Highly Stereoselective Isomerization of Ynones to Conjugated Dienones Catalyzed by Transition-Metal Complexes

Dawei Ma, Yihua Yu, and Xiyan Lu*

Shanghai Institute of Organic Chemistry, Academia Sinica, 345 Lingling Lu, Shanghai 200032, China
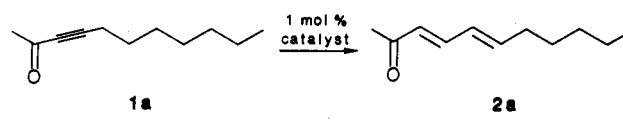
α,β-Ynones isomerize in the presence of a catalytic amount of $IrH_5(i\text{-}Pr_3P)_2$, $RuH_2(Ph_3P)_4$–Bu_3P, or $RuCl_2$-$(Ph_3P)_3$–Ph_3P in benzene at 35–80 °C to give (E,E)-$\alpha,\beta{:}\gamma,\delta$-dienones in high yield with high stereoselectivity. This experimentally simple and economically feasible (E,E)-$\alpha,\beta{:}\gamma,\delta$-dienone synthesis is illustrated with eight examples including several natural products such as capillone, $(3E,5E)$-octa-3,5-dien-2-one, $(4E,6E)$-octa-4,6-dien-3-one, 6-methyl-$(3E,5E)$-hepta-3,5-dien-2-one, $(3E,5E)$-nona-3,5-dien-2-one, and $(3E,5E)$-undeca-3,5-dien-2-one. The presence of excess ligands such as $n\text{-}Bu_3P$, $i\text{-}Pr_3P$, or Ph_3P makes the catalysts much more active. Both 4-nonyn-2-one and 3,4-nonadien-2-one gave $(3E,5E)$-nona-3,5-dien-2-one under the catalysis of $IrH_5(i\text{-}Pr_3P)_2$, implying that allenone is the possible reaction intermediate. The stoichiometric reacton of 1-phenyl-2-hexyn-1-one with $IrH_5(i\text{-}Pr_3P)_2$ gave $[2,3,4,5\text{-}\eta^4\text{-}1\text{-phenyl-}(2E,4E)\text{-hexa-2,4-dien-1-one}]hydridobis(triisopropylphosphine)iridium. This η^4-dienone metal complex may be regarded as the possible key intermediate in controlling the stereoselectivity.

Introduction

(E,E)-$\alpha,\beta{:}\gamma,\delta$-Dienones are well known as common flavor constituents in tea, tobacco, and foods.[1] In addition, they often serve as useful intermediates in the synthesis of natural products such as isogregatins B, isoaspertetronins,[2] (–)-rothrockene,[3] (S)-plectaniaxanthin,[4] heterocycles,[5] and polycyclic compounds.[6] Several methods for the synthesis of these compounds involving Knoevenagel condensation,[4,7] Wittig–Horner reaction,[2c,6a] Claisen rearrangement,[8] and addition–elimination reaction[9] have been developed. Many of them, however, follow lengthy procedures and strong basic conditions and/or give a mixture of geometrical isomers in poor yield[6a] and are not suitable for large scale preparation. On the other hand, intramolecular hydrogen-transfer reaction of olefins catalyzed by transition-metal complexes has attracted much attention in recent years,[10] but intramolecular hydrogen-transfer reactions

Table I. Effect of the Catalysts in the Stereoselective Isomerization of 3-Undecyn-2-one[a]

entry	catalyst	time, h	conv,[b] %
1	$IrH_5(i\text{-}Pr_3P)_2$	24	99
2	$ReH_7(i\text{-}Pr_3P)_2$	24	98
3	$RuH_2(n\text{-}Bu_3P)_4$	24	83
4	$RuH_2(Ph_3P)_4$	20	20
5	$RuH_4(Ph_3P)_3$	20	25
6	$RuCl_2(Ph_3P)_3$	24	20
7	$RhH(Ph_3P)_4$	24	5
8	$RhCl(Ph_3P)_3$	24	4
9	$[Ir(cod)Cl]_2$	24	0
10	$RuCl_3\cdot 3H_2O$	24	0
11	$RhCl_3\cdot 3H_2O$	24	0

[a] Reaction condition: Ynone (1a) (1.6 mmol), catalyst (0.016 mmol), and benzene (2 mL) at 60 °C. [b] Estimated by GC using the normalization method with calibration.

related to carbon–carbon triple bonds are rare.[11] Suzuki and Moro-oka have reported the isomerization of acetylenic ethers to dienol ethers under the catalysis of a ruthenium hydride complex,[11a] but their reaction is not stereoselective. In the course of our study on the transition-metal hydride complex catalyzed organic synthesis,[12] a novel stereoselective isomerization of α,β-ynones to (E,E)-dienones catalyzed by dihydridotetrakis(triphenylphosphine)ruthenium, $RuH_2(Ph_3P)_4$, was reported as a communication.[13a] Trost also reported the isomerization of ynones to dienones under the catalysis of palladium-(0).[13b] In our communication,[13a] 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 $IrH_5(i\text{-}Pr_3P)_2$, $ReH_7(i\text{-}Pr_3P)_2$, and RuH_2-$(Bu_3P)_4$ and/or by adding excess phosphine ligand as

(1) (a) Heydanek, M. G.; McGorrin, R. J. *J. Agric. Food Chem.* **1981**, *29*, 950. (b) Heydanck, M. G.; McGorrin, R. J. *J. Agric. Food Chem.* **1981**, *29*, 1093. (c) Greenberg, M. J. *J. Agric. Food Chem.* **1981**, *29*, 1276. (d) Habu, T.; Flath, R. A.; Mon, T. R.; Marton, J. F. *J. Agric. Food Chem.* **1985**, *33*, 249. (e) Murray, K. E.; Shipton, J.; Whitfield, F. B.; Last, J. H. *J. Sci. Food Agric.* **1976**, *27*, 1093. (f) Greenberg, M. J. *J. Agric. Food Chem.* **1981**, *29*, 831. (g) Josephson, D. B.; Lindsay, R. C.; Stuiber, D. A. *Can. Inst. Food Sci. Technol. J.* **1984**, *17*, 178; *Chem. Abstr.* **1984**, *101*, 228706z. (h) Demole, E.; Berthet, D. *Helv. Chim. Acta* **1972**, *55*, 1866.

