Selective Linear Codimerization of Terminal Acetylenes and 1,3-Butadienes Catalyzed by (η^4-1,5-Cyclooctadiene)(η^6-1,3,5-cyclooctatriene)ruthenium(0)-Trialkylphosphine

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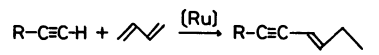
The reaction of terminal acetylenes with 1,3-butadienes catalyzed by (η^4-1,5-cyclooctadiene)(η^6-1,3,5-cyclooctatriene)ruthenium [Ru^0(COD)(COT)]-PR$_3$ (R=ethyl, butyl, octyl) in various solvents at 80 °C afforded linear codimers in good to excellent yield with high chemo-, regio-, and stereoselectivities. Reactions of deuterated acetylenes were also examined.

Recently, much attention has been focused on finding novel organic reactions catalyzed by ruthenium complexes.[1–18] With regard to carbon–carbon bond formation, however, characteristic organic syntheses with ruthenium catalysts are still limited.[1–9] In the course of our study on organic syntheses catalyzed by low-valent ruthenium complexes,[1,2] the first example of the selective linear codimerization of terminal aliphatic acetylenes and 1,3-butadienes catalyzed by dihydridotetrakis(trialkylphosphine)ruthenium [RuH$_2$(PR$_3$)$_4$, R= ethyl or butyl] has been found.[2] We now report a novel and versatile catalytic system, (η^4-1,5-cyclooctadiene)(η^6-1,3,5-cyclooctatriene)ruthenium [Ru(COD)-(COT)]-PR$_3$ system, for this linear codimerization. The optimum reaction conditions, the effects of various phosphine ligands and solvents, and the reaction path of the codimerization are investigated.

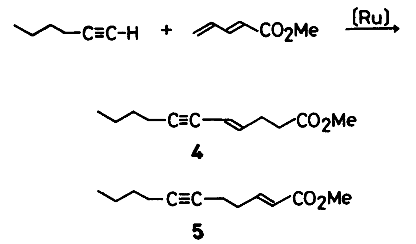
Results and Discussion

1-Hexyne and 3,3-dimethyl-1-butyne readily reacted with 1,3-butadiene in the presence of a catalytic amount of Ru(COD)(COT)-PBu^n$_3$ in benzene at 80 °C for 4 h to give (*E*)-3-decen-5-yne (**1**) and (*E*)-7,7-dimethyl-3-octen-5-yne (**2**), respectively (Table 1, Runs 1 and 2). The reaction of ethyl 2-ethoxycarbonyl-4-pentynoate with 1,3-butadiene gave ethyl (*E*)-2-ethoxycarbonyl-6-nonen-4-ynoate (**3**) in 80% yield (Run 3). On the other hand, the reaction of 1-hexyne with methyl (*E*)-2,4-pentadienoate gave two isomers of the codimer, **4** and **5**, respectively (Run 4, Eq. 2).



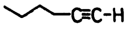
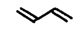
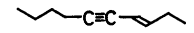
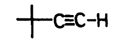
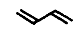
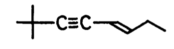
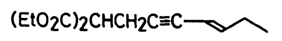
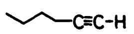
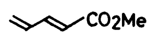
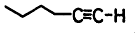
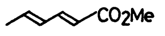
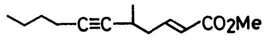
1,2,and 3 (1)

R= n-Bu, t-Bu, (EtO$_2$C)$_2$CHCH$_2$.
[Ru]=Ru(COD)(COT)-PR'$_3$ (R'=Et, n-Bu, n-C$_8$H$_{17}$)



(2)

Table 1. Linear Codimerization of Acetylenes with 1,3-Dienes Catalyzed by Ru(COD)(COT)-PBu^n$_3$[a)]

Run	Acetylene	1,3-Diene	Product	Yield/%[b)]
1				**1** 94
2				**2** 96
3[c)]	(EtO$_2$C)$_2$CHCH$_2$C≡C-H			**3** 80(57)
4[d)]			 	**4** (32) 4/5=64/36 **5**
5[e)]				**6** (45)

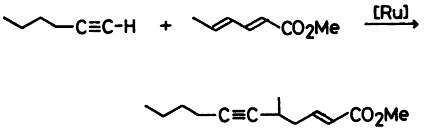
a) Acetylene, 10 mmol; Diene, 20 mmol; Ru(COD)(COT), 0.1 mmol; PBu^n$_3$, 0.2 mmol; Solvent, Benzene 5.0 cm^3; 80 °C; 4 h. b) Determined by GLC based on the amount of acetylene. Isolated yields were given in the parentheses. c) Ru(COD)(COT), 0.2 mmol; PBu^n$_3$, 0.4 mmol; 80 °C; 20 h. d) Acetylene, 10 mmol; Diene, 15 mmol; 80 °C, 8 h. e) 80 °C; 8 h.

