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FACILE SYNTHESIS OF (2E,4E)-DIENOIC ESTERS VIA STEREOSELECTIVE ISOMERIZATION OF 2-YNOIC ESTERS

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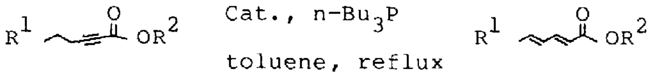
Abstract: (2E,4E)-Dienoic esters were synthesized stereoselectively from the corresponding 2-ynoic esters in high yield under the catalysis of an iridium hydride or ruthenium hydride complex.

Recently, we reported the highly stereoselective synthesis of (E,E)-α,β-γ,δ-dienones via isomerization of α,β-ynones effected by transition metal complexes.[1] The isomerization of alkynes to conjugated dienes can represent a useful synthetic approach due to the ready accessibility and elaboration of alkynes.[2] (2E,4E)-Dienoic esters are valuable synthetic intermediates,[3] while some (2E,4E)-dienoic esters such as (2E,4E)-decadienoic esters are also aromatic substances.[3a,4] Herein, we wish to report the $IrH_5(i\text{-}Pr_3P)_2$ or $RuH_2(Ph_3P)_4$ catalyzed isomerization of 2-ynoic esters as a practical synthetic method for the preparation of (2E,4E)-dienoic esters.



1 2

A typical procedure is as follows: A mixture of **1c** (4 mmol), $RuH_2(Ph_3P)_4$ (0.04 mmol) and n-Bu_3P (0.24 mmol) in toluene (4 mL) was heated at reflux for 28 h. After removal of the solvent, the red residue was distilled under reduced pressure. The product **2c** was obtained in 90% yield as a colorless oil. The results are shown in the Table.

In the absence of n-Bu_3P, the $IrH_5(i\text{-}Pr_3P)_2$ catalyzed isomerization of methyl 2-heptynoate (**1a**) gave poor yield, but this reaction gave complete conversion by adding 4 mol% of n-Bu_3P (compare entries 1 and 2). Complex $IrH_5(i\text{-}Pr_3P)_2$ has higher catalytic activity than $RuH_2(Ph_3P)_4$ (compare entries 1 and 3).

The high stereoselectivity of the reaction is shown by ^1H NMR spectra. As (E,E)-α,β-γ,δ-dienones,[1a] the stereochemistry of (2E,4E)-dienoic esters can be determined by ^1H NMR using C_6D_6 as solvent,[5] while using $CDCl_3$ or CCl_4 as solvent gave difficultly recognized spin-spin coupling constant of H_3 and H_4.[3] To the best of our knowledge, although there have appeared many methods involving the Wittig reaction and the elimination reaction for preparing (2E, 4E)-dienoic esters, only a few of them gave exclusively (2E,4E)-dienoic esters.[3] Therefore, our results may provide a convenient and useful method for

Table. Isomerization of 2-ynoic esters to (2E,4E)-dienoic esters catalyzed by $IrH_5(i\text{-}Pr_3P)_2$ or $RuH_2(Ph_3P)_4$[a]

Entry	Ynoic esters(**1**) R^1	R^2	Catalyst	$n\text{-}Bu_3P$/cat.	Temp. (^oC)	Time (h)	Yield of **2**[b] (%)
1	C_2H_5	CH_3(**1a**)	$IrH_5(i\text{-}Pr_3P)_2$	0	80	24	48[c]
2	**1a**		$IrH_5(i\text{-}Pr_3P)_2$	4	80	30	87
3	**1a**		$RuH_2(Ph_3P)_4$	0	80	24	0[c]
4	**1a**		$RuH_2(Ph_3P)_4$	6	80	24	58[c]
5	$n\text{-}C_5H_{11}$	CH_3(**1b**)	$IrH_5(i\text{-}Pr_3P)_2$	4	80	24	92
6	$n\text{-}C_5H_{11}$	C_2H_5(**1c**)	$RuH_2(Ph_3P)_4$	6	110	28	90
7	C_2H_5	C_2H_5(**1d**)	$RuH_2(Ph_3P)_4$	6	110	30	86
8	CH_3	CH_3(**1e**)	$IrH_5(i\text{-}Pr_3P)_2$	4	110	24	85
9	CH_3	C_2H_5(**1f**)	$RuH_2(Ph_3P)_4$	6	110	30	88
10	$n\text{-}C_3H_7$	CH_3(**1g**)	$IrH_5(i\text{-}Pr_3P)_2$	4	110	24	89
11	$n\text{-}C_3H_7$	C_2H_5(**1h**)	$IrH_5(i\text{-}Pr_3P)_2$	4	110	24	90

a: Reaction condition: entries 1-5 were carried out in benzene; entries 6-12 were carried out in toluene.
b: Isolated yield. All products gave satisfactory IR, ^1H NMR and MS data.
c: Determined by ^1H NMR spectra.

the highly stereoselective synthesis of (2E,4E)-dienoic esters.

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5. Taking **2c** as an example: ^1H NMR(200 MHz, C_6D_6): 0.85(t, 3H), 1.0(t, 3H), 1.20(m, 6H), 1.80(m, 2H), 4.10(q, 2H), 5.70(dt, J_{54}=15.2 Hz, J_{56}=7.0 Hz, 1H), 5.85(dd, J_{43}=10.8 Hz, J_{45}=15.2 Hz, 1H), 5.90(d, J_{23}=15.4 Hz, 1H), 7.52(dd, J_{32}=15.4 Hz, J_{34}=10.8 Hz, 1H).

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