(2) (a) Clemo, N. G.; Pattenden, G. *Tetrahedron Lett.* **1982**, *23*, 585. (b) Miyata, O.; Schmidt, R. R.; *Tetrahedron Lett.* **1982**, *23*, 1793. (c) Clemo, N. G.; Pattenden, G. *J. Chem. Soc., Perkin Trans. 1* **1985**, 2407.

(3) Barbachyn, M. R.; Johnson, C. R.; Glick, M. D. *J. Org. Chem.* **1984**, *49*, 2746.

(4) Dumont, v. R.; Pfander, H. *Helv. Chim. Acta* **1984**, *67*, 1283.

(5) (a) Wendelin, W.; Schramm, H.-W.; Blasi-Rabassa, A.; *Monatsch. Chem.* **1985**, *116*, 385. (b) Moskal, J.; van Stralen, R.; Postma, D.; Van Leusen, A. M. *Tetrahedron Lett.* **1986**, *27*, 2173.

(6) (A) Hanessian, S.; Hodges, P. J.; Sahoo, S. P.; Roy, P. J. *Tetrahedron Lett.* **1986**, *27*, 2949. (b) Hoffmann, W.; Janitschke, L. Ger. Offen. DE 3,500,057; *Chem. Abstr.* **1986**, *105*, 227081.

(7) (a) Surber, W.; Thens, V.; Colombi, L.; Schinz, H. *Helv. Chim. Acta* **1956**, *39*, 1229. (b) Grunanger, P.; Grieco, D. *Gazz. Chim. Ital.* **1958**, *88*, 296. (c) Jones, G. In *Organic Reactions*; Cope, A. C., Ed.; John Wiley: New York, 1967; Vol. 15, p 204.

(8) Cookson, R. C.; Gopalan, R. *J. Chem. Soc., Chem. Commun.* **1978**, 608.

(9) (a) Sakai, T.; Seko, K.; Tsuji, A.; Utaka, M.; Takeda, A. *J. Org. Chem.* **1982**, *47*, 1101. (b) Kuwajima, I.; Hoshino, S.; Tanaka, T.; Shimizu, M. *Tetrahedron Lett.* **1980**, *21*, 3209. (c) Molander, G. A.; Singaram, B.; Brown, H. C. *J. Org. Chem.* **1984**, *49*, 5024. (d) Naf, F.; Decorzant, R. *Helv. Chim. Acta* **1974**, *57*, 1309.

(10) (a) Colquhoun, H. M.; Holton, J.; Thompson, D. J.; Twigg, M. V. *New Pathways for Organic Synthetic Practical Applications of Transition Metals*; Plenum Press: New York, 1984; p 173. (b) Johnstone, R. A. W.; Wibey, A. H.; Entwistle, I. D. *Chem. Rev.* **1985**, *85*, 129.

(11) (a) Hiral, K.; Suzuki, H.; Moro-oka, Y.; Ikawa, T. *Tetrahedron Lett.* **1980**, *21*, 3413. (b) Shvo, Y.; Blum, Y. *J. Organomet. Chem.* **1982**, *238*, C79. (c) Sheng, H.; Lin, S.; Huang, Y. *Tetrahedron Lett.* **1986**, *27*, 4893.

(12) (a) Lin, Y.; Ma, D.; Lu, X. *Tetrahedron Lett.* **1987**, *28*, 3115. (b) Lin, Y.; Ma, D.; Lu, X. *Acta Chim. Sin.* **1988**, *46*, 93. (c) Lu, X.; Lin, Y.; Ma, D.; *Pure Appl. Chem.* **1988**, *60*, 1299. (d) Lin, Y.; Ma, D.; Lu, X. *J. Organomet. Chem.* **1987**, *323*, 407.

(13) (a) Ma, D.; Lin, Y.; Lu, X.; Yu, Y. *Tetrahedron Lett.* **1988**, *29*, 1045. (b) Trost. B. M.; Schmidt, T. *J. Am. Chem. Soc.* **1988**, *110*, 2303.

Table II. Effect of the Phosphine Ligands in the Stereoselective Isomerization of 1a[a]

$$\text{1a} \xrightarrow[\text{R}_3\text{P}]{\text{catalyst}} \text{2a}$$

entry	catalyst	ligand	ligand/ cat.	temp, °C	convn,[b] %
12	IrH$_5$(i-Pr$_3$P)$_2$		0	35	0
13	IrH$_5$(i-Pr$_3$)P$_2$	n-Bu$_3$P	2	35	28
14	IrH$_5$(i-Pr$_3$P)$_2$	n-Bu$_3$P	4	35	48
15	IrH$_5$(i-Pr$_3$P)$_2$	n-Bu$_3$P	6	35	73
16	IrH$_5$(i-Pr$_3$P)$_2$	n-Bu$_3$P	8	35	98
17	IrH$_5$(i-Pr$_3$P)	n-Bu$_3$P	16	35	98
18	IrH$_5$(i-Pr$_3$P)$_2$	i-Pr$_3$P	8	35	99
19	IrH$_5$(i-Pr$_3$P)$_2$	Ph$_3$P	2	35	16[c]
20	IrH$_5$(i-Pr$_3$P)$_2$	Ph$_3$P	8	35	30[c]
21	RuH$_2$(Ph$_3$P)$_4$	i-Pr$_3$P	8	35	99
22	RuH$_2$(Ph$_3$P)$_4$	n-Bu$_3$P	8	35	99
23	RuH$_2$(Ph$_3$P)$_4$	Ph$_3$P	8	60	98
24	RuCl$_2$(Ph$_3$P)$_3$	Ph$_3$P	10	60	98
25	RuCl$_2$(Ph$_3$P)$_3$	n-Bu$_3$P	8	35	15[c]
26	RhH(Ph$_3$P)$_4$	n-Bu$_3$P	8	35	69[c]
27	[Ir(cod)Cl]$_2$	Ph$_3$P	10	60	98
28	[Ir(cod)Cl]$_2$	n-Bu$_3$P	10	60	40
29	RuCl$_3$·3H$_2$O	n-Bu$_3$P	10	60	0
30	RuCl$_3$·3H$_2$O	Ph$_3$P	10	60	45