Table 2. The Ru-Catalyzed Linear Codimerization of 1-Hexyne and 1,3-Butadiene[a]
— Effects of Reaction Conditions

Run	Catalyst[b]	PBu^n_3	Reaction temp	Reaction time	Yield of (*E*)-3-decen-5-yne[c]
	mmol	mmol	°C	h	%
6	0.025	0.05	80	8	78
7	0.05	—	80	8	1
8	0.05	0.05	80	8	76
9	0.05	0.1	80	8	94
10	0.05	0.2	80	8	94
11	0.05	1.0	80	8	59
12	0.05	0.1	40	8	25
13	0.05	0.1	60	8	93
14	0.05	0.1	100	8	79
15	0.05	0.1	80	1	51
16	0.05	0.1	80	2	78
17	0.05	0.1	80	4	95
18	0.1	0.2	80	8	94
19	0.2	0.4	80	8	89(73)

a) 1-Hexyne, 10 mmol; 1,3-Butadiene, 20 mmol; Benzene, 5.0 cm^3. b) Catalyst=Ru(COD)(COT) (COD=cyclooctadiene, COT=cyclooctatriene). c) Determined by GLC based on the amount of 1-hexyne. Isolated yield was given in the parentheses.

The reaction of 1-hexyne with methyl (*E*,*E*)-2,4-hexadienoate gave methyl (*E*)-5-methyl-2-undecen-6-ynoate (**6**) in 45% yield (Run 5, Eq. 3). The optimum mole ratio of 1,3-diene/acetylene was 2 to perform the codimerization suppressing the homooligomerization of the acetylene. The high chemo-, regio-, and stereoselectivities observed are almost the same as those found in the reactions catalyzed by $RuH_2(PBu^n_3)_4$.[2] Since the preparation of Ru(COD)(COT) is much easier than that of $RuH_2(PBu^n_3)_4$ and the present catalyst system is easily modified by adding an appropriate phosphine, the present catalyst system is regarded to be an improved one. The effects of the amount of catalyst, the ratio of PBu^n_3/Ru, the reaction temperature and the reaction time in the reaction of 1-hexyne with 1,3-butadiene were examined and the results are summarized in Table 2. In the absence of PBu^n_3 under the reaction conditions shown in Run 7 of the Table 2, the yield of the codimer **1** was 1%. When a catalytic amount of PBu^n_3 was added, the yield of the codimer **1** increased dramatically (94%) (Run 9). The effect of the amount of the catalyst is shown in Fig. 1. The maximum yield of the codimer **1** was obtained by using 0.5 mol% of Ru(COD)(COT) and 1.0 mol% of PBu^n_3 at 80 °C for 4—8 h (yield 95%). The effect of the mole ratio PBu^n_3/Ru(COD)(COT) is shown in Fig. 2. When the ratio was 2—4, the codimer **1** was obtained in 94% yield. When the ratio was 20, the yield of the codimer decreased to 59%.



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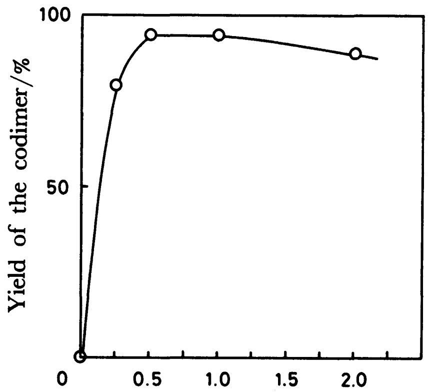


Fig. 1. The effect of the amount of catalyst. 1-Hexyne, 10 mmol; 1,3-Butadiene, 20 mmol; 80 °C; 8 h; PBu^n_3/Ru(COD)(COT)=2.

