

Ruthenium-catalyzed formal [4 + 2] cycloaddition of alkynes with alkenes: formation of cyclohexenedicarboxylates via isomerization of alkynes and successive Diels–Alder reaction

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Abstract

Formal [4 + 2] cycloaddition of alkynes with electron-deficient alkenes, which affords 3,6-dialkyl-4-cyclohexene-1,2-dicarboxylates, was achieved using $\text{Ru}(\eta^6\text{-1,3,5-cyclooctatriene})(\eta^2\text{-dimethyl fumarate})_2$ as a catalyst. The reaction mechanism consists of two steps, isomerization of an alkyne to conjugated dienes and successive Diels–Alder reaction of the generated dienes with an electron-deficient alkene.

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1. Introduction

In recent years, metal-catalyzed co-oligomerizations of alkynes and alkenes have been widely developed which are represented by cycloadditions [1] and linear coupling reactions [2,3]. Among the 1:1 cycloadditions of alkynes and alkenes, [2 + 2] reaction is well known, where strained alkenes such as 2-norbornene and 2,5-norbornadiene react with alkynes to give cyclobutenes in the presence of several late transition metal catalysts [4–7]. Pd-catalyzed intramolecular version has also been developed to yield tricyclic compounds [8]. Formal [3 + 2] cycloaddition of propargyl halides with alkenes gives halocyclopentenes via allenyl cation intermediates [9].

During the course of our investigation on the codimerizations of unsaturated hydrocarbons, we found an apparent '[4 + 2] cycloaddition' of simple alkynes with electron-deficient dimethyl fumarate to give *trans*-4-cyclohexene-1,2-dicarboxylates. The catalyst most suitable for this reaction is a zerovalent ruthenium complex with olefinic ligands, $\text{Ru}(\text{cot})(\text{dmfm})_2$ [1; cot = 1,3,5-cyclooctatriene, dmfm = dimethyl fumarate] [10,11], which was reported by us previously and is prepared by the reaction of $\text{Ru}(\text{cod})(\text{cot})$ [cod = 1,5-cyclooctadiene] with 2 equiv of dimethyl fumarate or dimethyl maleate [10]. The results and a proposed reaction mechanism of the formal [4 + 2] cycloaddition are described herein.

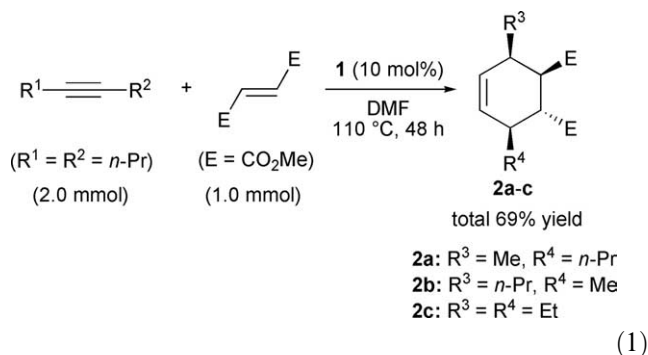
2. Results and discussion

Treatment of dimethyl fumarate with 4-octyne (2 fold excess) in the presence of **1** as a catalyst (10 mol%) in

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DMF at 110 °C for 48 h gave a mixture of cycloadducts, dimethyl 3,6-dialkyl-4-cyclohexene-1,2-dicarboxylates **2a–c**, in total 69% yield (Eq. (1)). The product consists of a mixture of two diastereomers (**2a** and **2b**) and a regioisomer (**2c**) in the ratio of 1.5:1.5:1.



Catalytic activity of several ruthenium complexes in the formal [4 + 2] cycloaddition of 4-octyne with dimethyl fumarate was examined (Table 1). Ru(cod)(cot) gave cyclohexenedicarboxylates in a moderate yield (entry 2). Under the present reaction conditions, Ru(cod)- (cot) would be converted into a highly active catalyst **1** in situ by the reaction with dimethyl fumarate [10]. Ru₃(CO)₁₂, which is a representative zerovalent catalyst, was not active (entry 3). RuHCl(CO)(PPh₃)₃ and RuCl₂(PPh₃)₃ were less effective and afforded the cycloadducts in lower yields (entries 4 and 5). Other ruthenium complexes such as RuH₂(PPh₃)₄, CpRuCl(cod), Cp*RuCl(cod) and RuCl₃ · 3H₂O were ineffective.

