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Two-step allylic carbon insertion between ketone carbonyl and α carbons giving α-quaternary α-vinyl ketones

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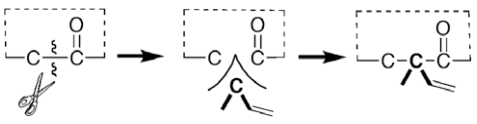
ABSTRACT

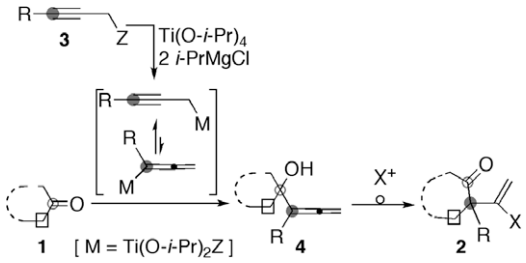
Ketones **1** were converted to α-quaternary α-vinyl ketones **2** by a two-step formal allylic carbon insertion between ketone carbonyl and α carbons, which involves the reaction of **1** with propargyltitanium reagents, derived from propargyl carbonates **3** and a divalent titanium reagent Ti(O-*i*-Pr)$_4$/2*i*-PrMgCl, and the following rearrangement of the resulting α-allenyl alcohols **4** with NBS.

Insertion of a carbon atom into a carbon–carbon bond is of interest as a versatile synthetic means for chain elongations at an internal position or ring expansions of cyclic compounds, thereby allowing for unique transformations of the molecular framework, but it is relatively difficult compared to chain extensions at the terminal positions.[1] Efforts have been devoted to realize such transformation and many methylene insertion reactions (homologation) and related reactions have been developed, which involve α-diazo insertions,[2] reactions with β-oxido carbenoids,[3] (semi)-pinacol-type rearrangements,[4] ring expansions through radical processes[5] and other reactions.[6] Herein disclosed is a formal two-step allylic carbon insertion reaction between ketone carbonyl and α carbons, providing α-vinyl ketones with an α-quaternary carbon (Scheme 1).

The present two-step reaction is outlined in Scheme 2, which involves a selective allenyl addition reaction to cyclic and acyclic ketones **1** followed by a rearrangement reaction of the resulting tertiary α-allenyl alcohols **4** with electrophilic reagents (X^+). The π-donative nature of the allenyl moiety[7] in **4** is desirable for the generation of a carbocation intermediate in the pinacol-type rearrangement of **4** to **2**, as exemplified by the related rearrangement of acyclic secondary α-allenyl alcohols with electrophilic reagents to α-vinyl aldehydes having an α-quaternary carbon developed by



Scheme 1. Conceptual scheme of allylic carbon insertion to ketones.



Scheme 2. Plan for two-step conversion of ketones **1**–**2** by allenylation and rearrangement (Z: leaving group).

Ma and co-workers.[8] In addition, Pd-catalyzed rearrangement/ring expansion reaction of 1-(1,2-dienyl)cyclobutanols (1-allenylcyclobutanols) have been reported,[9] where the allenyl π-coordinated Pd was proposed as an initial intermediate. In order to selectively allenylate the ketones, we used allenyl/propargyl titanium reagents derived from propargyl compounds **3** (*Z* = leaving group) and a divalent titanium reagent, Ti(O-*i*-Pr)$_4$/2*i*-PrMgCl.[10] Readily available propargyl alcohol derivatives **3** can be used as the allenylating agent and can give nearly complete selectivity of α-allenyl alcohols with high yields.[11]

According to the reaction sequence shown in Scheme 2, we carried out this two-step reaction on a variety of cyclic ketones **1** with propargyl substrates **3** and *N*-bromosuccinimide (NBS) as an electrophilic reagent. The results are summarized in Table 1, where the crude mixture of an allenyl alcohol **4** derived from **1** and **3** was used directly for the next rearrangement reaction and, therefore, the yields listed are the overall yields of these two steps. The ^{1}H NMR analysis of the crude **4** showed exclusive formation of an allenyl alcohol **4**, where the corresponding homopropargylic alcohol was not detected. In all cases, this two-step reaction provided