[a] Reaction condition: 1a (1.6 mmol), catalyst (0.016 mmol), and corresponding amount of R$_3$P in benzene (2 mL) for 24 h. [b] Estimated by GC using the method described in Table I. No isomer was found in all reactions. [c] The reaction gave quantitative yield by further heating for 10 h at 60 °C.

catalyst instead of RuH$_2$(Ph$_3$P)$_4$ was found to give products in higher yield at much mild conditions. Herein, we report the details of these catalytic isomerizations with respect to the influences of catalysts and ligands. Several natural products such as aroma components of foods were synthesized by using this simple and convenient method.

Results and Discussion

Effect of Catalysts. α,β-Ynones isomerized readily in the presence of a suitable transition-metal catalyst at 60 °C to give corresponding (E,E)-α,β:γ,δ-dienones. The activity of various transition-metal catalysts was examined with respect to the isomerization of 3-undecyn-2-one (1a). Representative results are shown in Table I. All reactions gave a single product, $(3E,5E)$-undeca-3,5-dien-2-one (2a), as determined by GC. The catalysts with trialkyl-phosphines as ligands such as IrH$_5$(i-Pr$_3$P)$_2$, ReH$_7$(i-Pr$_3$P)$_2$, and RuH$_2$(Bu$_3$P)$_4$ showed the highest catalytic activity. Those catalysts with triphenylphosphine as ligands, RuH$_2$(Ph$_3$P)$_4$, RuCl$_2$(Ph$_3$P)$_3$, RhH(Ph$_3$P)$_4$, and RhCl-(Ph$_3$P)$_3$, showed lower catalytic activity, while the catalysts without phosphine ligands, RuCl$_3$·3H$_2$O, RhCl$_3$·3H$_2$O, and [Ir(cod)Cl]$_2$, showed no catalytic activity.

Effect of Ligand. The presence of excess phosphine ligands such as Ph$_3$P, n-Bu$_3$P, and i-Pr$_3$P influenced significantly the activity of the catalysts. Isomerization of 1a using 1 mol % IrH$_5$(i-Pr$_3$P)$_2$ as catalyst did not occur at 35 °C, but this reaction gave 28% conversion by adding 2 mol % n-Bu$_3$P after 24 h. With the increase of the ratio of n-Bu$_3$P to IrH$_5$(i-Pr$_3$P)$_2$, the conversion of the reaction increased as shown in Table II.

Besides IrH$_5$(i-Pr$_3$P)$_2$, other catalysts also displayed high activity by adding phosphine ligands. The results on the isomerization of 1a are shown in Table II. The effect of n-Bu$_3$P is nearly similar to that of i-Pr$_3$P but is much greater than that of Ph$_3$P (compare entries 16, 18, and 20; 21, 22, and 23). The metal hydrides, IrH$_5$(i-Pr$_3$P)$_2$, RuH$_2$(Ph$_3$P)$_4$, and RuH(Ph$_3$P)$_4$, gave the best results. Chloride complex, RuCl$_2$(Ph$_3$P)$_3$, needs a higher temperature to give complete conversion. It is surprising that for
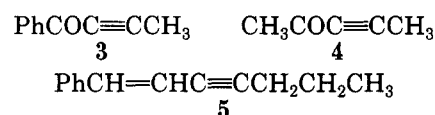
[Ir(cod)Cl]$_2$ and RuCl$_3$·3H$_2$O adding Ph$_3$P gave better results than that of n-Bu$_3$P (compare entries 27 and 28, 29 and 30).

Catalytic Isomerization of α,β-Ynones to Dienones. Three catalytic systems were used to examine the catalytic isomerization of various α,β-ynones. Representative results are shown in Table III.

Several natural products were synthesized readily from this reaction in high yield and high stereoselectivity, such as 1-phenyl-$(2E,4E)$-hexa-2,4-dienone (capillone, 2b), a component of artemisia and capillaraer with medicinal properties;[14] $(3E,5E)$-octa-3,5-dien-2-one (2c), a major flavor component of Oat Groats,[1a,b] green tea,[1c] and meal,[1g] $(4E,6E)$-octa-4,6-dien-3-one (2d), a constituent of mouse urine possibly used in chemical communication,[15] 6-methyl-$(3E)$-hepta-3,5-dien-2-one (2e), a major odor component of Rooibos Tea[1d] and aroma component of tobacco,[1h] and $(3E,5E)$-nona-3,5-dien-2-one (2f) and $(3E,5E)$-undeca-3,5-dien-2-one (2a), important odor compounds of meal flavor volatile.[1e,f]

The absence of other stereoisomers was confirmed by GC and ^{1}H NMR spectra. The stereochemistry of α,β: γ,δ-dienones 2 was first determined by ^{1}H NMR spectra using CDCl$_3$ as solvent, which showed the characteristic signals of a double-doublet peak at about 7.0 ppm ($J = 15.5$–16.0 Hz) due to C$_\beta$H, indicating α,β-trans geometry. Unfortunately, the chemical shifts of C$_\alpha$H, C$_\gamma$H, and C$_\delta$H are too close to give spin–spin coupling constants for C$_\gamma$H and C$_\delta$H.[16] The chemical shifts of C$_\gamma$H and C$_\delta$H could be shifted by using C$_6$D$_6$ as solvent according to the "aromatic solvent induced shifts" principle[17] and then $J_{\gamma,\delta} = 15.5$–16.0 Hz was observed by simple decoupling technique, indicating γ,δ-trans geometry.

