Stereoselective isomerization of acetylenic derivatives as a new methodology in organic synthesis

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Abstract--The transition metal catalyzed isomerization reactions of acetylenic derivatives were studied. ($\underline{E}$,$\underline{E}$)-Conjugated dienones, dienoic esters and dienoic amides were synthesized from corresponding α,β-ynones, 2-ynoic esters and 2-ynoic amides, respectively. 2-Ynols were first isomerized to the corresponding 2-enones or 2-enals. The reactions can be accomplished simply, in high yield, and stereoselectively. It is proposed that allenic compounds are initially formed as the main intermediates and then isomerized further to the products. A convenient and potential useful methodology is provided for the preparation of important intermediates in the synthesis of natural products.

INTRODUCTION

The practical and mechanistic aspects of double bond migration have been attracted much attention in recent years (ref. 1, 2). The highly enantioselective isomerization of prochiral allylamine to optically active enamine by a chiral Rh catalyst has been used as the key step in the industrial synthesis of (-)-menthol (ref. 3). On the other hand, alkynes exhibit a rich coordination chemistry and are increasingly recognized as valuable and versatile reagents for organometallics and organic synthesis (ref. 4). In recent years, it was demonstrated that transition metal complexes mediate the irreversible isomerization of substituted acetylenes to allenes (ref. 5, 6):

$$RCH_2C\equiv CE \xrightarrow{\quad\quad} RCH=C=CHE$$
$$\quad\quad MnL_3 \quad\quad\quad\quad\quad MnL_3$$
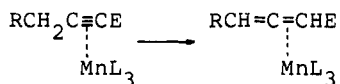
Another example was observed in the unusual reaction of phenyl propene with trans-[ReCl(N$_2$)(dppe)$_2$] to give the 2-phenylallene complex; it was produced by a 1,3-hydrogen migration of the parent alkynes (ref. 6, 7). However, the catalytic chemistry related to this field has not thus far been extensively explored. In this paper, we wish to review several novel transition metal catalyzed reactions based on the isomerization of acetylenic derivatives to prepare the useful intermediates in organic synthesis.

## ISOMERIZATION OF ACETYLENIC DERIVATIVES TO SUBSTITUTED CONJUGATED DIENES

Transition metal catalyzed isomerization of α,β-ynones to α,β-γ,δ-dienones

($\underline{E}$,$\underline{E}$)-α,β-γ,δ-Dienones are well known as common flavor constituents in tea, tobacco and foods. In addition, they often serve as useful intermediates in the synthesis of natural products. Moro-oka reported the isomerization of acetylenic ethers to dienol ethers under the catalysis of ruthenium hydride complex, but the reaction is not stereoselective (ref. 8). In the course of our study on the transition metal hydride complexes catalyzed organic synthesis (ref. 9), it was found that a novel stereoselective isomerization of α,β-ynones to ($\underline{E}$,$\underline{E}$)-dienones could be catalyzed by RuH$_2$(Ph$_3$P)$_4$ (ref. 10). Two other groups also reported the isomerization of ynones to dienones under the catalysis of transition metal complexes (ref. 11). In our communication,

(ref. 10), it was described that a higher reaction temperature is necessary
when R^1 in compound 1 is an alkyl group. On further study of this reaction,
using $IrH_5(\underline{i}\text{-}Pr_3P)_2$ (3), $RuH_2(\underline{n}\text{-}Bu_3P)_4$ and $RuCl_2(Ph_3P)_3$ and adding excess
phosphine ligand as catalyst instead of $RuH_2(Ph_3P)_4$ were found to give prod-
ucts in higher yield at much mild conditions (ref. 12).

R^1: CH_3, C_2H_5, C_6H_5

R^2: CH_3, C_2H_5, $\underline{n}\text{-}C_3H_7$, $\underline{n}\text{-}C_5H_{11}$

R^3: H, CH_3
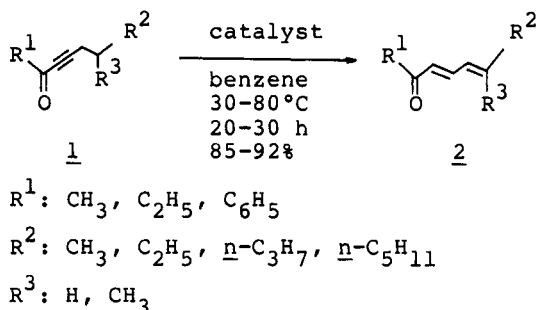
No isomerization of 1-phenyl-2-butyn-1-one (4) and 3-pentyn-2-one (5) occur-
red under the catalysis of 3 at 60-80°C, implying that an α,β-ynone with $C_\delta H$
is necessary for this reaction in order to convert to the thermodynamically
more stable dienone. This reaction was also not applicable to an alkyne
without a polar substituent, for example, 1-phenyl-1-hepten-3-yne (6) did
not give isomerization product at 80°C under the catalysis of 3 indicating
that the polarization of the triple bond and the conjugation of the carbonyl
group in the products do play an important role in this reaction.