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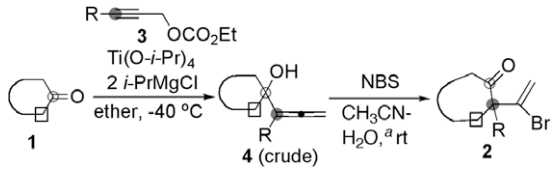
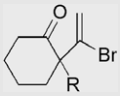
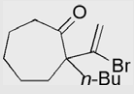
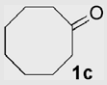
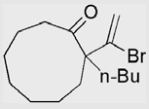
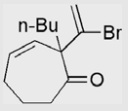
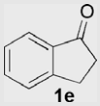
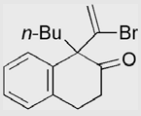
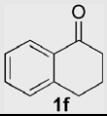
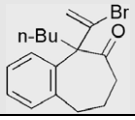
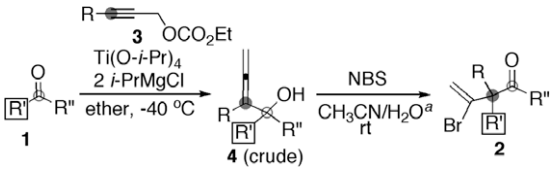
Table 1
Ring expansion reaction of cyclic ketones[a]

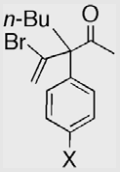
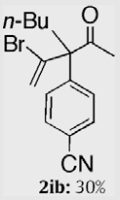
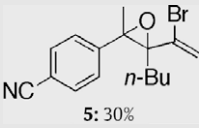
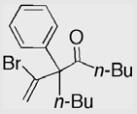
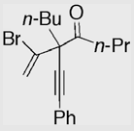
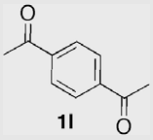
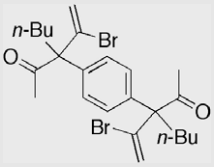


Run	1	3[b]	Product 2	Yield[c]
1		**3a** (R = Me)		**2aa**: R = Me, 38%
2		**3b** (R = *n*-Bu)		**2ab**: R = *n*-Bu, 66%
3		**3c** (R = Ph)		**2ac**: R = Ph, 59%
4		**3b**		**2bb** 79% (58%)[d] (23%)[e] (trace)[f]
5		**3b**		**2cb:** 40%
6		**3b**		**2db**: 70%
7		**3b**		**2eb**: 57%
8		**3b**		**2fb**: 47%

[a] $CH_3CN:H_2O$ = 15:1 (v/v).
[b] For runs 1–6, 1.3 equiv of **1** and 1.0 equiv of **3** were used. For runs 7 and 8, 1.0 equiv of **1** and 1.3 equiv of **3** were used.
[c] Isolated yield.
[d] The reaction with NBS in dry CH_3CN.
[e] The reaction with NBS in dry CH_2Cl_2.
[f] The reaction with NBS in DMF.

Table 2
Quaternary carbon insertion to acyclic ketones[a]



Run	1	3[b]	Product 2	Yield[c]
1	**1g** (R′ = Ph, R″ = Me)	**3b**		**2hb** (X = H): 70%
2	**1h** (R′ = ρ-$MeOC_6H_4$, R″ = Me)	**3b**		**2gb** (X = OMe): 85%
3	**1i** (R′ = ρ-NC-C_6H_4, R″ = Me) **1i**	**3b**	 **2ib:** 30%	 **5:** 30%
4	**1j** (R′ = R″ = *n*-Bu)	**3c**		**2jc**: 31%
5	**1k** (R′ = –C≡CPh, R″ = *n*-Pr)	**3b**		**2kb**: 50%
6[d]		**3b**		**2lb**: 25%[e]

[a] $CH_3CN:H_2O$ = 15:1 (v/v).
[b] For run 5, 1.3 equiv of **1** and 1.0 equiv of **3** were used. For runs 1–4 and 6, 1.0 equiv of **1** and 1.3 equiv of **3** were used.
[c] Isolated yield.
[d] 1.0 equiv of **1l** and 2.6 equiv of **3** were used.
[e] 2.6 equiv of NBS was used.

the corresponding rearrangement (ring expansion) product in moderate to good yield.