No isomerization of 1-phenyl-2-butyn-1-one (3) and 3-pentyn-2-one (4) occurred under the catalysis of IrH$_5$-(i-Pr$_3$P)$_2$ 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 (5) did not give

$$\text{PhCOC} \equiv \text{CCH}_3 \qquad \text{CH}_3\text{COC} \equiv \text{CCH}_3$$
$$\text{3} \qquad\qquad\qquad\qquad \text{4}$$

$$\text{PhCH} = \text{CHC} \equiv \text{CCH}_2\text{CH}_2\text{CH}_3$$
$$\text{5}$$

isomerization product at 80 °C under the catalysis of IrH$_5$(i-Pr$_3$P)$_2$, 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. The high catalytic activity of IrH$_5$(i-Pr$_3$P)$_2$ could be shown by the reaction of 3-octyn-2-one (1c) with 0.1 mol % of IrH$_5$(i-Pr$_3$P)$_2$ in benzene at reflux to give $(3E,5E)$-octa-3,5-dien-2-one (2c) in 86% isolated yield (entry 37). The sterically hindered α,β-ynone can influence the reactivity, for example, 6-methyl-3-heptyn-2-one (1e) did not isomerize at 60 °C under the catalysis of IrH$_5$(i-Pr$_3$P)$_2$ and the starting material was recovered, but this reaction gave almost quantitatively 6-methyl-$(3E)$-hepta-3,5-dien-2-one (2e) at 80 °C (compare entries 41 and 42).

It is worth noting that isomerization of α,β-ynones catalyzed by RuCl$_2$(Ph$_3$P)$_3$ and Ph$_3$P gave high yield and
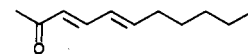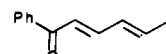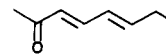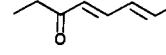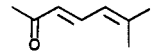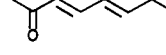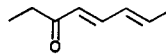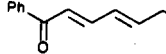
(14) Sze, C. Q.; Chen, Y. S. African, 79 00,375, *Chem. Abstr.* 1979, *93*, 120256.

(15) Schwende, F. J.; Wiesler, D.; Jorgenson, J. W.; Carmack, M.; Novotny, M. *J. Chem. Ecol.* 1986, *12*, 277.

(16) References 2c, 9a, and 9c. ^{1}H NMR in CDCl$_3$ gave a broad peak of C$_\alpha$H, C$_\gamma$H, and C$_\delta$H.

(17) Laszlo, P. In *Progress in NMR Spectroscopy*; Emsley, J. W.; Feeney, J.; Sutchffe, L. H., Eds.; Pergamon: 1967; p 231.

Table III. Highly Stereoselective Isomerization of α,β-Ynone 1 to (E,E)-α,β:γ,δ-Dienone 2 with Transition-Metal Catalysts[a]

entry	compd	R¹	R²	R³	cat.[b]	temp, °C	time, h	product	yield,[c] %
31	1a	CH_3	n-C_5H_{11}	H	A	60	24	**2a**	92
32	1a	CH_3	n-C_5H_{11}	H	C	60	28	**2a**	87
33	1b	Ph	CH_3	H	A	60	20	**2b**	87
34	1b	Ph	CH_3	H	B	35	28	**2b**	89
35	1b	Ph	CH_3	H	C	60	24	**2b**	88
36	1c	CH_3	C_2H_5	H	A	60	24	**2c**	87
37	1c	CH_3	C_2H_5	H	A	80	30	**2c**	86[d]
38	1c	CH_3	C_2H_5	H	B	35	28	**2c**	86
39	1d	C_2H_5	CH_3	H	A	60	24	**2d**	88
40	1d	C_2H_5	CH_3	H	B	35	28	**2d**	86
41	1e	CH_3	CH_3	CH_3	A	60	24		0[e]
42	1e	CH_3	CH_3	CH_3	A	80	24	**2e**	90
43	1e	CH_3	CH_3	CH_3	C	80	24	**2e**	85
44	1f	CH_3	n-C_3H_7	H	A	60	24	**2f**	92
45	1f	CH_3	n-C_3H_7	H	B	35	28	**2f**	89
46	1g	C_2H_5	C_2H_5	H	A	60	24	**2g**	88
47	1h	Ph	C_2H_5	H	A	60	20	**2h**	86

[a] Reaction condition: 1 (5 mmol), catalyst (0.05 mmol), benzene (5 mL). [b] Catalyst: A, IrH₅(i-Pr₃P)₂; B, RuH₂(Ph₃P)₄ + 8n-Bu₃P; C, RuCl₂(Ph₃P)₃ + 10Ph₃P. [c] Isolated yield. [d] Reaction condition: 1c (30 mmol), IrH₅(i-Pr₃P)₂ (0.03 mmol), benzene (5 mL). [e] Starting material was recovered.

