Tandem Platinum Dichloride Catalysis and Thermal Reaction of Enynes: Versatile Synthetic Platform Based on Bicyclo[4.1.0]hept-2-enes

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Abstract: A tandem platinum dichloride-catalyzed cycloisomerization and rearrangement reaction of enynes leads to the formation of 2,4-pentadienals, 1-aryl-tetrahydro-1*H*-indenes, or 3-methylene-4-vinyl-cyclohex-1-enes; depending upon the substituent(s) and tether group of the enynes, the platinum dichlor-ide-catalyzed cycloisomerization products, bicyclo-

[4.1.0]hept-2-enes, undergo a Claisen rearrangement, a 1,5-hydrogen shift, or a vinylcyclopropane rearrangement.

Keywords: 1,3-alkyl migration; cycloisomerization; homogeneous catalysis; 1,5-hydrogen migration; olefin isomerization; platinum; vinylcyclopropanes

Introduction

Transition metal-catalyzed cycloisomerization reactions can provide a variety of cyclic scaffolds from readily available starting materials that are not easily obtained by conventional synthetic methods.^[1] Bicyclo[4.1.0]hept-2-ene derivatives (a) are one class of the products which can be easily obtained by transition metal-catalyzed cycloisomerization of 1,6enynes,^[2] typically utilizing Pt(II) and Au(I) as the catalyst. Recently, a restricted range of enantioselective processes also has been reported.^[3] The unique structure of bicyclo[4.1.0]hept-2-ene derivatives can give rise to an array of interesting characteristic transformations, but their use in the synthesis of more complex compounds is still rare (Scheme 1).^[4] Echavarren et al.^[4d,e] reported an oxidative ring opening of 3-oxabicyclo[4.1.0]hept-4-enes giving oxepanes, dihydrofurans or 3,4-dihydro-2H-chromenes. Very recently, this transformation has been used in the synthesis of GSK1360707F.^[5]

Under these circumstances, we have been exploring the possible utilization of bicyclo[4.1.0]heptenes in organic synthesis further. A few years ago, we had used cyclopropyl-substituted bicyclo[4.1.0]hept-2-enes in a carbonylative [3+3+1] cycloaddition reaction.^[4a] Recently, we reported^[4b,c] on a PtCl₂-catalyzed cycloisomerization of dienynes and a subsequent Cope rearrangement to create synthetically useful heterocyclic molecules, such as bicyclo[3.2.2]nonadienes, and 1,6,7,9a-tetrahydrocyclohepta[c]pyrans and -pyridines (Scheme 1).

From these previous studies, we envisioned PtCl₂catalyzed bicyclizations of enynes leading to bicyclo-[4.1.0]hept-2-ene and a range of subsequent rearrangements, depending upon the substituents (Scheme 2). Finally, we found that bicyclo[4.1.0]hept-2-ene derivatives can selectively undergo a Claisen rearrangement, a [1,5] hydrogen shift, or a vinylcyclopropane rearrangement depending upon the substituent(s) and tether groups in the envne substrates. Here, we reported a tandem PtCl₂-catalyzed cycloisomerization and rearrangement reaction of envnes to 2,4-pentadienals, 1-aryltetrahydro-1H-inproduce denes, or 3-methylene-4-vinylcyclohex-1-enes.

Results and Discussion

Synthesis of 2,4-Pentadienals from Allyl Propargyl Ethers

We initially studied a $PtCl_2$ -catalyzed isomerization of oxygen-tethered enynes. We selected **1** as the basic substrate, because the rearrangement occurred only in the presence of an aryl substituent at the internal



Scheme 1. Transition metal-catalyzed cycloisomerization and consecutive reactions.



Scheme 2. Platinum-catalyzed cycloisomerization and consecutive reactions.

carbon of an alkene group. Three years ago, we communicated the formation of 2,4-pentadienal from bicyclo[4.1.0]hept-2-ene.^[4a] However, only one example was reported at that time.

When **1** was treated with 2.5 mol% $PtCl_2$ in toluene at 110 °C for 1 h, a mixture of **1a**, **1b**, and **1c** was obtained in 44%, 5%, and 10% yields, respectively. A Claisen rearrangement and a consecutive hydrogen shift of **1a** took place with 2,4-dienals **1c** being obtained (Scheme 3).

We investigated the best conditions for obtaining **1**c using **1** as a model substrate (Table 1). When a reaction was carried out in toluene using 2.5 mol% PtCl₂ at 110 °C (entries 1–3), the yields and distribution of the products varied depending on the reaction time and temperature. As the reaction time increased, the yield of **1**c increased. However, a prolonged reaction



Scheme 3. PtCl₂-catalyzed cycloisomerization and sequential rearrangements.