The results of a rearrangement reaction in several different solvent(s), shown in run 4 of Table 1, revealed that the reaction proceeded in CH_3CN or CH_2Cl_2. Among them, wet CH_3CN ($CH_3CN:H_2O$ = ~15:1, v/v) gave better results, similar to the results reported for the rearrangement of acyclic secondary allenyl alcohols by Ma and co-workers.[8] As a substituent R in the substrate propargyl carbonates, aliphatic and aromatic groups could be utilized (runs 1–3). The rearrangement reaction of the allenyl alcohols derived from unsymmetrical ketones **1d–f** proceeded regioselectively with cleavage of the sp^2-carbon-carbonyl carbon bond to provide the corresponding non-conjugated ketones **2db**, **2eb** and **2fb**, respectively (runs 6–8).

The molecules obtained by the present two-step process shown in Tables 1 and 2 have keto and vinyl bromide moieties useful for further transformation.[8] For example, Pd-catalyzed Sonogashira[12] coupling (phenylacetylene, 5 mol % of $Cl_2Pd(PPh_3)_2$, 15 mol % of CuI, piperidine, THF, rt) and Suzuki–Miyaura[13] coupling (styrene, 9-BBN, THF then K_3PO_4, 5 mol % of Cl_2Pd(dppf), THF, 70 °C) of **2ab** proceeded smoothly with alkyne and organoborane counterparts to yield the corresponding products **6** and **7**, respectively, in high yields (Fig. 1) [dppf: 1,1′-bis(diphenylphosphino)ferrocene]. Treatment of **2ab** with *n*-BuZnI in the presence of Cl_2Pd(dppf) catalyst reduced alkenyl bromide to afford **8** having a vinyl group at the α-position.

Next, we discuss on an extension of the present two-step transformation to reactions with acyclic ketones. The results are shown in Table 2, where the yields listed are the overall yields of these two steps. In all cases, the allenylation of the ketones was nearly quantitative and had exclusive regioselectivity. Ma and co-workers have shown an example of α-quaternary ketone formation from acyclic tertiary 2,3-allenol **4** (R = Et, R′ = Ph, R″ = Me), derived from acetophenone by In-mediated allenylation with 1-bromo-2-pentyne (30% yield), giving the corresponding **2** in 83% yield by the reaction with Br_2.[8b] Similarly, the reaction of α-allenyl alcohols **4hb** and **4gb**, prepared from acetophenone (**1g**) and its derivatives

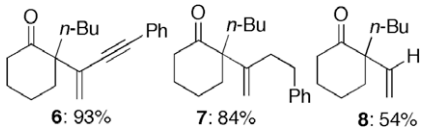
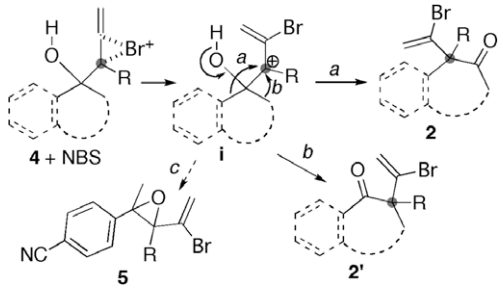


Figure 1. Derivatization products from **2ab**.



Scheme 3. Proposed reaction mechanism.