Scheme I
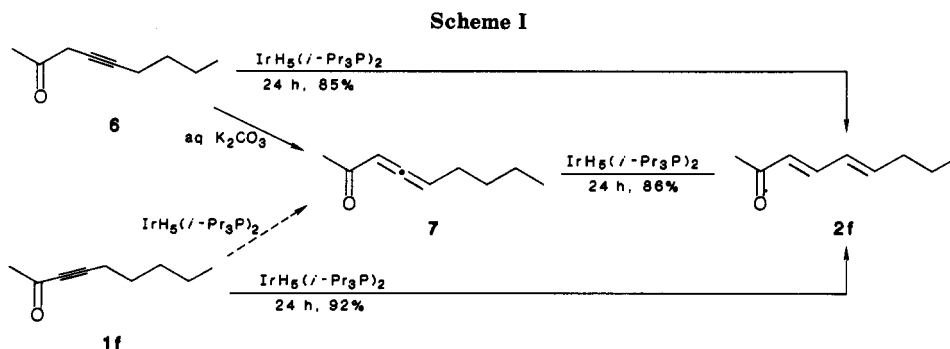
high stereoselectivity, too (entries 32, 34, and 43). Considering that RuCl₂(Ph₃P)₃ and Ph₃P are more stable to air and conveniently available, this catalytic system might provide a practical route to synthesize (E,E)-α,β:γ,δ-dienones from α,β-ynones.

Reaction Mechanism. It was suggested that the possible intermediate for this reaction may be a α,β:β,γ-dienone.[13] 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.[18] 3,4-Nonadien-2-one (7) was prepared from 4-nonyn-2-one (6) according to the known method[19] to investigate the reac-

(18) (a) Landor, P. D. In *The Chemistry of the Allenes*; Landor, S. R., Ed.; Academic Press: London, 1982; Vol. 1, p 119. (b) Schupter, H. F.; Coppola, G. M. *Allenes in Organic Synthesis*; John Wiley and Sons: New York, 1984; p 153.

(19) (a) Brandsma, L.; Verkruijsse, H. D. *Synthesis of Acetylenes, Allenes and Cumulenes*; Elsevier: Oxford, 1981; p 101, 236. (b) Huntsman, W. D.; Yin, T.-K. *J. Org. Chem.* **1983**, *48*, 3813.

Scheme II

Scheme III[a]

[a] [IrH] = L_nIrH(i-Pr$_3$P)$_2$; R^3 ≤ R^2.
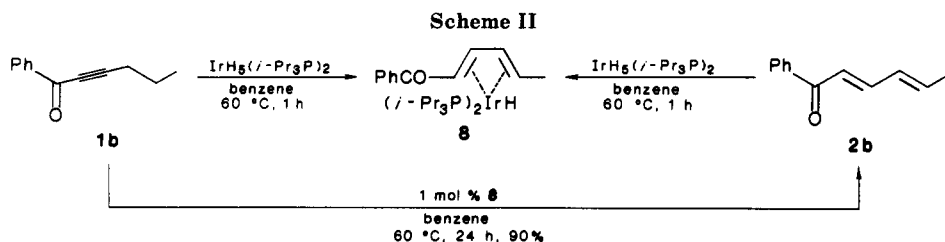
tion mechanism of this reaction. The fact that all **6, 7,** and **1f** could isomerize to (3E,5E)-nona-3,5-dien-2-one (**2f**) by the catalysis of IrH$_5$(i-Pr$_3$P)$_2$ in benzene at 60 °C in high yield supports the suggested mechanism. Both **6** and **1f** may isomerize first under IrH$_5$(i-Pr$_3$P)$_2$ catalysis to the same intermediate **7**, which is then isomerized further to **2f** (Scheme I).

Equimolar amount of IrH$_5$(i-Pr$_3$P)$_2$ and 1-phenyl-2-hexyn-1-one (**1b**) reacted at 60 °C in benzene to give [2,3,4,5-η^4-phenyl-(2E,4E)-hexa-2,4-dien-1-one]hydrido-bis(triisopropylphosphine)iridium complex (**8**) as determined by IR, ^{1}H NMR, ^{13}C NMR, and mass spectra with comparison to the reported data of the analogous complexes.[20] The same complex was also obtained and characterized by ^{1}H NMR from the reaction of IrH$_5$(i-Pr$_3$P)$_2$ and 1-phenyl-(2E,4E)-hexa-2,4-dien-1-one (**2b**) (Scheme II). The ^{1}H NMR spectra showed J_{23} = J_{34} = J_{45} = 8 Hz, indicating the syn,syn geometry.[20b] Complex **8** could catalyze the isomerization of **1b** to give **2b** in high yield (Scheme II). These results showed that the (η^4-dienone)metal complex might be regarded as the possible reaction intermediate.

A plausible reaction mechanism with respect to IrH$_5$-(i-Pr$_3$P)$_2$ was shown in Scheme III. Other transition-metal complexes may be similar to this mechanism. The catalytically active species seems to be the coordinatively unsaturated complex L$_n$IrH(i-Pr$_3$P)$_2$,[21] which will coordinate to the triple bond first to form **9**. After addition and elimination of metal hydride,[22] $\alpha,\beta:\beta,\gamma$-dienone **11** may be formed first, the metal hydride adds to **11** to produce the intermediate **12** (the more stable trans isomer can be formed predominantly), and then syn elimination of intermediate **12** occurs 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.[23] *syn,syn*-(Dienone)hydridobis(triisopropylphosphine)iridium (**14**) is formed. Finally, ynone replaces the dienone to form **2**.