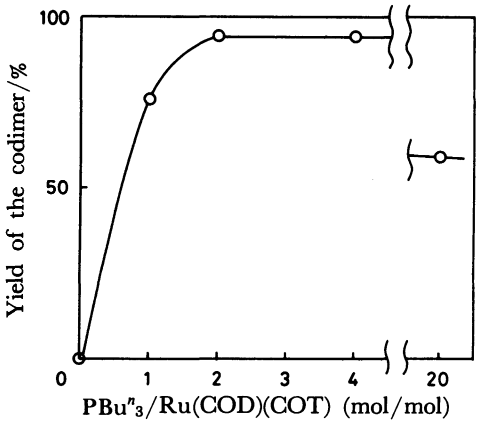


Fig. 2. The effect of the mole ratio PBu^n_3/Ru(COD)(COT). 1-Hexyne, 10 mmol; 1,3-Butadiene 20 mmol; Ru(COD)(COT) 0.5 mol%; 80 °C; 8 h.

The effect of various phosphine ligands on the codimerization of 1-hexyne and 1,3-butadiene is summarized in Table 3. When triethylphosphine, tributylphosphine, or trioctylphosphine was added, the reaction proceeded rapidly and afforded the (*E*)-3-decen-5-yne (**1**) in the yields of 87, 95, and 90%, respectively (Runs 20—22). Trimethylphosphine, triisopropylphosphine, and tricyclohexylphosphine were not effective. When PEt_3, PBu^n_3, $P(C_8H_{17}{}^n)_3$, PMe_3, PPr^i_3, and $P(c\text{-}C_6H_{11})_3$ were compared, alkylphosphines with 130° of cone angle were effective. Neither phosphine ligands with an aryl group nor triisopropylphosphite with 130° of cone angle was effective.

The effects of various solvents on the codimerization of acetylenes and 1,3-butadiene are summarized in Table 4. The polarity of the solvents (benzene, THF, toluene, CH_3CN, CH_2Cl_2, DMF, or acetone) does not appreciably affect the yield of the codimers; the corresponding codimers were obtained in excellent yields (Runs 1, 2, 23—28). In pyridine, no reaction occurred (Run 29).

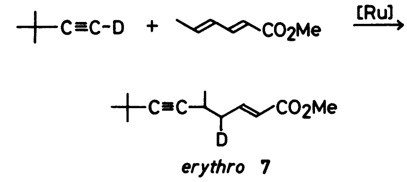
No codimer was obtained in the reactions of 1,3-butadiene with 3-hexyne, 2-propyn-1-ol, 2-methyl-3-butyn-2-ol, 2-propynyl acetate, ethyl 2-propynyl carbonate, 1-methoxy-2-propyne, or methyl propiolate.

Table 3. The Ru-Catalyzed Linear Codimerization of 1-Hexyne and 1,3-Butadiene with Phosphine Ligands[a,b)]

Run	Ligand (cone angle°)		Yield of (*E*)-3-decen-5-yne[c)] %
20	PEt_3	(132)	87
21	PBu^n_3	(130)	95
22	$P(C_8H_{17}{}^n)_3$	(—)	90

a) 1-Hexyne, 10 mmol; 1,3-butadiene, 20 mmol; Ru(COD)(COT), 0.05 mmol; Ligand, 0.1 mmol; Benzene, 5.0 cm³; 80 °C; 4 h. b) PMe_3(118°), PPr^i_3(160°), $P(c\text{-}C_6H_{11})_3$(170°), PMe_2Ph(122°), $PMePh_2$(136°), PPh_3(145°), P(*o*-Tol)$_3$(194°), 1,2-Bis(diphenylphosphio)ethane, 1,2-Bis(diethylphosphino)ethane, and $P(OPr^i)_3$(130°) were not effective. c) Determined by GLC based on the amount of 1-hexyne.