1 h by the reaction with **3b** and a divalent titanium, with NBS proceeded with a 1,2-shift of the aryl moiety to produce the corresponding non-conjugated ketones **2hb** and **2bg** in 70% and 85% overall yields, respectively (runs 1–2). However, the reaction starting from **1i** having an electron-withdrawing group (CN) at the 4 position yielded an equal amount of the rearrangement product **2ib** and the epoxide **5** (run 3). Alkyl group migration in the α-allenyl alcohol derived from aliphatic ketone **1j** was possible to produce the corresponding rearrangement product **2jc**, albeit low yield (run 4). Treatment of the allenyl intermediate derived from ynone **1k** with NBS rearranged an alkynyl group selectively (run 5). As exemplified in run 6, a tandem reaction starting from diketone such as **1l** was possible, although the reaction was not optimized.

As illustrated in Scheme 3, it may be proposed that the rearrangement reaction proceeds through a carbocation intermediate **i** generated by the reaction of allenyl alcohol **4** with NBS. When an unsymmetrical ketone was utilized as a starting material, the carbon migration from **i** occurred predominantly with an sp^2 or sp carbon (path *a*) to provide non-conjugated ketone product **2** selectively. This trend is similar to that observed in other cationic 1,2-migrations that proceed by pinacol-type rearrangement.[1,4] When a rearrangement is slow, **i** competitively undergoes epoxide formation (path *c*) as seen in the reaction of **1i** (run 3 in Table 2).

In summary, we have demonstrated that the two-step reaction involving a highly regioselective allenylation of ketones by utilizing allenyl/propargyl-titanium reagents, derived from propargyl carbonates and a Ti(O-*i*-Pr)$_4$/2*i*-PrMgCl reagent, followed by rearrangement by treatment with NBS of the resulting tertiary α-allenyl alcohols provides a facile means for ring-expansion or one-carbon elongation of ketones by a formal allylic carbon insertion between carbonyl and α carbons.[14,15] Although the yield obtained was not necessarily high, the method might be synthetically useful because of the production of highly functionalized α-quaternary ketones which are otherwise difficult to prepare.[16] In addition, optimization of the reaction conditions for an individual substrate may improve the yield. Application of the method to synthesis of biologically active compounds is underway.