The isomerization of olefins often yields a carbon–carbon double bond with lower stereoselectivity.[24] The isomerization of acetylenic ethers catalyzed by ruthenium hydride gave also poor stereoselectivity.[11a] The present reaction
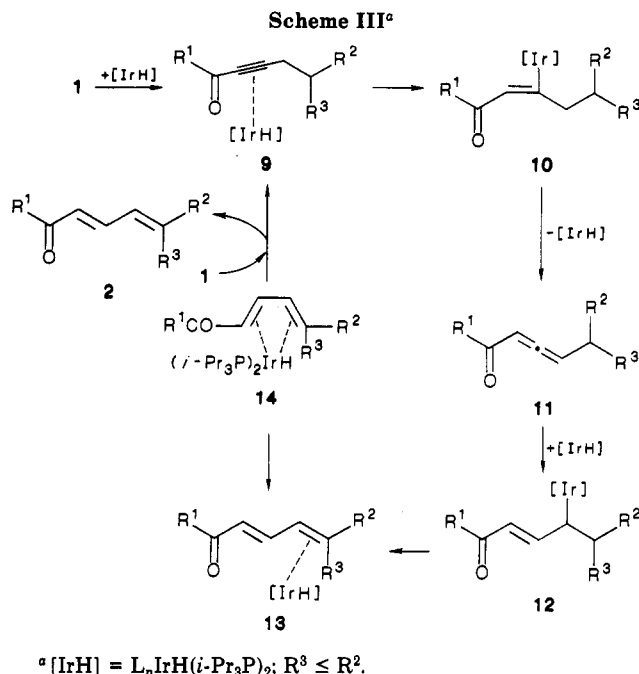
gave only (E,E)-dienones even at high temperature (140 °C).[13] So there might be another factor that controls the stereochemistry besides the general configuration control. Knox and Lillya have reported isomerization of *anti*-(dienone)tricarbonyliron complexes to their syn isomer by base or acid at room temperature or more slowly by thermal reaction without catalyst.[25] It is possible that the high stereoselectivity of the present reaction is controlled by the formation of *syn,syn*-(dienone)metal complex. After the elimination reaction of **12**, four possible (η^4-dienone)metal complexes may be produced and the less stable isomers may isomerize to the thermally more stable isomer **14**, which may also give contribution to the E,E stereochemistry of the dienone.

Experimental Section

The boiling points are uncorrected. All reactions were carried out under a prepurified nitrogen atmosphere. Benzene was distilled from sodium and benzophenone under a nitrogen atmosphere. ^{1}H and ^{13}C NMR spectra were recorded on an EM-360 or Varian XL-200 spectrometer. Chemical shifts are reportd as δ values in parts per million with Me$_4$Si as an internal standard. Infrared spectra were taken as liquid films with an IR-440 instrument. Mass spectral data were obtained with electron ionization on a Finnigan 4021 spectrometer. High resolution mass spectral data were determined on Finnigan-MAT8430 spectrometer. GC analysis were performed on a 102 G instrument using a PEG 20000 column (3 m × 5 mm) at 180 °C.

Materials. The complexes IrH$_5$(i-Pr$_3$P)$_2$,[20a] ReH$_7$(i-Pr$_3$P)$_2$,[12d] RuH$_2$(Bu$_3$P)$_4$,[26] RuH$_2$(Ph$_3$P)$_4$,[27] RuH$_4$(Ph$_3$P)$_3$,[27] RuCl$_2$(Ph$_3$P)$_3$,[28]

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

(21) Although complex **8** was isolated from the reaction mixture, it is still not certain whether the active species is IrH(i-Pr$_3$P)$_2$, a highly coordination unsaturated species, or L$_n$IrH(i-Pr$_3$P)$_2$ where L represents hydride, tertiary phosphine, or solvents.

(22) (a) Alper, H.; Hachem, K. *J. Org. Chem.* **1980**, *45*, 2269. (b) Sasson, Y.; Rempel, G. L. *Tetrahedron Lett.* **1974**, 4133. (c) Cole-Hamilton, D. J.; Wilkinson, G. *Nouv. J. Chim.* **1977**, *1*, 141.

(23) Yamamoto, A. *Organotransition Metal Chemistry–Fundamental Concepts and Applications*; John Wiley and Sons: New York, 1986; p 384.

(24) (a) Suzuki, H.; Koyama, Y.; Moro-oka, Y.; Ikawa, T. *Tetrahedron Lett.* **1979**, 1415. (b) Taber, D. F.; Gunn, B. P. *J. Org. Chem.* **1979**, *44*, 450. (c) Corrless, H. A. J.; Haywood, D. J. *J. Chem. Soc., Chem. Commun.* **1980**, 980.

(25) (a) Greaves, E. O.; Knox, G. R.; Rauson, P. L.; *J. Chem. Soc., Chem. Commun.* **1969**, 1124. (b) Frederibsen, J. S.; Graf, R. E.; Gresham, D. G.; Lillya, C. P. *J. Am. Chem. Soc.* **1979**, *101*, 3863.

RhH(Ph$_3$P)$_4$,[29] RhCl(Ph$_3$P)$_3$,[30] and [Ir(cod)Cl]$_2$[31] were prepared according to the reported methods. α,β-Ynones were prepared by the reaction of an aldehyde with the acetylenic carbanion followed by oxidation with Jones reagent;[32] compound, boiling point, and yield are as follows: **1a**,[33] 90–92 °C/2 mm, 86%; **1b**,[34] 121–123 °C/0.35 mm, 89%; **1c**, 84–85 °C/19 mm (lit.[35] 93–95 °C/25 mm), 93%; **1d**,[36] 85–86 °C/18 mm, 88%; **1e**, 85–86 °C/19 mm, 87%; **1f**,[33] 89–90 °C/12 mm, 86%; **1g**, 87–88 °C/10 mm (lit.[35] 108–110 °C/22 mm), 92%; **1h**, 130–131 °C/0.35 mm (lit.[34] 106–108 °C/0.5 mm).

Catalytic Activity of Various Metal Complexes. A mixture of 3-undecyn-2-one (**1a**) (1.6 mmol) and catalyst (0.016 mmol) in benzene (2 mL) was heated at 60 °C for 20–24 h. The conversion of **1a** was estimated by the GC analysis of the reaction mixture. The results with various catalysts are shown in Table I.

Effect of Phosphine Ligand. A mixture of **1a** (1.6 mmol), catalyst (0.016 mmol) and R$_3$P (0.032–0.256 mmol, R = *n*-Bu, *i*-Pr, or Ph) in benzene (2 mL) was heated at 35–60 °C for 24 h. The conversion of **1a** was estimated by GC analysis of the reaction mixture. The results with various catalysts and phosphine ligands are shown in Table II.