To obtain information on the reaction mechanism, the reactions of 1-pentyne-1-*d* or 3,3-dimethyl-1-butyne-1-*d* with 1,3-butadiene, methyl (*E,E*)-2,4-hexadienoate, or methyl (*E*)-2,4-pentadienoate were carried out. In the reaction of 3,3-dimethyl-1-butyne-1-*d* with methyl (*E,E*)-2,4-hexadienoate, erythro methyl (*E*)-5,8,8-trimethyl-2-nonen-6-ynoate-4-*d* (**7**) was obtained as a sole product (Eq. 4). The deuterium is introduced selectively at the 4 position of the codimer in a cis addition pathway.[2b)] The reaction of 1-pentyne-1-*d* with methyl (*E*)-2,4-pentadienoate gave four isomers of the codimer, **8—11**. The ratio (**8**+**9**)/(**10**+**11**) was 6/4 and both ratios, **8**/**9** and **10**/**11** were 1/1 (Eq. 5). The reaction of 3,3-dimethyl-1-butyne-1-*d* with methyl (*E*)-2,4-pentadienoate also gave a result similar to that described above. It should be noted that no deuterium was introduced into the olefinic groups of the products. The reaction of 1-pentyne-1-*d* with 1,3-butadiene gave, to our surprise, (*E*)-3-



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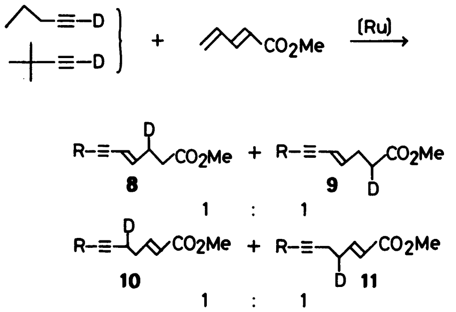
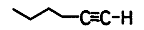
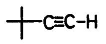
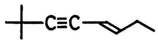
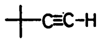
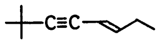
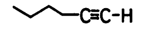
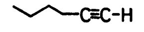
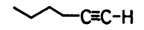
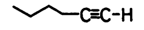
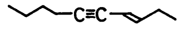
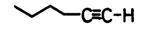
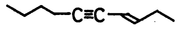
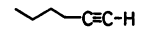
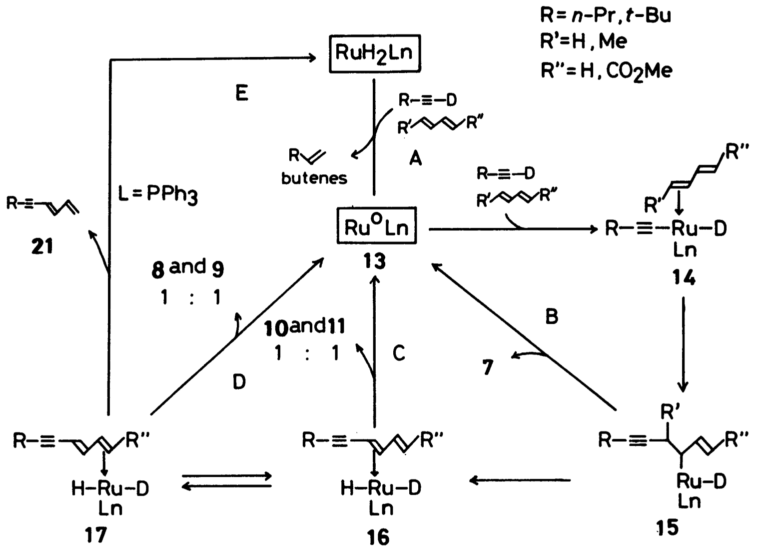


(5)

Table 4. The Ru-Catalyzed Linear Codimerization of Terminal Acetylenes with 1,3-Butadiene—Solvent Effects[a)]

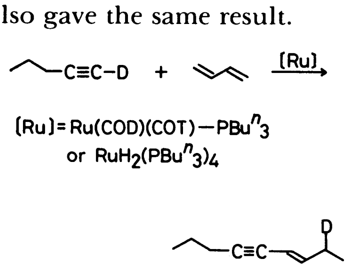
Run	Acetylene	Solvent	Product	Yield/%[b)]
1		Benzene		**1** 94
2		Benzene		**2** 96
23		THF		**2** 96(91)
24		Toluene		**1** 88
25		CH_3CN		**1** 91(82)
26		CH_2Cl_2		**1** 85
27		DMF		**1** 97
28		Acetone		**1** 88
29		Pyridine	—	0

a) Acetylene, 10 mmol; 1,3-Butadiene, 20 mmol; Ru(COD)(COT), 0.1 mmol; PBu^n_3, 0.2 mmol; Solvent, 5.0 cm³; 80 °C; 4 h. b) Determined by GLC based on the amount of acetylene. Isolated yields were given in the parentheses.