Several internal alkynes were used in the reaction (Table 2). 6-Dodecyne also afforded a mixture of three isomers (entry 2). Noteworthy is that in the case of 3-hexyne the cycloaddition proceeded regio- and stereo-selectively, and the sole product was obtained in 39% yield (entry 3). As an unsymmetrical alkyne, 3-octyne was reacted with dimethyl fumarate to give the same products as in entry 1 in relatively lower yield (entry 4). In entries 3 and 4, conversions of dimethyl fumarate were comparatively low and many small amount of byproducts were detected by GC analyses. When dimethyl maleate was

used instead of dimethyl fumarate, the products were not *cis*-1,2-dicarboxylates but *trans* isomers (entry 5). This result is reasonably explained by the rapid isomerization of dimethyl maleate to dimethyl fumarate catalyzed by **1** [10]. Except for entry 3, the products obtained under these reaction conditions were a mixture of two diastereomers and a regioisomer (the ratio was constantly 1.5:1.5:1), and the other isomers were not obtained. Other electron-deficient alkenes such as quinones, maleic anhydride and maleimides, which directly reacted with the catalyst to deactivate, were not applicable.

To elucidate the mechanism, following experiments were carried out. In the presence of **1** (10 mol%), a DMF solution (2 mL) of 4-octyne (2.0 mmol) was treated at 110 °C for 48 h affording a mixture of conjugated C₈-dienes, which were confirmed by comparing with the products prepared by Wittig reaction of butyraldehyde with a crotyl phosphonium salt. This fact strongly indicates that the first step of the present reaction is an isomerization of an alkyne to conjugated dienes. Actually, a small amount of C₈-dienes were detected in the reaction of 4-octyne and dimethyl fumarate in the presence of **1**. Isomerizations of *functionalized alkynes* to conjugated dienes have been known to be catalyzed by either late-transition metal hydride complexes [12–15] or PPh₃ [16]. However, no report of the isomerization of simple internal aliphatic alkynes to conjugated dienes could be found, probably because of the low regio- and stereo-selectivity.

A plausible mechanism of the present formal [4 + 2] cycloaddition is shown in Scheme 1. The mechanism consists of two parts, first isomerization of an alkyne to conjugated dienes and second Diels–Alder reaction of the generated dienes with dimethyl fumarate. A ruthenium hydride species **4** would be generated initially, where the hydride should be derived from either the cyclooctatriene ligand or a dimethyl fumarate ligand on **1**. Although the ruthenium hydride species has not yet been successfully detected, a supporting evidence for the generation of the hydride species from **1** via sp² C–H bond activation of dimethyl fumarate has been found [11c]. The hydride species **4** then interacts with an alkyne (**5**), subsequent insertion gives **6** and β-hydrogen elimination leads to an allene complex **7**. Reinsertion of allene to the Ru–H bond (**8**, **9**) followed by β-hydrogen elimination gives conjugated dienes along with the regeneration of **4**. Since the regio- and stereo-selectivity cannot be perfectly controlled, several conjugated dienes are formed at this stage. For instance, the isomerization of 4-octyne would give not only (2*E*, 4*E*)-, (2*E*, 4*Z*)-, (2*Z*, 4*E*)- and (2*Z*, 4*Z*)-octadienes, but also other regioisomers such as 1,3- and 3,5-octadienes. In spite of this complexity, the cycloadducts converged on a single or three isomers. This could be interpreted as follows; the generated several conjugated

Table 1
Catalytic activity of several ruthenium complexes in the formal [4 + 2] cycloaddition of 4-octyne with dimethyl fumarate^a

Entry	Catalyst	Yield (%) ^b
1	Ru(cot)(dmfm) ₂ (1)	69
2	Ru(cod)(cot)	52
3	Ru ₃ (CO) ₁₂	0
4	RuHCl(CO)(PPh ₃) ₃	19
5	RuCl ₂ (PPh ₃) ₃	11

^a 4-Octyne (2.0 mmol), dimethyl fumarate (1.0 mmol), Ru catalyst (10 mol%), DMF (2.0 mL) under Ar at 110 °C for 48 h.

^b GC yield.