Isomerization of α,β-Ynones Catalyzed by IrH$_5$(i-Pr$_3$P)$_2$, RuH$_2$(Ph$_3$P)$_4$–8Ph$_3$P, or RuCl$_2$(Ph$_3$P)$_3$–10Ph$_3$P. A mixture of **1** (5 mmol), catalyst (0.05 mmol), R$_3$P (0–0.5 mmol, R = *n*-Bu, Ph), and benzene (5 mL) was heated at 60–80 °C for 16–24 h. After cooling and removal of the solvent, the red residue was distilled under reduced pressure and **2** was obtained as a colorless oil.

(**3E,5E**)-**Undeca-3,5-dien-2-one (2a):** colorless liquid; IR (neat) 3050, 1680, 1640, 1610 cm^{-1}; ^{1}H NMR (200 MHz, C$_6$D$_6$) 6.94 (dd, J_{43} = 15.6 Hz, J_{45} = 10.2 Hz, 1 H), 5.92 (d, J_{34} = 15.6 Hz, 1 H), 5.78 (dd, J_{54} = 10.2 Hz, J_{56} = 15.0 Hz, 1 H), 5.68 (dt, J_{67} = 6.7 Hz, J_{65} = 15.0 Hz, 1 H), 1.90 (s, 3 H), 1.82 (m, 2 H), 1.16 (m, 6 H), 0.86 (t, 3 H); MS, *m/e* 166 (M$^+$), 109, 95.

1-Phenyl-(2E,4E)-hexa-2,4-dien-1-one (2b): pale yellow crystal, mp 47–48 °C (from petroleum ether); IR (KBr) 3045, 1665, 1620, 1590 cm^{-1}; ^{1}H NMR (200 MHz, C$_6$D$_6$) 7.95 (m, 2 H), 7.57 (dd, J_{32} = 15.0 Hz, J_{34} = 11.0 Hz, 1 H), 7.15 (m, 3 H), 6.75 (d, J_{23} = 15.0 Hz, 1 H), 6.03 (dd, J_{43} = 11.0 Hz, J_{45} = 15.0 Hz, 1 H), 5.72 (dq, J_{54} = 15.0 Hz, J_{56} = 7.0 Hz, 1 H), 1.48 (d, 3 H); ^{13}C NMR (C$_6$D$_6$) 190.28, 145.52, 140.94, 139.63, 133.04, 131.54, 129.32, 124.28, 19.28; MS, *m/e* 172 (M$^+$), 157, 105, 77.

(**3E,5E**)-**Octa-3,5-dien-2-one (2c):** colorless liquid; IR (neat) 3040, 1670, 1620 cm^{-1}; ^{1}H NMR (200 MHz, C$_6$D$_6$) 6.90 (dd, J_{43} = 15.6 Hz, J_{45} = 10.0 Hz, 1 H), 5.93 (d, J_{34} = 15.6 Hz, 1 H), 5.83 (dd, J_{54} = 10.0 Hz, J_{56} = 15.1 Hz, 1 H), 5.68 (dt, J_{65} = 15.1 Hz,

J_{67} = 6.1 Hz, 1 H), 1.89 (s, 3 H), 1.80 (dq, 2 H), 0.77 (t, 3 H); MS, *m/e* 124 (M$^+$), 109, 85.

(**4E,6E**)-**Octa-4,6-dien-3-one (2d):** colorless liquid; IR (neat) 3050, 1680, 1640 cm^{-1}; ^{1}H NMR (200 MHz, C$_6$D$_6$) 7.04 (dd, J_{54} = 15.5 Hz, J_{56} = 10.1 Hz, 1 H), 5.92 (d, J_{45} = 15.5 Hz, 1 H), 5.78 (dd, J_{65} = 10.1 Hz, J_{67} = 15.1 Hz, 1 H), 5.63 (dq, J_{76} = 15.1 Hz, 1 H), 2.15 (q, 2 H), 1.52 (d, 3 H), 0.99 (t, 3 H); MS, *m/e* 124 (M$^+$), 109, 95.

6-Methyl-(3E)-hepta-3,5-dien-2-one (2e): colorless liquid; IR (neat) 3050, 1680, 1640, 1605 cm^{-1}; ^{1}H NMR (200 MHz, C$_6$D$_6$) 7.37 (dd, J_{43} = 15.6 Hz, J_{45} = 11.4 Hz, 1 H), 5.95 (d, J_{34} = 15.6 Hz, 1 H), 5.73 (d, J_{54} = 11.4 Hz, 1 H), 1.92 (s, 3 H), 1.43 (d, 6 H); MS, *m/e* 124 (M$^+$), 109, 95.

(**3E,5E**)-**Nona-3,5-dien-2-one (2f):** colorless liquid; IR (neat) 3050, 1680, 1635 cm^{-1}; ^{1}H NMR (200 MHz, C$_6$D$_6$) 6.92 (dd, J_{43} = 15.9 Hz, J_{45} = 10.0 Hz, 1 H), 5.92 (d, J_{34} = 15.9 Hz, 1 H), 5.79 (dd, J_{54} = 10.0 Hz, J_{56} = 15.5 Hz, 1 H), 5.63 (dt, J_{65} = 15.5 Hz, J_{67} = 6.3 Hz, 1 H), 1.92 (s, 3 H), 1.84 (m, 2 H), 1.12 (m, 2 H), 0.76 (t, 3 H); MS, *m/e* 138 (M$^+$), 123, 95.

(**4E,6E**)-**Nona-4,6-dien-3-one (2g):** colorless liquid; IR (neat) 3040, 1670, 1620 cm^{-1}; ^{1}H NMR (200 MHz, C$_6$D$_6$) 7.09 (dd, J_{54} = 15.6 Hz, J_{56} = 10.2 Hz, 1 H), 5.94 (d, J_{45} = 15.6 Hz, 1 H), 5.87 (dd, J_{65} = 10.2 Hz, J_{67} = 15.7 Hz, 1 H), 5.71 (dt, J_{76} = 15.7 Hz, J_{78} = 6.3 Hz, 1 H), 2.17 (q, 2 H), 1.82 (dq, 2 H), 1.03 (t, 3 H), 0.78 (t, 3 H); MS, *m/e* 138 (M$^+$), 109, 57.