PhCOC≡CCH$_3$ CH$_3$COC≡CCH$_3$ PhCH=CHC≡CCH$_2$CH$_2$CH$_3$

4   5   6
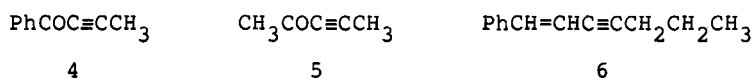
It was suggested that the possible intermediate for this reaction may be α,
β-β,γ-dienone (ref. 8, 10, 11). Although the catalyzed isomerization of α,β-
ynones to α,β-β,γ-dienone has hardly been reported, there have appeared many
examples about the base catalyzed isomerization of β,γ-ynones to α,β-β,γ-
dienones (ref. 13). To investigate the reaction mechanism of this reaction,
3,4-nonadien-2-one (8) was prepared from 4-nonyn-2-one (7) according to the
known method (ref. 14). The fact that all 7, 8 and 9 could isomerize to
(3E,5E)-nonandien-2-one (10) by the catalysis of 3 in benzene at 60°C in
high yield supports the suggested mechanism. Both 7 and 9 may isomerize
first under the catalysis of 3 to the same intermediate 8 which is then
isomerized further to 10 (Scheme 1).

Scheme 1
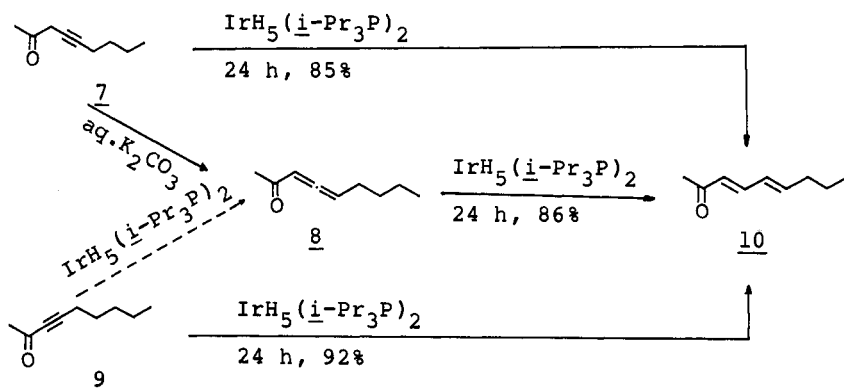
Equimolar amount of 3 and 1-phenyl-2-hexyn-1-one (11) reacted at 60°C in
benzene to give 2,3,4,5-tetrahapto-[1-phenyl-(2E,4E)-hexadien-1-one]mono-
hydridobis(triisopropylphosphine)iridium complex (12) as determined by IR,
^{1}H NMR, ^{13}C NMR and mass spectra with comparison to the reported data of
the analogous complexes (ref. 15). The same complex was also obtained and
characterized by ^{1}H NMR from the reaction of 3 and 1-phenyl-(2E,4E)-hexa-
dien-1-one (13) (Scheme 2). The ^{1}H NMR spectra showed J_{23}=J_{34}=J_{45}=8 Hz,