Entry	Catalyst [mol%]	Temp. [°C]	Time [h]	Yield [%]		
				1 a	1b	1c
1	2.5	110	1	44	5	10
2	2.5	110	4	_	4	68
3	2.5	110	21	_	_	11
4	1.3	90	10	15	_	32
5	1.3	110	4	3	-	81 (74 ^[b])
6 ^[c]	1.3	130	1	_	_	64

Table 1. PtCl₂-catalyzed cycloisomerization of oxygen-tethered enynes followed by sequential rearrangements.^[a]

^[a] Yields and isomeric ratio determined by ¹H NMR versus methyl benzoate as an internal standard.

^[b] Isolated yields.

^[c] Xylene was used as a solvent.

time (21 h; entry 3) was detrimental; probably the aldehyde **1c** was decomposed by heat. Varying the amount of catalyst had an effect on the yield, which could be reduced to 1.3 mol%. The best yield (81% by NMR; 74% isolated yield) was obtained when the reaction was carried out in the presence of 1.3 mol% of PtCl₂ in toluene at 110 °C for 4 h. Only a small amount of **1a** (3%) was observed. We next investigated the $PtCl_2$ -catalyzed cycloisomerization of a variety of oxygen-tethered enynes and a subsequent rearrangement (Table 2).

The reaction time varied depending on the substrate. The reaction afforded the corresponding products in reasonable to high yields with a high preference for the (2E, 4E)-stereoisomer. The diastereomeric ratio of each compound was determined by the ¹H NMR spectrum of the crude product. In the case of entry 2, the (2Z,4E)-stereoisomer 2c, having a different geometry at C-2, was obtained in 5% yield. Interestingly, only (2E, 4E)-stereoisomers were observed for entries 4 and 6. The stereoselectivity was highly sensitive to the steric bulkiness (entries 1 and 2 vs. 3 and 5), but rather insensitive to the electronic effect of the aryl group (entries 1 vs. 9 and 10). An enyne bearing a 4-MeOC₆H₄ instead of a phenyl group gave a poor yield (21%) at 110°C. However, when the reaction was conducted at 140°C, the yield increased to 71%. A substrate having $4-CF_3C_6H_4$ gave a higher yield (77%) at 110°C. The structure of the aldehyde produced was confirmed by X-ray diffraction analysis of **4c** (Figure 1).

Table 2. PtCl ₂ -catalyzed cycloisomerization	of a variety of O-tethered envi	nes and subsequent thermal	rearrangements.[a]

Entry	Substra	Time [h]		Product	Yield [%] ^[b] (4 <i>E</i> /4Z	
1	1a	O Ph	4	1c	Ph H 4 0 2	74 (14/1)
2 ^[c] 3 4 ^[d] 5	2a $(R^1 = Ph)$ 3a $(R^1 = Me)$ 4a $(R^1 = cyclopropyl)$ 5a $(R^1 = vinyl)$	O Ph Ph	2 4 3 2	2c 3c 4c 5c	Ph H O R ¹	78 (7.7/1) 79 (6/1) 77 58 (6/1)
6	6a		6	6с	Ph	48
7 8	7a $(R^2 = p$ -CH ₃ OC ₆ H ₄) 8a $(R^2 = p$ -CF ₃ C ₆ H ₄)		24 24	7c 8c	H O	71 (10/1) 77 (12/1)

^[a] Reaction conditions: 0.3 mmol of substrate and 1.3 mol% PtCl₂ were reacted in 6 mL toluene at 110 °C.

^[b] Isolated yield.

^[c] **2c** was obtained in 5% yield.

^[d] In xylene at 140°C.



Figure 1. X-ray crystallography of 4c.

Synthesis of 1-Aryltetrahydro-1*H*-indenes from Enynes

We next studied a PtCl₂-catalyzed reaction of oxygentethered enynes bearing an aryl group at the terminal position of the alkene. When compound **9** was treated with 1.3 mol% PtCl₂ in toluene at 80 °C for 2 h, a cyclopropanated product **9a** instead of a dienal was isolated in 69% yield. Heating the isolated **9a** in toluene at 110 °C for 12 h gave 9-phenyloctahydroindeno[2,1c]pyran, **9d**, in 92% yield [Eq. (1)].