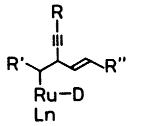
Scheme 1.

nonen-5-yne-2-*d* (**12**) as the sole product. Deuterium was introduced selectively at the 2 position of the codimer (Eq. 6). The reaction catalyzed by $\mathrm{RuH_2(PBu^n{}_3)_4}$ also gave the same result.



12 (6)

No clear-cut mechanism which explains these complicated results can be offered at the present time. Obviously, the mechanism of the formation of **7** is different from that of **12** because the position of the deuterium introduced is essentially different. The reaction path of the formation of the linear codimers **7** and **8**—**11** can be explained as follows (Scheme 1). Taking into account that both $\mathrm{Ru(COD)(COT)\text{–}PBu^n{}_3}$ and $\mathrm{RuH_2(PBu^n{}_3)_4}$ show almost the same catalytic activities and the identical distributions of the deuterium introduced in the reaction of deuterated acetylene (Eqs. 5 and 6), the reaction mechanism should be the same for both catalysts. The first step of the catalytic cycle would be the oxidative addition of acetylene to a zerovalent ruthenium complex **13** such as $\mathrm{Ru(PR_3)_n}$ derived by the reaction of Ru(COD)(COT) with trialkylphosphines or by the reaction of $\mathrm{RuH_2(PBu^n{}_3)_4}$ with the dienes or acetylenes. It has been reported that the reaction of $\mathrm{RuH_2(PPh_3)_4}$ with olefins such as ethylene or styrene gives zerovalent ruthenium complexes $\mathrm{Ru(olefin)(PPh_3)_3}$[20] at the early step of the reaction.[21] The formation of a zerovalent ruthenium complex was also reasonably assumed in the [2+2] cross addition of norbornenes with acetylenes catalyzed by $\mathrm{RuH_2(PPh_3)_4}$.[1] Then the η^2-coordination of the diene to the complex gives **14**. Insertion of the diene into the Ru-alkynyl bond would give **15**. If acetylene, instead of the diene, coordinates and inserts into the Ru-alkynyl bond, homooligomerization of acetylene proceeds. To prevent the insertion of acetylene, the mole ratio 2 of 1,3-diene/acetylene was required. When R′ and R″ in **15** are Me and $\mathrm{CO_2Me}$, respectively, i.e. in the reaction of methyl (*E*,*E*)-2,4-hexadienoate, the reductive elimination of the ligands would give **7** selectively. Considering the high chemo- and regioselectivity of the reaction and the fact that deuterium is not introduced into the olefinic groups of **8**—**11**, the formation of an intermediate **18** with a branched skeletone or **19** derived by the insertion of the diene into the Ru-D bond is ruled out. Complex **18** will not give a linear codimer. Once **19** is formed, the formation of **8**—**11** having no deuterium at the olefinic group and the distributions of the deuterium can not be explained (vide infra).



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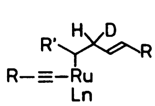
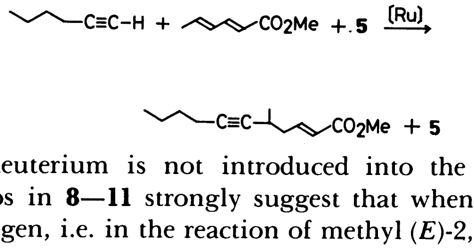


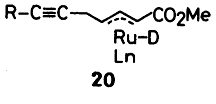
19

The possibility of the isomerization of **5** to **4** was investigated. The reaction of 1-hexyne with methyl (*E*,*E*)-2,4-hexadienoate was carried out in the presence of **5**; product **6** was obtained and **5** was recovered without the formation of **4** (Eq. 7). This fact and that