indicating the syn,syn-geometry. Complex 12 could catalyze the isomerization of 11 to give 13 in high yield. These results showed that the η4-dienone metal complex might be regarded as the possible reaction intermediate.
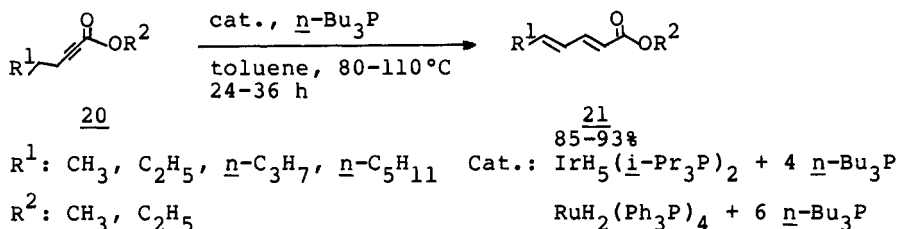
Scheme 2
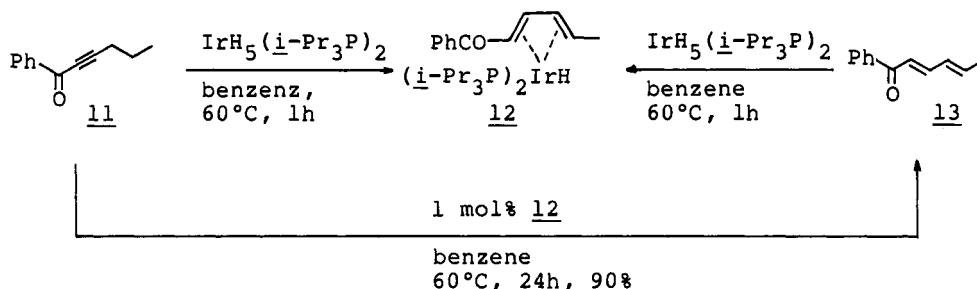
A plausible reaction mechanism with respect to iridium pentahydride complex 3 was shown in Scheme 3. Other transition metal complexes may be similar to this mechanism. The catalytically active species seems to be the coordinatively unsaturated complex [IrH] which will coordinate to the triple bond first to form 14. After addition and elimination of metal hydride (ref. 16), $\alpha,\beta-\beta,\gamma$-dienone (16) may be formed first, the metal hydride adds to 16 to produce the intermediate 17 (the more stable trans-isomer can be formed predominantly), and then syn-elimination of intermediate 17 occur in such a fashion that the terminal alkyl group adopts a trans orientation with respect to the vinyl group in order to minimize the steric interactions during the metal hydride elimination. Syn,syn-(dienone)monohydridobis(triisopropylphosphine)iridium (19) is formed. Finally, ynone replaces the dienone to form 2.

Scheme 3
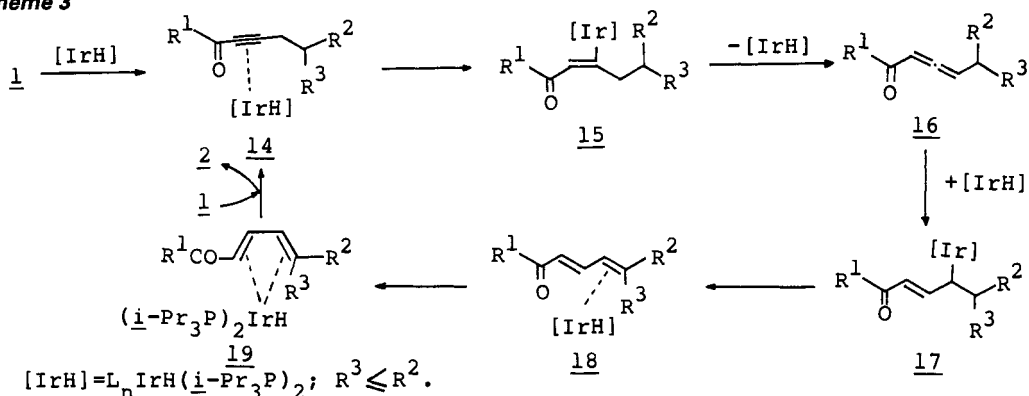
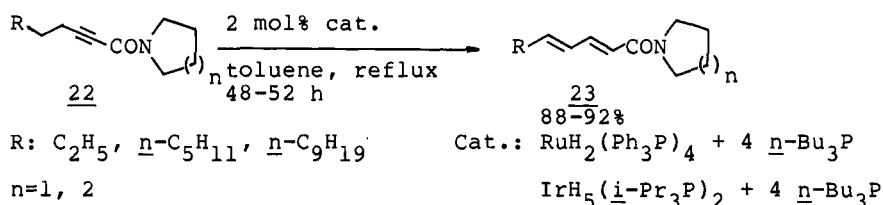## Isomerization of 2-ynoic esters to (2E,4E)-dienoic esters

(2E,4E)-Dienoic esters are valuable synthetic intermediates. Some of them such as (2E,4E)-decadienoic esters are also aromatic substances. We found that the iridium or ruthenium complex (in the presence of excess trialkylphosphine) catalyzed isomerization of 2-ynoic esters provides a synthetic method for the preparation of (2E,4E)-dienoic esters. The reaction is highly stereoselective as shown by ^{1}H NMR. Complex 3 has higher catalytic activity than RuH$_2$(Ph$_3$P)$_4$ (ref. 17):

R^1: CH$_3$, C$_2$H$_5$, n-C$_3$H$_7$, n-C$_5$H$_{11}$ Cat.: IrH$_5$(i-Pr$_3$P)$_2$ + 4 n-Bu$_3$P

R^2: CH$_3$, C$_2$H$_5$ RuH$_2$(Ph$_3$P)$_4$ + 6 n-Bu$_3$P

To the best of our knowledge, although there have appeared many methods
involving the Wittig rection and the elimination reaction for preparing
(2E,4E)-dienoic esters, only a few of them gave exclusively (2E,4E)-
dieoic esters. Therefore, our results may provide an convenient and useful
method for the highly stereoselective synthesis of (2E,4E)-dienoic esters.

