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ISOMERIZATION OF PROPARGYLIC ALCOHOLS CATALYZED BY AN IRIDIUM COMPLEX

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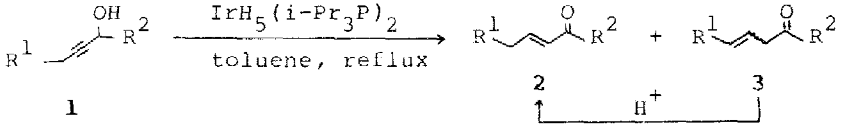
Abstract: α,β-Enones were synthesized by the isomerization of propargylic alcohols catalyzed by an iridium pentahydride complex.

α,β-Enones are well known as important intermediates in organic synthesis, especially in the synthesis of natural products.[1] A series of new approaches has been reported for the preparation of this class of compounds including the Horner-Emmons-Wadsworth reaction, elimination and condensation reactions.[1,2] Many of them, however, follow lengthy procedures and need starting materials not easy to prepare. The synthesis of α,β-enones using propargylic alcohols as starting materials should be also beneficial due to the ready accessibility and elaboration of the latter. Indeed, the synthetic route of α,β-enones from propargylic alcohols by reduction with lithium aluminium hydride followed by oxidation with chromic anhydride has been proved of value.[3] The transformation of trimethylsilylated propargyl alcohols to α,β-enones using butyl lithium has been reported.[4] On the other hand, the transition metal complexes catalyzed double bond migration of allylic alcohols to ketones or aldehydes has been widely studied in recent years,[5] however, a successful example of isomerization of propargylic alcohols to α,β-enones catalyzed by transition metal complexes remains elusive.[6] The failure to obtain the thermodynamically prefered α,β-enones seems to result from the large kinetic energy barrier between 2-yn-1-ols and α,β-enones. Recently, we reported that the metal complexes with alkyl phosphines such as $IrH_5(i\text{-}Pr_3P)_2$ are more effective catalysts for the isomerization of α,β-ynones and 2-ynoic esters than those with aryl phosphines,[7] which stimulates us to apply $IrH_5(i\text{-}Pr_3P)_2$ as a catalyst to the isomerization of propargylic alcohols. Herein, we wish to report our recent results of this reaction.



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The isomerization reaction could easily be carried out by heating propargylic alcohols (1, 5 mmol) with $IrH_5(i\text{-}Pr_3P)_2$ (0.05 mmol) in toluene at reflux for about 24 h. After cooling, the products were separated from the catalyst and a small amount of polymers by distillation under reduced pressure. ^1H NMR spectra showed the formation of two isomers, (E)-α,β-enones (**2**)[8] and β,γ-enones (**3**), in the ratio of about 4 to 1. The results of the isomerization for various propargylic alcohols are shown in the Table. This reaction was not applicable to the propargylic alcohol with a terminal triple bond (e.g. 1-octyn-3-ol) or with bulky substituents (e.g. 1-trimethylsilyl-1-octyn-3-ol). Lengthening the reflux time could make the yield lower (compare entries 2 and 3).

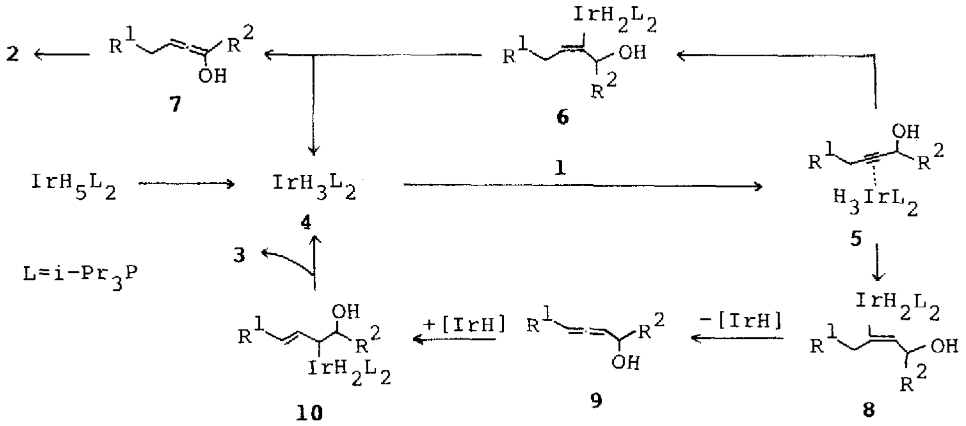
Table. Isomerization of propargylic alcohols catalyzed by $IrH_5(i\text{-}Pr_3P)_2$