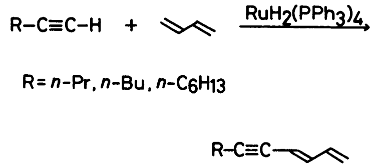
(7)

the deuterium is not introduced into the olefinic groups in **8**—**11** strongly suggest that when R′ is a hydrogen, i.e. in the reaction of methyl (*E*)-2,4-pentadienoate, *β*-elimination of **15** easily occurs giving the equilibrium mixture of a deuteridohydrido(η^2-dienyne)-ruthenium complex **16** and its isomer **17**. The hydrogenation of the coordinated dienyne in **16** or **17** gives two pairs of olefins (**10** and **11**), and (**8** and **9**), in both pairs the equivalent amount of deuterium is introduced in the methylene groups and no deuterium is introduced into the olefinic groups. In these steps the zerovalent ruthenium complex **13** is reproduced (path C and D). It is unlikely that a π-allyl complex such as **20** plays the role of the key intermediate



20

because the formation of **8**—**11** can not be explained. As has been reported in the previous paper,[2b)] when the ligand L is triphenylphosphine and R″ is hydrogen in **16** or **17**, i.e. in the reaction of 1,3-butadiene, the dissociation of the dienyne easily occurs giving **21** (path E, Eq. 8). The main reason of the dissociation

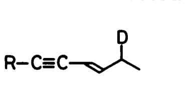


R = n-Pr, n-Bu, n-C$_6$H$_{13}$

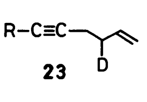
21 (8)

of **21** would be a larger cone angle of triphenylphosphine (145°) than that of tributylphosphine (130°).[22)]

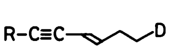
The explanation of the reaction path of the codimerization of 1-pentyne-1-*d* with 1,3-butadiene is confusing. The reaction path shown in the Scheme 1 should give **23** or the mixture of **12** and **22**; however, the result shows that the deuterium is selectively introduced into the 2 position of **12**. It is unlikely that the isomerization of **23** gives **12**, because in this case **24** should be detected in the products.



12



23



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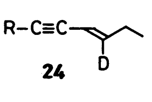

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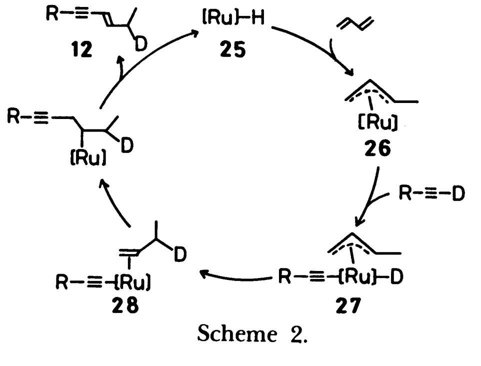
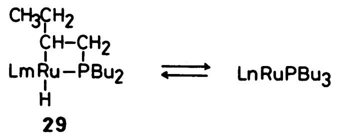
A speculated reaction path explaining these unusual results is shown in Scheme 2. If a monohydridoruthenium species **25** is present, a catalytic cycle via a π-allyl ruthenium complex could give **12** selectively. The first step of the reaction is a formation of a π-allyl ruthenium complex **26** by the coordination of 1,3-butadiene to hydridoruthenium species followed by the insertion of 1,3-butadiene to the hydrido-ruthenium bond. Oxidative addition of the 1-pentyne-1-*d* affords a π-allylalkynyldeuteridoruthenium complex **27**. Reductive elimination of the η^3-allyl group and the deuteride gives the alkynyl(π-olefin) complex **28**; insertion of the olefin into the alkynyl-Ru bond and β-elimination would give **12** selectively and the hydridoruthenium species again. As for the monohydridoruthenium species, it should be pointed out that complex **29** would be formed by the intramolecular oxidative addition of β-hydrogen of the tributylphosphine ligand (Eq. 9). Quite recently, similar intramolecular oxidative addition of an alkyl group of an alkylphosphine ligand has been reported.[19)]



Scheme 2.



$$\mathrm{LmRu(H)\text{–}PBu_2(CH_2CH(CH_2CH_3))} \rightleftarrows \mathrm{LnRuPBu_3} \qquad (9)$$

29

In conclusion, a versatile catalytic system for the selective linear codimerization of terminal acetylenes with 1,3-dienes was found providing a novel convenient tool for the construction of carbon skeletones with acetylenic and olefinic groups.

