities, while carbonates (entries 4–6, Table 3) gave very high regioselectivities. This unambiguously demonstrates that the carbonate functionality is necessary for obtaining high selectivity. It is noted that for the Boc-substituted starting material **1p**, the yield of the product under $PtCl_4$ catalysis was very low (entry 4, Table 3). Instead, most of the material was converted to a bimolecular decarboxylative product. This indicates the participation of the butyoxyl oxygen in stabilizing cationic intermediates, making the *t*-Bu group more labile as previously observed.[17] This might be the reason for the high regioselectivity observed in the kinetic products obtained with *conditions A*. Under *conditions B*, however, all variants afforded the thermodynamic products in good yields with very high selectivities, demonstrating the generality of the catalytic isomerization process.

The pentannulation of secondary acetate derivatives is known to be challenging;[9c] we found that the same is true

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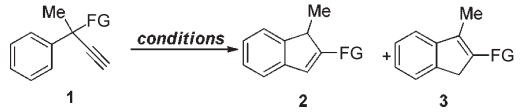
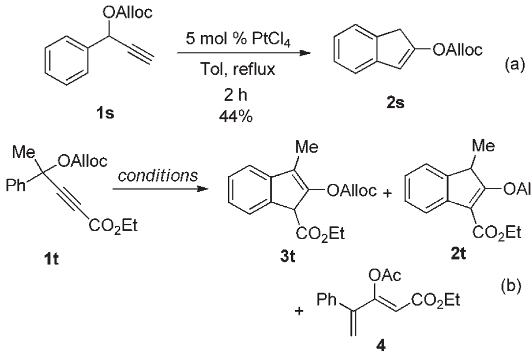
Table 3. Functional Group Effects on Reactivity and Selectivity



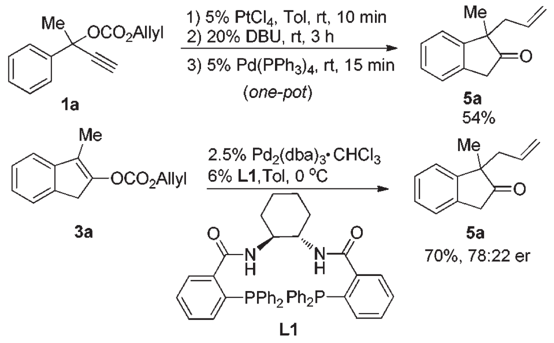
entry	FG	conditions A yield^a/%	conditions A **2**/**3**^{b}	conditions B yield^a/%	conditions B **2**/**3**^{b}
1	Ac (**1m**)	42 (**2m**/**3m**)	83/17	75 (**3m**)	<1/99
2	Bz (**1n**)	72 (**2n**/**3n**)	79/21	82 (**3n**)	<1/99
3	Piv (**1o**)	77 (**2o**/**3o**)	72/28	78 (**3o**)	<1/99
4	Boc (**1p**)	22 (**2p**/**3p**)	92/8	55 (**3p**)	<1/99
5	Cbz (**1q**)	66 (**2q**)	95/5	50 (**3q**)	<1/99
6	CO_2Et (**1r**)	66 (**2r**)	>94/6	73 (**3r**)	<1/99

^{a} Isolated yields. ^{b} Ratio determined by ^1H NMR of crude product.

Scheme 3. Reactivity of Related Substrates



Scheme 4. Synthesis of 2-Indanone **5a** Bearing an α-Quaternary Stereogenic Center



for secondary carbonates. The proclivity for pentannulation was examined with secondary allyl carbonate **1s**. Carbonate **1s** required a higher temperature (110 °C) to give indene **2s** in moderate 44% yield (Scheme 3a). Pentannulation of the corresponding acetate, reported by Ohe, provided 17% yield of the corresponding indene using $PtCl_2$.[9c] Elevated temperatures were also required for allyl propargyl substrate **1t**. Under $PtCl_4$ catalysis, **1t** gave a mixture of indenes **2t** and **3t** as well as diene **4** in 57% combined yield (Scheme 3b). Following the conditions reported by Sarpong, a similar yield and ratio of products was observed for **1t**.[9b,14] Attempts to apply base-catalyzed isomerization was not successful for $PtCl_4$ or the Sarpong protocol.[18]

Incorporation of an enol carbonate into the indenyl products presents a unique opportunity to explore allyl transfer reactions.[19] In particular, use of products **3** in such a reaction would grant access to a benzylic all-carbon quaternary stereocenter, which is difficult to install in a selective manner.[19d] As shown in Scheme 4, a sequential one-pot transformation to 2-indanone **5a** could be efficiently realized. The process is rapid, high yielding (> 83% per step), and completely regioselective. Moreover, the facile access to indene **3a** allowed us to validate the installation of the required quaternary center asymmetrically. The asymmetric Tsuji–Trost reaction of **3a** using the standard Trost DACH ligand **L1** afforded **5a** in 70% yield with an *er* of 78:22 (Scheme 4).

In conclusion, we have developed a facile synthesis of regioisomeric functionalized indenes that relies on a propargyl carbonate Rautenstrauch rearrangement. The use of Pt(IV) complexes and the carbonate functionality were shown to be crucial for obtaining high regioselectivity of the kinetic isomer. The thermodynamic isomer could be formed by a sequential Rautenstrauch cyclization followed by base-catalyzed isomerization.

In addition, we demonstrated a tandem one-pot Rautenstrauch/isomerization/Tsuji–Trost reaction sequence for the synthesis of 2-indanones that possess an all-carbon quaternary stereocenter. The asymmetric variant of the Tsuji–Trost reaction opens a new avenue for obtaining 2-indanones enantioselectively. These results validate the synthetic usefulness of the current methodology in the preparation of highly functionalized indene derivatives. Future work will focus on understanding the nature of the propargyl carbonate on selectivity and use of this method in natural product synthesis.

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Supporting Information Available. Procedures for synthesis of starting materials and products as well as copies of NMR spectra of all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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(18) The substrate with alkyl substitution on the alkyne is acid sensitive, prone to elimination, and decomposed during flash chromatography purification.

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The authors declare no competing financial interest.