As expected, the vinylcyclopropane rearrangement of **9a** to **9d** needs a high reaction temperature and a long reaction time. However, the reaction temperature was much lower than those for the thermal rear-



Table 3. A consecutive reaction of PtCl₂-catalyzed cycloisomerization and vinylcyclopropane rearrangement.^[a]

Entry			Subst	rate		Time [h]	Product		Yield [%] ^[b]
		X	Ar	R			H _{Ar} R		
1	9	0	Ph	H		18		9d	80
23	10	N IS O	Ph Ph	н Ме		24 24		10a 11d	80 34
4	12	NTs	$p-CH_3OC_6H_4$	H		24		11d 12d	68
5	13	NTs	p-CH ₃ C ₆ H ₄	Н		24		13d	74
		R ¹	R ²	R ³	$ \begin{array}{c} $		TsN H Ph		
6	14	Н	Н	Me		22		14d	59 ^[c]
7	15	Н	Me	Me		24		15d	36 ^[d]
8	16	Ph	Ph	Н		18		16d	57
9	17	Н	Ph	Н		3		17d	48 ^(c)

^[a] *Reaction conditions:* 0.3 mmol of substrate and 5 mol% PtCl₂ were reacted in 6 mL toluene at 120 °C.

^[b] Isolated yield.

^[c] Isolated as a mixture with **14a** in 10% yield.

^[d] Isolated as a mixture with **15a** in 36% yield.

^[e] Isolated as a mixture with **17a** in 19% yield.

182 **a**

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rangement of unactivated vinylcyclopropanes to cyclopentenes.^[6] Compared to the formation of **1c** from **1**, the formation of **9d** from **9** shows the importance of the position of a substituent in the enyne substrate. Thus substituents affect both the direction of the transformations and their activation barriers.

We investigated a consecutive sequence of $PtCl_2$ catalyzed cycloisomerization and thermal reaction in a one-pot reaction. When the same reaction was carried out at 120 °C, the total yield was improved to 80%. We further screened the consecutive reactions of $PtCl_2$ -catalyzed cycloisomerization and vinylcyclopropane rearrangement with a variety of dienynes having a phenyl group at the terminal carbon of an alkene moiety. The results are compiled in Table 3.

Compounds having a cyclopenta[c]pyridine or a cyclopenta[c]pyran skeleton were obtained in reasonable to high yields. However, a dienyne bearing a gemdisubstituted alkene moiety (entry 3) afforded a rather lower yield (34%). Dienynes (entries 2, 4, and 5: 67–80%) bearing a cyclic olefin gave higher yields than those having an acyclic olefin (entries 6–9: 36– 59%). The structure of the product was confirmed by X-ray diffraction analysis of **16d** (Figure 2).

However, dienynes bearing no phenyl group at the terminal carbon of an alkene group gave only cyclopropanated products in high yields (18 and 19: [Eq. (2)]). Thus, it seems that the presence of an aryl substituent at the terminal carbon of an alkene group is a





Figure 2. X-ray crystal structure of 16d.

prerequisite for the generation of the cyclopentene products.^[7]

Synthesis of 3-Methylene-4-vinylcyclohex-1-enes

We next investigated a $PtCl_2$ -catalyzed reaction of Otethered dienynes bearing a methyl group at the olefinic terminal carbon. We expected that this type of the substrate would be transformed to the 2,4-dienal of Eq. (1), but when substrate **20** was reacted with 1.3 mol% of $PtCl_2$ in xylene at 140 °C for 24 h, a methylene-4-vinylcyclohexene derivative, **20e**, was isolated in 65% yield [Eq. (3)]. Thus, a subtle change in the substitution leads to a quite different reaction product. The product was derived from a cycloisomerization followed by a [1,5] hydrogen shift.^[8]

The scope of the reaction was further studied with a variety of dienynes having a methyl group at the olefinic terminal carbon (Table 4). The reaction temperature was highly dependent upon the substrate itself. In the case of **26**, a reaction temperature of 80 °C was chosen. In some cases, a reaction temperature of 140 °C was chosen, in order to enhance the thermal reaction. When significant decomposition of the products was observed at 140 °C, 100 °C was chosen as the reaction temperature. The yield found to be highly dependent upon the substituent at the alkene's inner carbon and on the concentration of the catalyst. When the substrate (**21**) in entry 2 was react-



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Entry			Substrate				Time [h]	Temp. [°C]	Product		Yield [%] ^[b]
		X	R ¹	R ²					$X \xrightarrow[R^2]{R^1}$		
1	20 ^[c]	0	Ph	Н			24	140		20e	65
2	21	0	Н	Me			48	140		21e	57 ^[e]
3	22	NTS	Ph	H			24	140		22e	78
4	23	NTS	p-CH ₃ OC ₆ H ₄	H			24	140		23e	69 62
3	24	INTS	п	п			48	100		24e	03
		X	\mathbf{R}^1	R ²	R ³	X R^3 R^2 R^1			$X \xrightarrow{R^3} R^2$		
6	25	NTs	Н	Н	Ph		24	140		25e	83
7	26 ^[d]	NTs	Н	Me	Ph		48	80		26e	87
8	27	NTs	Н	Me	Η		8	140		27e	65 ^[f]
9	28	NTs	Me	Me	Ph		24	100		28e	48
10	29	0	Н	Ph	Ph		24	140		29e	41
11	30 ^[c]	0	Ph	Н	Ph		8	140		30e	58
						TsN_Ph			TsN Ph		
12	31 ^[d]					,	20	140		31e	41 ^[g]

Table 4. A consecutive reaction of PtCl₂-catalyzed cycloisomerization and [1,5]-hydrogen shift.^[a]

^[a] Reaction conditions: 0.3 mmol of substrate and 5 mol% $PtCl_2$ were reacted in 6 mL xylene at the presented temperature.