Experimental

All boiling points were uncorrected. Infrared spectra were recorded on a Hitachi Model 215 spectrometer and NICOLET 5-MX spectrometer as films. Proton nuclear magnetic resonance spectra were obtained on a JNM-FX-100 or NICOLET NT-300NB spectrometer as 20% solutions with tetramethylsilane as an internal reference. Carbon-13 nuclear magnetic resonance spectra were obtained on a JNM-FX-100 spectrometer as 30% solutions with tetramethylsilane as an internal reference. Mass spectra were taken on a JMS-01SG mass spectrometer. Microanalyses were performed by the Laboratory for Organic Elemental Microanalysis at the Faculty of Pharmaceutical Science at Kyoto University. Gas chromatographic analysis (GLC) were carried out on a 1.5 m×3 mm diameter column with OV 17. 1-Hexyne, 1,3-butadiene, methyl (*E*,*E*)-2,4-hexadienoate, and solvents were commercial samples and were purified by distillation under an atmosphere of argon before use. 3,3-Dimethyl-1-butyne,[23)] 3,3-dimethyl-1-butyne-1-*d*,[24)] and 1-pentyne-1-*d*[24)] were prepared by the methods described in the literature. The complex Ru(COD)(COT) were prepared by the reported method.[25)] All the catalytic reactions were carried out under an atmosphere of argon.

General Reaction Procedure. The reaction of 1-hexyne with 1,3-butadiene is representative. A mixture of 1-hexyne (0.82 g, 10 mmol), 1,3-butadiene (20 mmol), Ru(COD)(COT) (0.063 g, 0.2 mmol), PBu$^n_3$ (0.08 g, 0.4 mmol), and benzene (5.0 cm^3) was heated in a heavy-walled sealed tube at 80 °C for 8 h. Careful vacuum distillation of the reaction mixture afforded 0.99 g (yield 73%) of (*E*)-3-decen-5-yne (**1**).

Other reactions were carried out in a similar manner. Codimers (**1**, **2**, **4**—**11**) were identified to be the products reported in the previous paper.[2b)]

Ethyl (*E*)-2-Ethoxycarbonyl-6-nonen-4-ynoate (3). Colorless liquid, bp 108 °C (25 mmHg) (1 mmHg=133.322 Pa); IR (neat) 1745 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=6.08 (1H, dt, J=15.9 and 6.6 Hz), 5.39 (1H, dt, J=15.9 and 1.8 Hz), 4.22 (4H, q, J=7.1 Hz), 3.54 (1H, t, J=7.8 Hz), 2.86 (2H, dd, J=7.8 and 1.8 Hz), 2.09 (2H, qd, J=7.4 and 6.6 Hz), 1.28 (6H, t, J=7.1 Hz), and 0.98 (3H, t, J=7.4 Hz); ^{13}C NMR ($CDCl_3$) δ=167.9 (s), 145.5 (d), 108.7 (d), 83.8 (s), 81.1 (s), 61.5 (t), 51.6 (d), 26.1 (t), 19.4 (t), 14.1 (q), and 13.0 (q). MS m/z: 252. Found: C, 66.65; H, 8.15%. Calcd for $C_{14}H_{20}O_4$: C, 66.65; H, 7.99%.

(*E*)-3-Nonen-5-yne-2-*d* (12). Colorless liquid, bp 80 °C (85 mmHg); IR (neat) 2217 and 955 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=6.08 (1H, dd, J=15.6 and 6.3 Hz), 5.45 (1H, dm, J=15.6 Hz), 2.26 (2H, td, J=7.2 and 1.8 Hz), 2.09 (1H, m), 1.54 (2H, qt, J=7.2 and 7.2 Hz), 0.99 (3H, dm, J=7.5 Hz), 0.99 (3H, t, J=7.2 Hz); ^{13}C NMR ($CDCl_3$) δ=144.2 (d), 109.6 (d), 88.4 (s), 79.5 (s), 25.9 (t, J_{C-D}=19.5 Hz), 22.6 (t), 21.6 (t), 13.6 (q), and 13.2 (q).

The reaction of 1-Hexyne with Methyl (*E,E*)-2,4-Hexadienoate in the presence of 5. A mixture of 1-hexyne (8.2 mg, 0.1 mmol), methyl (*E,E*)-2,4-hexadienoate (12.7 mg, 0.1 mmol), methyl (*E*)-2-undecen-6-ynoate (**5**) (20 mg, 0.1 mmol), Ru(COD)(COT) (0.32 mg, 1 mol%), PBu^n_3 (0.40 mg, 2 mol%), and benzene (0.05 cm^3) was heated at 60 °C for 4 h. The GLC analysis showed the formation of the codimer **6** (yield 30%) and that **5** was completely recovered without the formation of **4**.