Acknowledgement

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14. *Typical procedure*: To a mixture of **3b** (1.0 mmol) and Ti(O-*i*-Pr)$_4$ (1.3 mmol) in ether (10 mL) was added *i*-PrMgCl (2.6 mmol, 1.3 M in ether, 2.0 mL) at −40 °C. After being stirred for 1.5 h at this temperature, cyclohexanone (**1b**) (1.3 mmol) was added and then the mixture was gradually warmed to room temperature over 2 h. After addition of saturated aqueous $NaHCO_3$ (0.3 mL), NaF (1 g) and Celite (1 g), the mixture was filtered through a pad of Celite with ether. The filtrate was concentrated in vacuo to give a crude residue, which was directly used for the next reaction. To a solution of the residue in CH_3CN/H_2O (~15:1, v/v, 6 mL) was added portionwise NBS (1.3 mmol) at ambient temperature. After being stirred for 2–4 h, saturated aqueous $NaHCO_3$ (10 mL) was added. The mixture was extracted with ether, dried over $MgSO_4$ and concentrated in vacuo. The resulting residue was subjected to column chromatography on silica gel to afford **2bb** (0.79 mmol) in 79% yield.
15. *^{1}H NMR data of* **2** *(500 MHz, $CDCl_3$) δ*: *Compound* **2aa**; 5.71 (d, *J* = 2.5 Hz, 1H), 5.66 (d, *J* = 2.5 Hz, 1H), 2.62–2.71 (m, 1H), 2.34–2.45 (m, 2H), 1.99–2.08 (m, 1H), 1.42–1.90 (m, 4H), 1.25 (s, 3H). *Compound* **2ab**; 5.81 (d, *J* = 2.0 Hz, 1H), 5.70 (d, *J* = 2.0 Hz, 1H), 2.65 (dt, *J* = 5.5, 13.0 Hz, 1H), 2.31–2.42 (m, 2H), 1.99–2.07 (m, 1H), 1.05–1.91 (m, 10H), 0.90 (t, *J* = 7.3 Hz, 3H). *Compound* **2ac**; 7.25–7.42 (m, 5H), 5.74 (d, *J* = 2.5 Hz, 1H), 5.18 (d, *J* = 2.5 Hz, 1H), 2.70 (ddd, *J* = 4.0, 11.0, 14.5 Hz, 1H), 2.51–2.59 (m, 2H), 2.40 (dt, *J* = 15.0, 8.0 Hz, 1H), 1.70–1.92 (m, 4H). *Compound* **2bb**; 5.74 (d, *J* = 2.3 Hz, 1H), 5.70 (d, *J* = 2.3 Hz, 1H), 2.72 (dt, *J* = 2.9, 11.5 Hz, 1H), 2.38 (ddd, *J* = 2.9, 6.9, 11.5 Hz, 1H), 1.87–1.96 (m, 3H), 1.07–1.96 (m, 11H), 0.90 (t, *J* = 7.5 Hz, 3H). *Compound* **2cb**; 5.88 (d, *J* = 2.0 Hz, 1H), 5.81 (d, *J* = 2.0 Hz, 1H), 2.96–3.03 (m, 1H), 2.14 (dt, *J* = 14.9, 4.6 Hz, 1H), 0.97–2.05 (m, 18H), 0.91 (t, *J* = 7.0 Hz, 3H). *Compound* **2db**; 6.01 (d, *J* = 2.0 Hz, 1H), 5.97–6.03 (m, 1H), 5.79 (d, *J* = 2.0 Hz, 1H), 5.53 (dt, *J* = 12.0, 1.8 Hz, 1H),