^[b] Isolated yield.

[c] 1.3 mol% PtCl₂ was used. [d] 10 mol% PtCl was used.

^[d] 10 mol% PtCl₂ was used. ^[e] 33% of **21** was recovered

 $\begin{bmatrix} e \end{bmatrix}$ 33% of **21** was recovered.

^[f] Isolated as a mixture with **27a** in 9% yield.

^[g] 9% of **31** was recovered.

ed in the presence of 1.3 mol% PtCl₂, no reaction was observed, but 57% of the expected product (21e) with a 33% recovery of 21 was isolated in the presence of 5.0 mol% of PtCl₂. In the presence of 10 mol% of PtCl₂, all of the reactants were decomposed, that is, no isolable compound was observed. Interestingly, for oxygen-tethered substrates (20 and 30), a higher yield was observed when 1.3 mol% PtCl₂ was used instead of 5.0 mol% PtCl₂ (entries 1 and 11). Higher yields (> 80%) were observed with envnes having an aryl group at the alkene's inner position (entries 6 and 7). This observation is consistent with the acceleration of 1,5-homodienyl hydrogen migrations due to electronwithdrawing aryl substituents.^[9] Dienyne substrates (entries 2, 5, and 8) without a substituent at the alkene's inner position gave the expected product in reasonable yields (57–65%).

However, when a substrate bearing a methyl group at the alkene's inner position (32 in [Eq. (4)]) was re-



acted at 140 °C over a 4-day of a reaction period, compound **32a** was isolated in 78% with a trace amount of **32e**.

Thus it seems that the electronic effect of the substituent at the alkene's inner position has a profound effect on the yield of the reaction. When a dienyne (**31**) having an ethyl group instead of the methyl at the olefinic terminal carbon was used as a substrate (entry 12), the expected reaction occurred, but the yield decreased to 41%. Oxygen-tethered dienynes with a methyl group at the olefinic terminal carbon (entries 1, 2, 10 and 11) gave the expected products at slightly lower yields (41–65%) than those of N-Ts-tethered dienynes. It has been well documented^[6a] that a [1,5] hydrogen shift pathway competes with a vinylcyclopropane rearrangement when the 2-*cis* substituted groups at vinylcyclopropane contain at least one hydrogen atom at the α -position. However, our study shows that the 1,5-hydrogen shift is unique to dienyne substrates having a methyl group at the terminal carbon of the alkene moiety and is much preferred when dienynes have an aryl group at the inner position of an alkene.

Conclusions

We have demonstrated two reaction pathways leading to compounds which are difficult to prepare by conventional synthetic pathways: that is, two new rearrangements of bicyclo[4.1.0]hept-2-enes to 2,4-pentadienals, 1-aryltetrahydro-1H-indendes, or 3-methylene-4-vinylcyclohex-1-enes which are found as substructures in natural products having a diverse range of biological activities.^[10] The reaction pathways are highly sensitive to the identity and position of (a) substituent(s) at the alkene moiety. Thus we can predict the characteristics of a reaction product based on our studies. Readily available enynes are used as starting materials for the reaction. Moreover, the experimental simplicity is noteworthy. Further studies on the application of bicyclo[4.1.0]heptenes as molecular scaffolds and a comprehensive experimental and computational study will be reported in due course.

Experimental Section

General Procedure for the Tandem PtCl₂-Catalyzed Cycloisomerization and Thermal Reactions

PtCl₂ and toluene (or xylene, 2 mL) were added to a Schlenk flask equipped with a stirring bar and capped with a rubber septum. The substrate (0.3 mmol) and toluene (or xylene, 4 mL) were then added to the flask and heated. The resulting mixture was reacted until the substrate was completely consumed (reaction monitored by TLC). The product was purified by flash chromatography on a silica gel column by eluting with **n**-hexane/ethyl acetate.

Supporting Information

Characterization data (¹H and ¹³C NMR spectra, and HR-MS) for substrates (1–32) and products (**a**, **b**, **c**, **d**, and **e**), and crystal data of 4c (CCDC 778494) and 16d (CCDC 778495) (these data can also be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif) are available in the Supporting Information.

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