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References

1) T. Mitsudo, K. Kokuryo, T. Shinsugi, Y. Nakagawa, Y. Watanabe, and Y. Takegami, *J. Org. Chem.*, **44**, 4492 (1979).

2) a) T. Mitsudo, Y. Nakagawa, H. Watanabe, K. Watanabe, and Y. Watanabe, *J. Chem. Soc., Chem. Commun.*, **1981**, 496; b) T. Mitsudo, Y. Nakagawa, K. Watanabe, Y. Hori, H. Misawa, H. Watanabe, and Y. Watanabe, *J. Org. Chem.*, **50**, 565 (1985).

3) J. F. Knifton, *J. Am. Chem. Soc.*, **103**, 3959 (1981).

4) B. D. Dombeck, *J. Organomet. Chem.*, **250**, 467 (1983).

5) T. Nakano, K. Ohkawa, S. Ikemori, R. Hasegawa, R. Sako, H. Matsumoto, and Y. Nagai, *Nippon Kagaku Kaishi*, **1983**, 1770.

6) T. Nakano, K. Ohkawa, S. Ikemori, H. Matsumoto, and Y. Nagai, *Nippon Kagaku Kaishi*, **1983**, 1778.

7) N. Kamigata, J.-I. Ozaki, and M. Kobayashi, *J. Org. Chem.*, **50**, 5045 (1985).

8) H. Nagashima, K.-I. Ara, H. Wakamatsu, and K. Itoh, *J. Chem. Soc., Chem. Commun.*, **1985**, 518.

9) Y. Tsuji, H. Nishimura, K.-T. Huh, and Y. Watanabe, *J. Organomet. Chem.*, **286**, C44 (1985).

10) S.-I. Murahashi, K.-I. Ito, T. Naota, and Y. Maeda, *Tetrahedron Lett.*, **22**, 5327 (1981).

11) S.-I. Murahashi, K. Kondo, and T. Hakata, *Tetrahedron Lett.*, **23**, 229 (1982).

12) S. Cenini, M. Pizzotti, C. Crotti, F. Porta, and G. L. Monica, *J. Chem. Soc., Chem. Commun.*, **1984**, 1286.

13) M. Rotem and Y. Shvo, *Organometallics*, **2**, 1689 (1983).

14) Y. Blum and Y. Shvo, *J. Organomet. Chem.*, **282**, C7 (1985).

15) T. A. Smith, R. P. Aplin, and P. M. Maitlis, *J. Organomet. Chem.*, **291**, C13 (1985).

16) Y. Watanabe, Y. Tsuji, H. Ige, Y. Ohsugi, and T. Ohta, *J. Org. Chem.*, **49**, 3359 (1984).

17) Y. Tsuji, K.-T. Huh, Y. Ohsugi, and Y. Watanabe, *J. Org. Chem.*, **50**, 1365 (1985).

18) T. Mitsudo, Y. Hori, and Y. Watanabe, *J. Org. Chem.*, **50**, 1566 (1985).

19) B. Chaudret and R. Poilblanc, *Organometallics*, **4**, 1722 (1985).

20) S. Komiya, A. Yamamoto, and S. Ikeda, *J. Organomet. Chem.*, **42**, C65 (1972); *Bull. Chem. Soc. Jpn.*, **49**, 2552 (1976).

21) D. J. Cale-Hamilton and G. Wilkinson, *J. Chem. Soc., Chem. Commun.*, **1977**, 59.

22) C. A. Tolman, *Chem. Rev.*, **77**, 313 (1975).

23) W. L. Collier and R. S. Macomber, *J. Org. Chem.*, **38**, 1367 (1973).

24) A. F. Thomas, "Deuterium Labeling in Organic Chemistry," Appleton-Century-Croft, New York (1971), p. 57.

25) K. Itoh, H. Nagashima, T. Ohshima, N. Ohshima, and H. Nishiyama, *J. Organomet. Chem.*, **272**, 179 (1984).