### Isomerization of 2-ynoic amides to (2E,4E)-dienoic amides

Similarly, 2-ynoic amides could be isomerized to (2E,4E)-dienoic amides
under the catalysis of ruthenium or iridium complex with the addition of
excess trialkylphosphine. This isomerization of 2-ynoic amides requires
higher temperature and longer time than that of the 2-ynoic esters (ref.
18).

R: C_2H_5, n-C_5H_{11}, n-C_9H_{19} Cat.: $RuH_2(Ph_3P)_4$ + 4 n-Bu_3P

n=1, 2 $IrH_5(i$-$Pr_3P)_2$ + 4 n-Bu_3P

The highly stereoselective synthesis of (E,E)-α,β-γ,δ-dienones, (2E,4E)-
dienoic esters and (2E,4E)-dienoic amides via the isomerization of corres-
ponding acetylenic derivatives effected by transition metal complexes can
represent a useful synthetic approach due to the easy accessibility and
elaboration of substituted alkynes.

From above results, it is obvious that in order to carry out the isomeriza-
tion of the triple bond, a carbonyl group is necessary at the α-position of
the triple bond, and excess phosphine is important for this reaction. In
most cases, aliphatic phosphines are more active than the aromatic phos-
phines. The addition of excess phosphine may increase the electron density
of the transition metal and make the triple bond more active (ref. 4).

It was shown that the order of reactivity for the isomerization of the
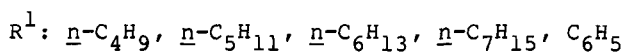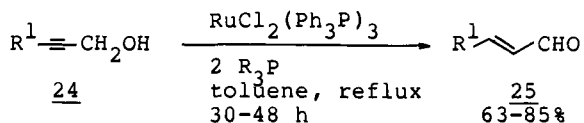substituted alkynes to substituted dienes is:

   R^1: Ph > alkyl > alkoxyl > amino group
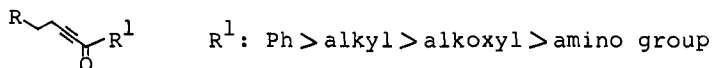
ISOMERIZATION OF PROPARGYLIC ALCOHOLS TO α,β-UNSATURATED CARBONYL COMPOUNDS

The conversion of 2-ynols to 2-enals or α,β-enones is still one of the
practical processes in the synthesis of natural products due to the easy
accessibility of ynols (ref. 19). The usual approach used consists of the
reduction with lithium aluminum hydride first followed by oxidation with a
suitable metal oxide, which needs multiple steps (ref. 19) and often leads
to considerable amount of environmentally hazardous wastes (ref. 20). This
conversion can be regarded as an isomerization process of the triple bond.
On the other hand, transition metal catalysts offer a mild approach for
hydrogen migrations and much attention has been directed toward the iso-
merization of olefinic alcohols. The transition metal complexes catalyzed
double bond migration of allylic alcohols to ketones or aldehydes has been
widely studied in recent years (ref. 1, 2). Many works related to the
intermolecular hydrogen transfer reactions between acetylenes and alcohols
have been reported, but it is quite surprising that 2-ynols have not been
employed as the starting materials for this synthetically useful isomeriza-
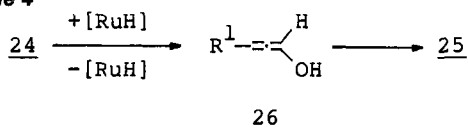tion reactions.

Isomerization of primary 2-ynols to 2-enals

Corey reported the isomerization of 2-octyl-1-ol to 2-octenal effected by
n-butyllithium (ref. 21), however, this procedure required the first conver-
sion of the 2-ynols to the ether derivatives and also provided a mixture of
2-octenal and the propargylic starting materials.