Entry	Ynol(**1**) R^1	R^2	Time (h)	Yield[a] (%)	Product[b] **2** : **3**[c]
1	n-C_6H_{13}	CH_3	28	90	81:19
2	n-C_3H_7	C_2H_5	28	91	81:19
3	n-C_3H_7	C_2H_5	40	70	80:20
4	n-C_4H_9	CH_3	24	92	78:22
5	n-C_3H_7	CH_3	24	90	76:24
6	i-C_3H_7	CH_3	24	88	83:17
7	C_2H_5	C_2H_5	28	87	80:20
8	n-C_3H_7	C_6H_5	30	85	85:15

a: Isolated yield.
b: All products have been fully characterized spectrally.
c: Determined by ^1H NMR spectra.

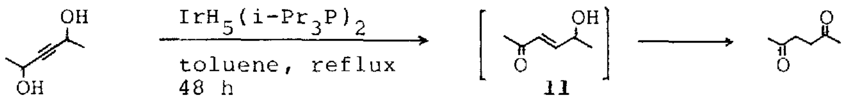
Although there has hardly been reported the isomerization of secondary propargylic alcohols to α,β-enones, the ruthenium complexes catalyzed isomerization of 2-butyn-1,4-diol to butyrolactone[9] and the reaction of the former with aliphatic primary amines to form pyrroles[10] have been reported. The α,β-enal was proposed to be the possible intermediate of these reactions but it was neither isolated nor determined. In addition, the isomerization of 4-hydroxy-2-alkynoates and 4-hydroxy-2-alkyn-1-ones to corresponding enones was achieved by using a base as the catalyst,[11] but the carboxyl or carbonyl group is necessary here for the isomerization. Therefore, to the best of our knowledge, our result is the first example of isomerization of propargylic alcohols to α,β-enones catalyzed by a transition metal complex.

In the present reaction, no evidence was found for the formation of α,β-ynones and allylic alcohols, implying that the reaction may proceed through a process of intramolecular hydrogen transfer reaction similar to the olefinic alcohols.[12] The possible reaction pathway may be depicted as follows. Complex $IrH_5(i\text{-}Pr_3P)_2$ will coordinate with the triple bond first, then the insertion of triple bond to Ir-H bond may occur to form **6** and **8**. The β-hydrogen elimination of **6** may give **7** which will isomerize to the α,β-enones **2** and regenerate **4** to complete the catalytic cycle. While the β-hydrogen elimination of **8** may produce allenic alcohols (**9**), to which the addition and elimination of iridium hydride will gererate **4** and the β,γ-enones **3**.



It is surprising that β,γ-enones could not further rearrange to α,β-enones under the present reaction conditions. Pure (E)-α,β-enones could be obtained by treating the reaction products with acids.[13] For example, after refluxing a mixture of (4E)-nonen-3-one and 5-nonen-3-one (4 mmol) with concentrated sulfuric acid (0.5 mmol) in formic acid (3 ml) for 0.5 h, (4E)-nonen-3-one was isolated as the only product in 58% yield. Thus, this reaction may provide an useful method for the preparation of α,β-enones from propargylic alcohols.

The significance of present method is further demonstrated by the isomerization of 3-hexyn-2,5-diol. Under the catalysis of 2 mol% of $IrH_5(i\text{-}Pr_3P)_2$, 3-hexyn-2,5-diol could rearrange to 2,5-hexadione in 70% yield. In this case, 5-hydroxy-3-hexen-2-one (**11**) may initially be formed, then through an intramolecular hydrogen transfer process of the formed allylic alcohol **11**,[12] 2,5-hexadione was obtained as the main product. Considering that the yndiols can be prepared easily by the reaction of



acetylenic dicarbanion with aldehydes, this procedure may offer a simple and convenient method for preparing 1,4-diketones.[14]

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