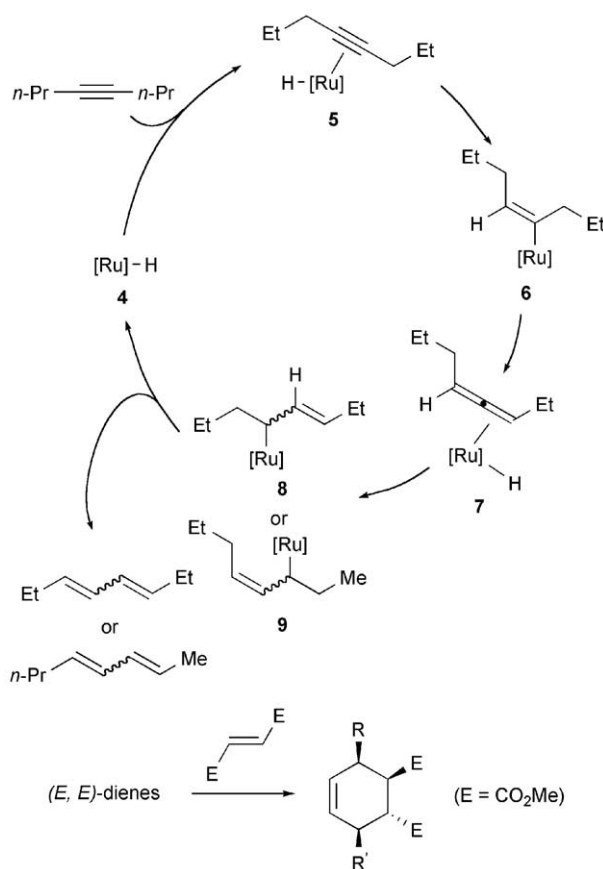
Table 2
Ru(cot)(dmfm)₂-catalyzed formal [4 + 2] cycloaddition of several internal alkynes with electron-deficient alkenes^a

Entry	Substrate			R ³	R ⁴	Yield (%) ^b
	R ¹	R ²	alkene			
1	<i>n</i> -Pr	<i>n</i> -Pr	dmfm	$\left\{ \begin{array}{l} \text{Me} \\ n\text{-Pr} \\ \text{Et} \end{array} \right.$	$\left. \begin{array}{l} n\text{-Pr} \\ \text{Me} \\ \text{Et} \end{array} \right\}$	69 (54)
2	<i>n</i> -C ₅ H ₁₁	<i>n</i> -C ₅ H ₁₁	dmfm			$\left\{ \begin{array}{l} n\text{-Pr} \\ n\text{-C}_5\text{H}_{11} \\ n\text{-Bu} \end{array} \right.$
3	Et	Et	dmfm	$\left\{ \begin{array}{l} \text{Me} \\ n\text{-Pr} \\ \text{Et} \end{array} \right.$	$\left. \begin{array}{l} \text{Me} \\ n\text{-Pr} \\ \text{Et} \end{array} \right\}$	
4	Et	<i>n</i> -Bu	dmfm			$\left\{ \begin{array}{l} \text{Me} \\ n\text{-Pr} \\ \text{Et} \end{array} \right.$
5	<i>n</i> -Pr	<i>n</i> -Pr	dmml ^c	$\left\{ \begin{array}{l} \text{Me} \\ n\text{-Pr} \\ \text{Et} \end{array} \right.$	$\left. \begin{array}{l} n\text{-Pr} \\ \text{Me} \\ \text{Et} \end{array} \right\}$	

^a Alkyne (2.0 mmol), alkene (1.0 mmol), **1** (10 mol%), DMF (2.0 ml) under Ar at 110 °C for 48 h.

^b GC yield. Figures in parentheses are isolated yield.

^c dmml, dimethyl maleate.



Scheme 1. A plausible mechanism of the formal [4 + 2] cycloaddition of 4-octyne with dimethyl fumarate.

dienes are in equilibrium each other catalyzed by the ruthenium hydride species, and only some dienes such as (2*E*, 4*E*)- and (3*E*, 5*E*)-octadiene, which are relatively

thermally stable and most reactive toward electron-deficient alkenes, can react to afford Diels–Alder adducts. Then the equilibrium would shift toward the formation of the consumed dienes. The lower yield of products in the reactions of 3-hexyne and 3-octyne (entries 3 and 4 in Table 2) would due to the relatively predominant formation of 1,3-dienes, which did not give the Diels–Alder adducts and might cause side reactions or deactivate the catalyst. Although the ruthenium catalyst was also expected to work as a Lewis acid to accelerate the Diels–Alder reaction, no remarkable effect was observed in this system.