We found that 2-ynols could isomerize to (2E)-enals under the catalysis of
$RuCl_2(Ph_3P)_3$ + R_3P (ref. 22):

$$R^1-\!\!\equiv\!\!-CH_2OH \xrightarrow[\substack{2\ R_3P \\ \text{toluene, reflux} \\ 30-48\ h}]{RuCl_2(Ph_3P)_3} R^1\diagdown\!\!\diagup\!\!\diagdown CHO$$

$$\underline{24} \qquad\qquad\qquad\qquad \underline{25}$$
$$63-85\%$$

R^1: $\underline{n}\text{-}C_4H_9$, $\underline{n}\text{-}C_5H_{11}$, $\underline{n}\text{-}C_6H_{13}$, $\underline{n}\text{-}C_7H_{15}$, C_6H_5

In the absence of a ligand or using triphenylphosphine as the ligand, the reaction did not take place and triisopropylphosphine is a more effective ligand than tributylphosphine. It is also found that 2-ynols with an aryl group are less reactive than that with an alkyl group.
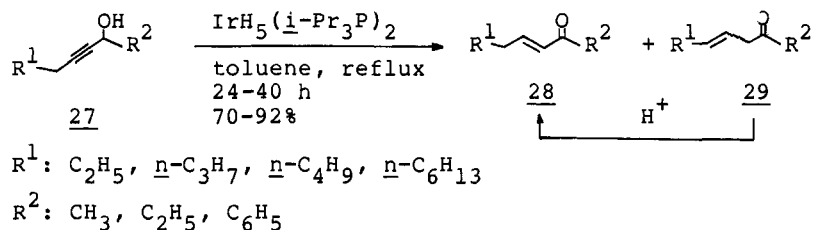
Scheme 4

$$\underline{24} \xrightarrow[-[RuH]]{+[RuH]} R^1-\!\!=\!\!\cdot\!\!\diagup_{OH}^{H} \longrightarrow \underline{25}$$

$$\underline{26}$$

The mechanism of this reaction may be similar to that of the isomerization of 2-ynones to dienones (ref. 10, 12). Ruthenium hydride species may be formed first from the reaction of propargylic alcohols and $RuCl_2(Ph_3P)_3$. After the addition and elimination of Ru-H, 1,2-dienol (26) was formed, which may further tautomerize to 25 (Scheme 4). This reaction is, to our knowledge, the first example of the isomerization of 2-ynols directly to the simple enals catalyzed by transition metal complexes.

Isomerization of secondary 2-ynols to α,β-enones

A number of intriguing methods have been deviced for the synthesis of α,β-enones, however, a successful example of isomerization of propargylic alcohols to α,β-enones catalyzed by transition metal complexes remains elusive.

$$R^1\diagdown\!\!\diagup^{OH}_{}\!\!\diagup R^2 \xrightarrow[\substack{\text{toluene, reflux} \\ 24-40\ h \\ 70-92\%}]{IrH_5(\underline{i}\text{-}Pr_3P)_2} R^1\diagdown\!\!\diagup\!\!\diagdown^{O}\!\!\diagup R^2 + R^1\diagdown\!\!\diagup\!\!\diagdown^{O}_{}R^2$$

$$\underline{27} \qquad\qquad\qquad\qquad \underline{28} \qquad\qquad \underline{29}$$
$$H^+$$

R^1: C_2H_5, $\underline{n}\text{-}C_3H_7$, $\underline{n}\text{-}C_4H_9$, $\underline{n}\text{-}C_6H_{13}$

R^2: CH_3, C_2H_5, C_6H_5

The isomerization reaction could easily be carried out by heating propargylic alcohols (27) with a catalytic amount of complex 3 in toluene at reflux for about 24 h. The products were shown to be two isomers, $(\underline{E})$-α,β-enones (28) and β,γ-enones (29) in the ratio of about 4 to 1 (ref. 23). This reaction was not applicable to the propargylic alcohol with a terminal triple bond (e.g. 1-octyn-3-ol) or with large substituents (e.g. 1-trimethylsilyl-1-octyn-3-ol). Lengthening the reflux time could make the yield lower.

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 (ref.9). The possible reaction pathway may be depicted as follows. Complex 3 will form 30 on heating and coordinate with the triple bond first, then the insertion of triple bond to Ir-H bond may occur to form 32 and 34. The β-hydrogen elimination of 32 may give 33 which will isomerize to the α,β-enones 28 and regenerate 30 to complete the catalytic cycle. While the β-hydrogen elimination of 34 may produce allenic alcohols (35), to which the addition and elimination of iridium hydride will gererate 30 and the β,γ-enones 29.

Pure $(\underline{E})$-α,β-enones could be obtained by treating the reaction products with acids. Thus, this reaction may provide an useful method for the preparation of α,β-enones from propargylic alcohols.