3.08 (ddd, *J* = 5.2, 8.1, 14.4 Hz, 1H), 2.49 (dt, *J* = 4.6, 9.2 Hz, 1H), 2.27–2.37 (m, 1H), 2.06–2.17 (m, 2H), 1.88 (ddd, *J* = 5.7, 12.0, 14.4 Hz, 1H), 1.02–1.81 (m, 6H), 0.92 (t, *J* = 7.2 Hz, 3H). *Compound* **2eb**; 7.18–7.31 (m, 4H), 5.96 (d, *J* = 2.3 Hz, 1H), 5.79 (d, *J* = 2.3 Hz, 1H), 3.03–3.20 (m, 2H), 2.91 (ddd, *J* = 6.3, 9.8, 16.1 Hz, 1H), 2.64–2.72 (m, 1H), 2.37 (dt, *J* = 4.6, 13.2 Hz, 1H), 1.85 (dt, *J* = 4.1, 12.6 Hz, 1H), 0.85–1.40 (m, 4H), 0.78 (t, *J* = 7.5 Hz, 3H). *Compound* **2fb**; 7.05–7.33 (m, 4H), 5.98 (d, *J* = 2.3 Hz, 1H), 5.89 (d, *J* = 2.3 Hz, 1H), 2.97 (dt, *J* = 10.9, 8.6 Hz, 1H), 2.89 (dt, *J* = 14.3, 6.4 Hz, 1H), 2.76 (dt, *J* = 14.4, 8.0 Hz, 1H), 2.46 (ddd, *J* = 5.2, 6.9, 12.0 Hz, 1H), 2.25 (ddd, *J* = 4.0, 12.6, 14.3 Hz, 1H), 2.16 (ddd, *J* = 4.6, 12.0, 14.3 Hz, 1H), 1.97–2.07 (m, 2H), 0.87–1.34 (m, 4H), 0.84 (t, *J* = 7.2 Hz, 3H). *Compound* **2gb**; 7.28–7.42 (m, 5H), 6.01 (d, *J* = 2.4 Hz, 1H), 5.92 (d, *J* = 2.4 Hz, 1H), 2.18–2.26 (m, 2H), 2.10 (s, 3H), 1.14–1.45 (m, 4H), 0.93 (t, *J* = 7.3 Hz, 3H). *Compound* **2hb**; 7.29 (d, *J* = 6.9 Hz, 2H), 6.88 (d, *J* = 6.9 Hz, 2H), 6.04 (d, *J* = 2.3 Hz, 1H), 5.90(d, *J* = 2.3 Hz, 1H), 3.81 (s, 3H), 2.15–2.21 (m, 2H), 2.09 (s, 3H), 1.35–1.44 (m, 2H), 1.13–1.33 (m, 2H), 0.93 (t, *J* = 7.2 Hz, 3H). *Compound* **2ib**; 7.65 (d, *J* = 8.6 Hz, 2H), 7.54 (d, *J* = 8.6 Hz, 2H), 6.15 (d, *J* = 2.3 Hz, 1H), 6.00 (d, *J* = 2.3 Hz, 1H), 2.16–2.22 (m, 2H), 2.17 (s, 3H), 1.31–1.42 (m, 2H), 1.08–1.17 (m, 2H), 0.90 (t, *J* = 7.5 Hz, 3H). *Compound* **2jc**; 7.26–7.39 (m, 5H), 6.07 (d, *J* = 2.3 Hz, 1H), 5.91 (d, *J* = 2.3 Hz, 1H), 2.38 (t, *J* = 7.5 Hz, 2H), 2.18–2.24 (m, 2H), 1.05–1.80 (m, 8H), 0.93 (t, *J* = 7.0 Hz, 3H), 0.79 (t, *J* = 7.0 Hz, 3H). *Compound* **2kb**; 7.42–7.45 (m, 2H), 7.31–7.37 (m, 3H), 6.52 (d, *J* = 1.5 Hz, 1H), 5.87 (d, *J* = 1.5 Hz, 1H), 2.90 (ddd, *J* = 7.0, 8.0, 18.0 Hz, 1H), 2.64 (ddd, *J* = 6.5, 7.5, 18.0 Hz, 1H), 1.91–2.05 (m, 2H), 1.60–1.73 (m, 2H), 1.22–1.47 (m, 4H), 0.94 (t, *J* = 7.5 Hz, 3H), 0.93 (t, *J* = 7.5 Hz, 3H). *Compound* **2lb**; 7.37 (s, 4H), 6.04 (d, *J* = 2.5 Hz, 2H), 5.92 (d, *J* = 2.5 Hz, 2H), 2.14–2.25 (m, 4H), 2.12 (s, 6H), 1.34–1.44 (m, 4H), 1.11–1.32 (m, 4H), 0.92 (t, *J* = 7.0 Hz, 6H). ^{1}H *NMR data of* ***5*** *(*500 MHz, *$CDCl_3$) d* 7.66 (d, *J* = 8.0 Hz, 2H), 7.43 (d, *J* = 8.0 Hz, 2H), 5.99 (d, *J* = 1.2 Hz, 1H), 5.79 (d, *J* = 1.2. Hz, 1H), 1.90 (ddd, *J* = 6.3, 9.2, 14.9 Hz, 1H), 1.60 (s, 3H), 1.10–1.37 (m, 4H), 0.80 (t, *J* = 7.4 Hz, 3H), 0.62 (ddd, *J* = 6.9, 9.2, 14.9 Hz, 1H).

16. Regarding production of acyclic α-quaternary α-vinyl carbonyl compounds, preparation of 2,2-dialkylbut-3-enoates from 4-chloro-2-alkylbut-2-enoates by the Lewis base-promoted S_N2' reaction with alkyl magnesium or zinc reagents has recently been reported: (a) Lee, Y.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2006**, *128*, 15604; (b) Kobayashi, K.; Ueno, M.; Naka, H.; Kondo, Y. *Chem. Commun.* **2008**, 3780.