3. Conclusion

A novel type of formal [4 + 2] cycloaddition of alkynes with alkenes was achieved. Although the isomerization of alkynes to dienes cannot yet be perfectly controlled, the combination with subsequent Diels–Alder reaction makes the present reaction intriguing as a one-pot cycloaddition of alkynes with alkenes.

4. Experimental

4.1. Materials and methods

All manipulations were performed under an argon atmosphere by standard Schlenk techniques. All solvents were distilled under argon over appropriate drying reagents (sodium or calcium hydride). Ru(cot)(dmfm)₂ (**1**) was synthesized as described in the literature [10]. Alkynes, dimethyl fumarate, dimethyl maleate

were obtained commercially and used without further purification.

4.2. Physical and analytical measurements

NMR spectra were recorded on a JEOL EX-400 (FT, 400 MHz (^1H), 100 MHz (^{13}C)) spectrometer. Chemical shifts (δ) for ^1H and ^{13}C are referenced to internal solvent resonances and reported relative to SiMe_4 . ^{13}C NMR Inadequate measurements were performed on a Bruker Dual Cryoprobe at Bruker BioSpin Corporation. IR spectra were recorded using a Nicolet Impact 410 FT-IR spectrometer. GC-MS studies were conducted on a Shimadzu GCMS-QP5000 instrument with 70-eV electron impact ionization. Elemental analyses were performed at the Microanalytical Center of Kyoto University. Analytical gas chromatography was performed on a Shimadzu GC-14B gas chromatograph with FID detection using a 3.2 mm i.d. \times 3 m glass column with 2% (w/w) silicone OV-17 liquid phase on a Chromosorb W(AW DMCS) support in 60/80 mesh. Biphenyl and 2-methylnaphthalene were used as internal standards. The products were purified on a Japan Analytical Industry Co. Ltd., Model LC-918 recycling preparative HPLC equipped with JAIGEL-1H and 2H columns (GPC) using CHCl_3 as an eluent.

4.3. General reaction procedure

The reaction of 4-octyne with dimethyl fumarate is representative. 4-Octyne (216 mg, 2.0 mmol) was added to a DMF solution (2.0 ml) of dimethyl fumarate (144 mg, 1.0 mmol) and $\text{Ru}(\text{cot})(\text{dmfm})_2$ (**1**) (50 mg, 0.10 mmol). The reaction mixture was stirred at 110 °C for 48 h. After evaporation of the solvent, flash column chromatography was carried out on MERCK silica gel 60 with a 1:20 ethyl acetate–hexane mixture as an eluent to remove the ruthenium catalyst. Further purification by recycling preparative HPLC gave a mixture of cycloadducts **2a–2c** (1.5:1.5:1). Structures of these products were determined by GC-MS, NMR (including ^{13}C Inadequate method), IR and elemental analysis.

4.3.1. ($1R^*,2R^*,3S^*,6R^*$)-Dimethyl 3-methyl-6-n-propyl-4-cyclohexene-1,2-dicarboxylate (**2a**), ($1R^*,2R^*,3R^*,6S^*$)-dimethyl 3-methyl-6-n-propyl-4-cyclohexene-1,2-dicarboxylate (**2b**) and ($1R^*,2R^*,3R^*,6S^*$)-dimethyl 3,6-diethyl-4-cyclohexene-1,2-dicarboxylate (**2c**)

Colorless liquid, b.p. 100–110 °C (0.2 mmHg). Anal. Calc. for $\text{C}_{14}\text{H}_{22}\text{O}_4$: C, 66.12; H, 8.72. Found: C, 66.35; H, 8.99%. IR spectrum (neat) 1738, 1436 cm^{-1} . For compound **2a** (or **2b**): ^1H NMR (CDCl_3 , 400 MHz) δ 5.69 (ddd, 1H, olefin, $J = 2.4, 5.2, 10.2$ Hz), 5.53 (dt, 1H, olefin, $J = 1.8, 10.2$ Hz), 3.72 (s, 3H, CO_2CH_3), 3.68 (s, 3H, CO_2CH_3), 3.12–3.06 (m, 1H, CHCO_2Me), 2.70–2.66 (m, 1H, CHMe), 2.35–2.26 (m, 1H, CHPr),