The significance of present reaction is further demonstrated by the isomerization of 3-hexyn-2,5-diol. Under the catalysis of 2 mol% of 3, 3-hexyn-2,5-diol could rearrange to 2,5-hexadione in 70% yield. In this case, 5-hydroxy-3-hexen-2-one (37) may be formed first, then through an intramolecular hydrogen transfer process of the formed allylic alcohol (37) (ref. 9), 2,5-

Scheme 5
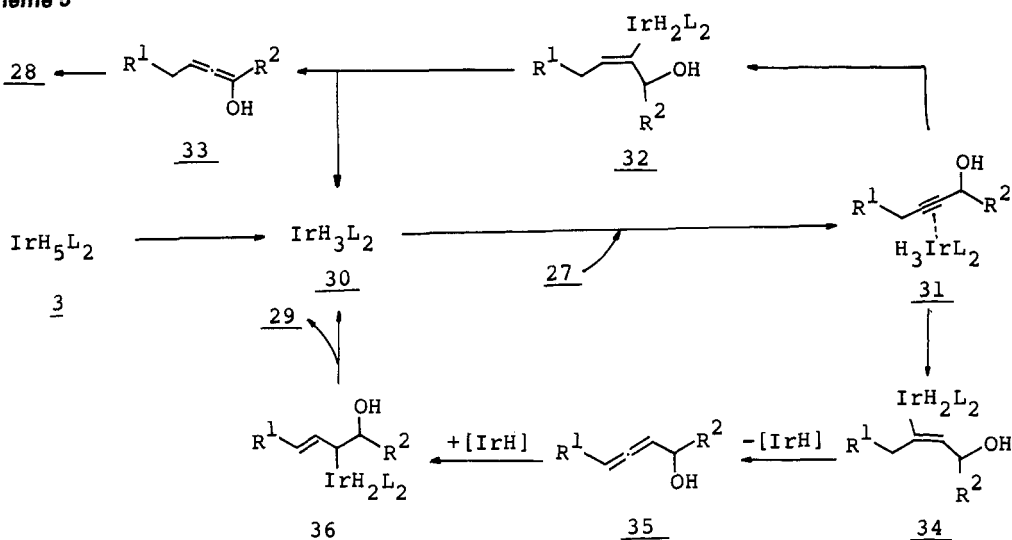
hexadione was obtained as the main product. Considering that the yndiols can be prepared easily by the reaction of acetylenic dicarbanion with aldehydes, this procedure may offer a simple and convenient method for preparing 1,4-diketones (ref. 24).
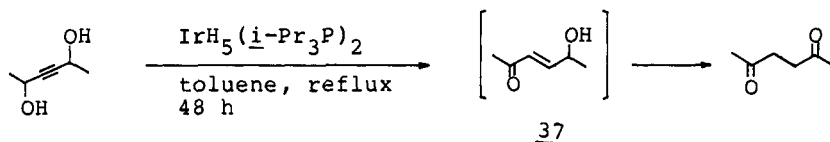
A NEW METHODOLOGY IN ORGANIC SYNTHESIS

As mentioned in the previous sections, (E,E)-conjugated dienones, dienoic esters, dienoic amides, α,β-enones and 2-enals has been synthesized by the isomerization of the corresponding acetylenic derivatives. In recent years, polyene ketones, polyene esters and polyene amides constitute a class of important compounds which occur widely in high plants. Such compounds are

R: CH_3 to $n-C_{11}H_{23}$
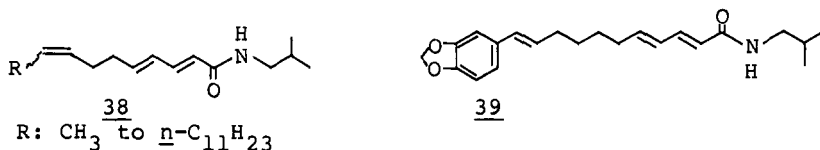
comparatively unstable and difficult to access, occurring only in small amount in plants (ref. 25, 26). Because of their importance as synthetic intermediates and the interesting insecticidal activity of polyene amide group (e.g., 38, 39), the development of methodology directed toward the synthesis of this class of compounds is an active area of research in organic synthesis. Crombie proposed compound 40 and 45 as the key inter-mediate for the synthesis of these natural occurring products (ref. 26). In addition, macrocyclic compounds with bactericidal and anticancer activity has been synthesized from 42 or 44 (ref. 27).


41: R=THP, $R^1=C_2H_5$, n=5

42: R=THP, $R^1=CH_3$, n=5

43: R=THP, $R^1=CH_3$, n=3

44: R=Bz, $R^1=CH_3$, n=5

Several methods for the synthesis of these key intermediates involving mainly Wittig-Horner reaction have been developed. Some of them, however, follow lengthy procedures and strong basic conditions, and/or give a mixture of geometrical isomers in poor yield and are not suitable for large scale preparation.