1-Phenyl-(2E,4E)-hepta-2,4-dien-1-one (2h): pale yellow liquid; IR (neat) 3050, 1660, 1620 cm^{-1}; ^{1}H NMR (200 MHz, C$_6$D$_6$) 7.93 (m, 2 H), 7.58 (dd, J_{32} = 15.0 Hz, J_{34} = 11.1 Hz, 1 H), 7.13 (m, 3 H), 6.76 (d, J_{32} = 15.0 Hz, 1 H), 6.06 (dd, J_{43} = 11.1 Hz, J_{45} = 15.0 Hz, 1 H), 5.79 (dt, J_{54} = 15.0 Hz, J_{56} = 6.8 Hz, 1 H), 1.86 (dq, 2 H), 0.81 (t, 3 H); MS, *m/e* 186 (M$^+$), 157, 105.

4-Nonyn-2-one (6) was prepared by oxidation of 4-nonyn-2-ol using a procedure similar to that of Brandsma and Verkruijsse:[19] IR (neat) 2250, 1720 cm^{-1}; ^{1}H NMR (CCl$_4$) 3.0 (s, 2 H), 2.1 (s, 3 H), 1.9 (m, 2 H), 1.5 (m, 4 H), 1.0 (t, 3 H); MS, *m/e* 138 (M$^+$); calcd exact mass for C$_9$H$_{14}$O 138.103, found 138.102.

3,4-Nonadien-2-one (7).[19a] A mixture of **6** (21.7 mmol), K$_2$CO$_3$ (3 mmol), and water (5 mL) was stirred at 35 °C for 4 h and the mixture was extracted three times with small portions of diethyl ether. The extract was dried over sodium sulfate and after removing the solvent, the product was purified by column chromatography on silica gel: yield 50%; IR 1950, 1680 cm^{-1}; ^{1}H NMR (CCl$_4$) 5.5 (m, 2 H), 2.2 (s, 3 H), 2.0 (m, 2 H), 1.4 (m, 4 H), 0.9 (t, 3 H); MS, *m/e* 138 (M$^+$).

Characterization of [2,3,4,5-η^4-1-Phenyl-(2E,4E)-hexa-2,4-dien-1-one]hydridobis(triisopropylphosphine)iridium. A solution of IrH$_5$(i-Pr$_3$P)$_2$ (0.08 mmol), 1-phenyl-2-hexyn-1-one (**1b**, 0.08 mmol), and benzene (2 mL) was heated at 60 °C for 1 h. The resulting red solution was evaporated to dryness to give a red oil; IR (Nujol) 1950, 1695, 1500, 1450 cm^{-1}; ^{1}H NMR (200 MHz, C$_6$D$_6$) 7.95 (m, 2 H), 6.90 (m, 3 H), 3.26 (dd, J_{23} = J_{34} = J_{45} = 8 Hz, 2 H; H$_3$ and H$_4$; this peak turned to single peak by irradiation at δ 1.6–1.8), 1.6–1.8 (m, 8 H; H$_2$, H$_5$, and PCH<; this peak turned to multiplet and doublet by irradiation at δ 0.7–1.0), 0.7–1.0 (m, 39 H, CH$_3$), –12.2 (dt, J_{PH} = 24 Hz, 1 H, IrH); ^{13}C NMR (C$_6$D$_6$) 198.59, 139.76, 133.23, 131.03, 56.75, 39.12, 32.48, 24.33, 15.76; MS, *m/e* 685 (M$^+$), 513, 512, 510, 508, 466, 424, 422, 160, 105, 76.

The same product is obtained as determined by ^{1}H NMR and ^{13}C NMR spectra if 1-phenyl-(2E,4E)-hexa-2,4-dien-1-one (**2b**) is used as starting material to react with IrH$_5$(i-Pr$_3$P)$_2$ in benzene at 60 °C for 1 h.

(26) Mitsudo, T.; Nakagawa, Y.; Watanabe, K.; Hori, Y.; Misawa, H.; Watanabe, H.; Watanabe, Y. *J. Org. Chem.* **1985**, *50*, 565.

(27) Harris, R. O.; Hota, N. K.; Sadavoy, L.; Yuen, J. M. C. *J. Organomet. Chem.* **1973**, *54*, 259.

(28) Holm, R. *Inorg. Synth.* **1970**, *12*, 238.

(29) Ahmad, N.; Levison, J. J.; Robinson, S. D.; Uttley, M. F. *Inorg. Synth.* **1974**, *15*, 58.

(30) Osborn, J. A.; Wilkinson, G. *Inorg. Synth.* **1967**, *10*, 67.

(31) Herde, J. L.; Lambert, J. C.; Senoff, C. V.; *Inorg. Synth.* **1974**, *15*, 18.

(32) Browden, K.; Hellbron, I. M.; Jones, E. R. H.; Weedon, B. C. L. *J. Chem. Soc.* **1946**, 39.

(33) Vasil'eva, R. L.; Li, M. L.; Shchelknnov, A. V. *Chem. Abstr.* **1977**, *87*, 5325.

(34) Yamada, K.; Miyaura, N.; Itoh, M.; Suzuki, A. *Synthesis* **1977**, 679.

(35) Garrilenlo, V. V.; Ivanov, L. L.; Zakharkin, L. I. *Zh. Obshch. Khim.* **1965**, *35*, 635; *Chem. Abstr.* **1965**, *63*, 55478g.

(36) Shaw, J. E.; Sherry, J. J. *Tetrahedron Lett.* **1971**, 4379.