2.58–2.55 (m, 1H, CHCO_2Me), 1.67–1.09 (m, 4H, $\text{CH}_2\text{CH}_2\text{CH}_3$), 0.91–0.85 (m, 6H, CHCH_3 and $\text{CH}_2\text{CH}_2\text{CH}_3$); ^{13}C NMR (CDCl_3 , 100 MHz) δ 176.18 (CO), 173.99 (CO), 130.79 (olefin), 128.53 (olefin), 51.70 (2C, CO_2CH_3), 46.68 (CHCO_2Me), 42.08 (CHCO_2Me), 39.53 (CHPr), 35.20 ($\text{CH}_2\text{CH}_2\text{CH}_3$), 31.22 (CHMe), 18.68 ($\text{CH}_2\text{CH}_2\text{CH}_3$), 16.91 (CHCH_3), 14.36 ($\text{CH}_2\text{CH}_2\text{CH}_3$). For compound **2b** (or **2a**): ^1H NMR (CDCl_3 , 400 MHz) δ 5.78 (ddd, 1H, olefin, $J = 2.4, 5.2, 9.8$ Hz), 5.47 (dt, 1H, olefin, $J = 1.8, 9.8$ Hz), 3.72 (s, 3H, CO_2CH_3), 3.68 (s, 3H, CO_2CH_3), 3.12–3.06 (m, 1H, CHCO_2Me), 2.58–2.55 (m, 1H, CHPr), 2.46 (t, 1H, CHCO_2Me , $J = 11.2$ Hz), 2.35–2.26 (m, 1H, CHMe), 1.67–1.09 (m, 4H, $\text{CH}_2\text{CH}_2\text{CH}_3$), 1.06 (d, 3H, CHCH_3 , $J = 7.2$ Hz), 0.91–0.85 (m, 3H, $\text{CH}_2\text{CH}_2\text{CH}_3$); ^{13}C NMR (CDCl_3 , 100 MHz) δ 176.11 (CO), 174.03 (CO), 131.20 (olefin), 128.44 (olefin), 51.70 (2C, CO_2CH_3), 46.77 (CHCO_2Me), 45.22 (CHCO_2Me), 35.74 (CHPr), 35.03 (CHMe), 34.89 ($\text{CH}_2\text{CH}_2\text{CH}_3$), 20.35 ($\text{CH}_2\text{CH}_2\text{CH}_3$), 19.89 (CHCH_3), 14.25 ($\text{CH}_2\text{CH}_2\text{CH}_3$). For compound **2c**: ^1H NMR (CDCl_3 , 400 MHz) δ 5.87 (ddd, 1H, olefin, $J = 2.4, 5.2, 10.8$ Hz), 5.57 (dt, 1H, olefin, $J = 1.8, 10.8$ Hz), 3.71 (s, 3H, CO_2CH_3), 3.67 (s, 3H, CO_2CH_3), 3.12–3.06 (m, 1H, CHCO_2Me), 2.66–2.60 (m, 1H, CHCO_2Me), 2.49–2.42 (m, 1H, CHEt), 2.35–2.26 (m, 1H, CHEt), 1.67–1.09 (m, 4H, $\text{CH}_2 \times 2$), 0.93 (t, 3H, Me, $J = 7.4$ Hz), 0.90 (m, 3H, Me); ^{13}C NMR (CDCl_3 , 100 MHz) δ 176.28 (CO), 174.14 (CO), 129.07 (olefin), 128.99 (olefin), 51.7 (2C, CO_2CH_3), 46.88 (CHCO_2Me), 41.95 (CHCO_2Me), 40.78 (CHEt), 37.62 (CHEt), 25.56 (CH_2), 25.50 (CH_2), 11.87 (Me), 9.64 (Me).