The discovery of the stereoselective isomerization of acetylenic derivatives to substituted dienes stimulates us to develope a new methodology for the synthesis of these polyene intermediates (<u>40</u>) instead of using the Wittig-Horner reaction to constitute the diene moiety in the molecule as shown in Scheme 6:

Scheme 6
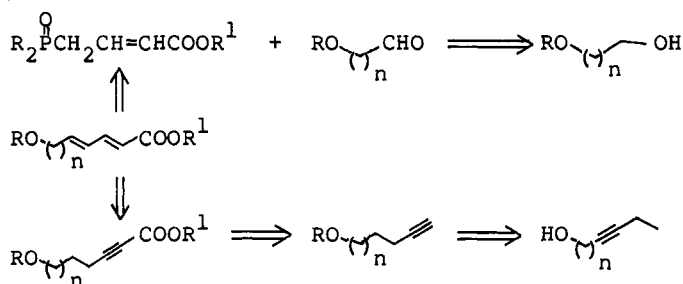
Thus, compound <u>41</u> was synthesized using the following method with an overall yield of 59%. Similarly, compound <u>42</u>-<u>45</u> were synthesized in high overall yield (ref. 28).
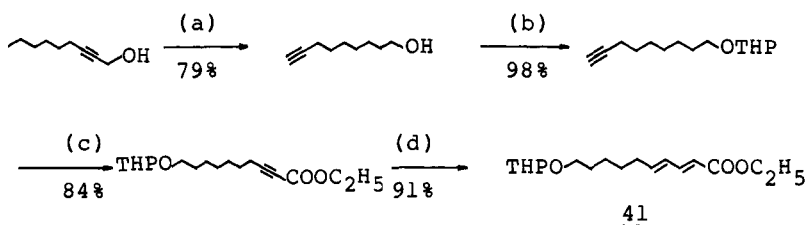
(a) NaH, ethylene diamine, 60-65°C, 5 h; (b) dihydropyran, H^+, 35°C, 5 h; (c) i: BuLi, -50--20°C, ii: ethyl chloroformate, -20-0°C; (d) $IrH_5(\underline{i}-Pr_3P)_2$ (1 mol%) + $\underline{n}-Bu_3P$ (4 mol%), toluene, reflux 30 h.

Compound <u>46</u>, which is an intermediate for synthesizing Leukotriene B$_3$ (ref. 29) could be also easily synthesized using this isomerization method:
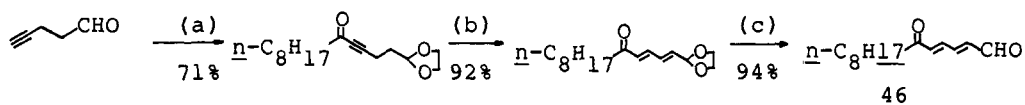
(a) i: ethylene glycol, TsOH, ii: BuLi, -50--20°C, iii: 1-nonanal, iv: PCC, dichloromethane; (b) $RuCl_2(Ph_3P)_3$ (1 mol%) + $\underline{n}-Bu_3P$ (8 mol%), benzene, reflux, 24 h; (c) acetone, TsOH

In summary, this work not only developes the novel stereoselective isomerization reactions of a serious of acetylenic derivatives but also provides a new methodology to synthesize substituted dienes with simple operation, at mild condition and in high overall yield. The new synthetic method may have practical uses in the synthesis of the important polyene natural products.

Acknowledgements

REFERENCES

1. P. A. Chaloner, <u>Handbook of Coordination Catalysis in Organic Chemistry</u>, p.403-424, Butterworths, London (1986).
2. H. M. Colquhoun, J. Holton, D. J. Thompson and M. V. Twigg, <u>New Pathways</u>

for Organic Synthesis. Practical Applications of Transition Metals, p.173-193, Plenum Press, New York (1984); R. A. W. Johnstone, A. H. Wiby and J. D. Entwistle, Chem. Rev. 85, 129-170 (1985); G. Brieger and T. J. Nestrick, Chem. Rev. 74, 567-580 (1974).

3. K. Tani, T. Yamagata, S. Akutagawa, H. Kumobayashi, T. Taketomi, H. Takaya, a. Miyashita, R. Noyori and S. Otsuka, J. Am. Chem. Soc. 106, 5208-5217 (1984).

4. S. Otsuka and A. Nakamura, Adv. Organometal. Chem. 14, 245-283 (1976).

5. M. Frabck-Neumann in Organometallics in Organic Synthesis, A. de Meijere and H. tom Dieck, eds., p.258-262 (1988).

6. A. J. L. Pombeiro, J. Organometal. Chem. 358, 273-282 (1988).

7. D. L. Hughes, A. J. L. Pombeiro, C. J. Pickett and R. L. Richards, J. Chem. Soc. Chem. Commun. 992-993 (1984).

8. K. Hirai, H. Suzuki, Y. Moro-Oka and T. Ikawa, Tetrahedron Lett. 21, 3413-3416 (1980).

9. X. Lu, Y. Lin and D. Ma, Pure Appl. Chem. 60, 1299-1306 (1988); Y. Lin, D. Ma and X. Lu, Acta Chim. Sinica (English edition) 272-274 (1988).