4.3.2. ($1R^*,2R^*,3S^*,6R^*$)-Dimethyl 3-n-pentyl-6-n-propyl-4-cyclohexene-1,2-dicarboxylate (**2d**), ($1R^*,2R^*,3R^*,6S^*$)-dimethyl 3-n-pentyl-6-n-propyl-4-cyclohexene-1,2-dicarboxylate (**2e**) and ($1R^*,2R^*,3R^*,6S^*$)-dimethyl 3,6-n-dibutyl-4-cyclohexene-1,2-dicarboxylate (**2f**)

Colorless liquid. Anal. Calc. for $\text{C}_{18}\text{H}_{30}\text{O}_4$: C, 69.64; H, 9.74. Found: C, 69.62; H, 9.53%. IR spectrum (neat) 1738, 1435 cm^{-1} . For compound **2d**, **2e** and **2f**: ^1H NMR (CDCl_3 , 400 MHz) δ 5.85–5.80 (m, 1H, olefin), 5.57 (d, 1H, olefin, $J = 10.8$ Hz), 3.72 (s, 3H, CO_2CH_3), 3.68 (s, 3H, CO_2CH_3), 3.08 (dd, 1H, CHCO_2Me , $J = 5.2, 11.0$ Hz), 2.61 (t, 1H, CHCO_2Me , $J = 11.0$ Hz), 2.57–2.50 (m, 1H, CHR), 2.35–2.24 (m, 1H, CHR), 1.56–1.11 (m, CH_2 of R), 0.94–0.85 (m, 3H, Me); ^{13}C NMR (CDCl_3 , 100 MHz) δ 176.30 (CO), 174.10 (CO), 129.08 (olefin), 129.03 (olefin), 51.72 (CO_2CH_3), 51.69 (CO_2CH_3), 51.66 (CO_2CH_3), 46.99, 46.96, 42.73, 42.69, 42.66, 39.76, 39.71, 39.63, 35.98, 35.94, 35.77, 35.28, 34.85, 32.91, 32.63, 32.57, 32.30, 32.04, 31.92, 29.36, 27.61, 26.86, 25.09, 22.92, 22.81, 22.64, 22.55, 22.53, 20.37, 18.75, 14.37 (Me), 14.27 (Me), 14.09 (Me), 14.07 (Me), 14.02 (Me), 13.96 (Me).

4.3.3. (1*R**2*R**,3*R**,6*S**)-Dimethyl 3,6-dimethyl-4-cyclohexene-1,2-dicarboxylate (2*g*)

Colorless liquid. IR spectrum (neat) 1738, 1733, 1436 cm^{-1} .

^1H NMR (CDCl_3 , 400 MHz) δ 5.66 (ddd, 1H, olefin, $J = 2.4, 4.8, 10.0$ Hz), 5.43 (dt, 1H, olefin, $J = 1.6, 10.0$ Hz), 3.73 (s, 3H, CO_2CH_3), 3.68 (s, 3H, CO_2CH_3), 3.09 (dd, 1H, CHCO_2Me , $J = 5.6, 11.5$ Hz), 2.70 (m, 1H, CHMe), 2.43 (t, 1H, CHCO_2Me , $J = 11.5$ Hz), 2.33 (m, 1H, CHMe), 1.06 (d, 3H, Me, $J = 6.8$ Hz), 0.87 (d, 3H, Me, $J = 7.6$ Hz). ^{13}C NMR (CDCl_3 , 100 MHz) δ 176.01 (CO), 173.92 (CO), 130.63 (olefin), 130.23 (olefin), 51.86 (CO_2CH_3), 51.70 (CO_2CH_3), 46.44 (CHCO_2Me), 44.55 (CHCO_2Me), 34.90 (CHMe), 31.16 (CHMe), 19.87 (CHCH_3), 16.99 (CHCH_3).

4.4. Synthesis of 2,4-octadienes

Crotyl chloride (2.36 g, 26.0 mmol) was added to a toluene solution (10 ml) of triphenylphosphine (6.53 g, 24.9 mmol), and the mixture was refluxed for 10 h. The formed white precipitate (phosphonium chloride) was filtered, washed with diethyl ether, and dried under vacuum. This phosphonium chloride (5.85 g, 16.6 mmol) and sodium amide (0.70 g, 18.0 mmol) were dissolved in THF, and cooled to -78°C . Butyraldehyde (1.45 g, 20.2 mmol) was added dropwise over 20 min, and stirring was continued for 40 min at -78°C . After the reaction mixture was stirred for further 2 h at room temperature, cooled pentane was added to precipitate triphenylphosphine oxide. After filtration, the filtrate was concentrated in vacuo cautiously to remove pentane. The residue was distilled under reduced pressure (50 mmHg, 100°C), which gave 2,4-octadienes (0.38 g, 3.46 mmol) as a mixture of four stereoisomers.

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