10. D. Ma, Y. Lin, X. Lu and Y. Yu, Tetrahedron Lett. 29, 1045-1048 (1988).

11. B. M. Trost and T. Schmidt, J. Am. Chem. Soc. 110, 2303-2305 (1988); Y. Inoue and S. Imaizumi, J. Mol. Cat. 49, L19-L21 (1988).

12. D. Ma, Y. Yu and X. Lu, J. Org. Chem. 54, 1105-1109 (1989).

13. P. D. Landor, in The Chemistry of the Allenes, Vol. 1, S. R. Landor (ed.) p.119, Academic Press, London (1982); H. F. Schupter, and G. M. Coppola, Allenes in Organic Synthesis, p.153, Wiley, New York (1984).

14. L. Brandsma and H. D. Verkruijsse, Synthesis of Acetylenes, Allenes and Cumulenes, pp.101, 236, Elsevier, Oxford (1981); W. D. Huntsman, and T-K. Yin, J. Org. Chem. 48, 3813-3814 (1983).

15. M. G. Clerici, S. D. Gioacchino, F. Maspero, E. Perrotti, and A. Zanobi, J. Organomet. Chem. 84, 379-388 (1975); (b) R. E. Graf and C. P. Liliya, J. Organomet. Chem. 122, 377-391 (1976); (c) D. Baudry, M. Ephritikhine and H. Felkin, J. Organomet. Chem. 224, 363-376 (1982); (d) D. Baudry, M. Ephritikhine, H. Felkin and J. Zabrzewski, Tetrahedron Lett. 25, 1283-1286 (1984).

16. H. Alper and K. Hachem, J. Org. Chem. 45, 2269-2272 (1980); Y. Sasson and G. L. Rempel, Tetrahedron Lett. 4133-4136 (1974); D. J. Cole-Hamilton and G. Wilkinson, Nouv. J. Chim. 1, 141-155 (1977).

17. D. Ma and X. Lu, Tetrahedron Lett. 30, 843-844 (1989).

18. D. Ma and X. Lu, to be published.

19. A. B. Shenvi and H. Gerlach, Helv. Chim. Acta, 63, 2426-2433 (1980); E. J. Corey, H. Park, A. Barton and Y. Nil, Tetrahedron Lett. 21, 4243-4246 (1980); H. Tanaka, K. Yoshida, Y. Itoh abd H. Imanaka, Tetrahedron Lett. 22, 3421-3422 (1981); T. Nakamura, M. Namiki and K. Ono, Chem. Pharm. Bull. 35, 2635-2645 (1987); B. P. Wijbergad, W. A. Speckamp, Tetrahedron Lett. 22, 5079-5082 (1981).

20. J. Muzart, Tetrahedron Lett. 28, 4665-4668 (1987) and references cited in.

21. E. J. Corey and S. Terashima, Tetrahedron Lett. 1815-1816 (1972).

22. D. Ma and X. Lu, J. Chem. Soc. Chem. Commun. 890-891 (1989).

23. D. Ma and X. Lu, Tetrahedron Lett. 30, 2109-2112 (1989).

24. For recent examples of synthesis and application of 1,4-diketones, see (a) A. Pecunioso and R. Menicagli, J. Org. Chem. 53, 2614-2617 (1988); (b) R. M. Moriarty, R. Penmasta and I. Prakash, Tetrahedron Lett. 28, 873-876 (1987); (c) M. Miyashita, T. Yanami, T. Kumazawa and A. Yoshikoshi, J. Am. Chem. Soc. 106, 2149-2156 (1984).

25. H. L. Sleeper and W. Fenical, J. Am. Chem. Soc. 99, 2367-2368 (1977).

26. L. Crombie and D. Fisher, Tetrahedron Lett. 26, 2481-2484 (1985); L. Crombie and D. Fisher, Tetrahedron Lett. 26, 2477-2480 (1985).

27. J. A. Marshall, J. E. Audia and B. G. Shearer, J. Org. Chem. 51, 1730-1735 (1986); K. Takada, M. Shinagawa, T. Koizumiand E. Yoshii, Chem. Pharm. Bull. 30, 4000-4005 (1982).

28. D. Ma, X. Lu and H. Shi, to be published.

29. J. Robach and J. Admas, Acc. Chem. Res. 18, 87-93 (1985).