Preparation of Z-Ala-OCH_3. To a solution of *N*-(benzyloxycarbonyl)alanine (447 mg, 2.0 mmol) and triethylamine (213 mg, 2.1 mmol) in methylene chloride (6 mL) at 0 °C was added methyl chloroformate (190 mg, 2.0 mmol). After 10 min of stirring at 0 °C, DMAP (23 mg, 0.2 mmol) was added and the resulting solution was stirred at 0 °C for 15 min. The reaction mixture was diluted with methylene chloride (40 mL) and washed with saturated $NaHCO_3$ (20 mL), 0.1 M HCl (10 mL), and saturated NaCl (30 mL). The aqueous layers were extracted with methylene chloride (20 mL). The combined extracts were dried over anhydrous $MgSO_4$ and evaporated to dryness. The residue was subjected to silica gel column chromatography with methylene chloride as an eluant to yield pure Z-Ala-OCH_3 (455 mg, 96%): NMR ($CDCl_3$) δ 1.40 (d, 3 H, J = 7), 3.73 (s, 3 H), 4.40 (q, 1 H, J = 7), 5.12 (s, 2 H), 5.52–5.95 (m, 1 H), 7.31 (b s, 5 H); IR (film) 1730, 1710 cm^{-1}.

Reaction of Caprylic–Ethyl Carbonate Anhydride with Caprylic Acid in the Presence of Triethylamine. To a solution of caprylic acid (288 mg, 2.0 mmol) and triethylamine (205 mg, 2.0 mmol) in methylene chloride (6 mL) at 0 °C was added ethyl chloroformate (220 mg, 2.0 mmol) and the resulting solution was stirred for 10 min at room temperature. The reaction mixture was diluted with methylene chloride (20 mL), washed with cold water (20 mL), and cold saturated NaCl (20 mL), dried over anhydrous $MgSO_4$, and evaporated to afford caprylic–ethyl carbonate anhydride (415 mg, 96%). To a solution of caprylic–ethyl carbonate anhydride (415 mg, 1.9 mmol) in methylene chloride (2 mL) at 0 °C was added a solution of caprylic acid (275 mg, 1.9 mmol) and triethylamine (202 mg, 2.0 mmol) in methylene chloride (3 mL). The resulting solution was stirred at 0 °C for 45 min, diluted with methylene chloride (30 mL), washed with saturated NaCl (20 mL), dried over anhydrous $MgSO_4$, and evaporated to dryness. The residue was distilled to afford caprylic anhydride (462 mg) in 90% yield. The product was identical with an authentic sample in spectral data and physical data.

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The First Selective Linear Codimerization of Terminal Acetylenes and 1,3-Dienes Catalyzed by Dihydridotetrakis(trialkylphosphine)ruthenium Complexes

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1,3-Butadiene and its derivatives reacted with aliphatic terminal acetylenes in the presence of a catalytic amount of $RuH_2(P\text{-}n\text{-}Bu_3)_4$ or $RuH_2(PEt_3)_4$ in benzene at 60–100 °C to give linear codimers in high yields with high chemo-, regio-, and stereoselectivity. For example, the reaction of 1,3-butadiene with 1-hexyne afforded (*E*)-3-decen-5-yne quantitatively. Methyl (*E*)-2,4-hexadienoate reacted with 1-hexyne to give methyl (*E*)-5-methyl-2-undecen-6-ynoate in 86% yield. When this reaction was used, a skeleton of a terpenoid was constructed. The reaction of 1-octyne with 1,3-butadiene in the presence of $RuH_2(PPh_3)_4$ afforded the oxidative cocoupling compound (*E*)-1,3-dodecadien-5-yne instead of the corresponding codimer. The deuterium distributions in the products of the reaction of 3,3-dimethyl-1-butyne-1-*d* with methyl (*E,E*)-2,4-hexadienoate and methyl (*E*)-2,4-pentadienoate were examined.

Introduction

Recently, organic synthesis catalyzed by ruthenium complexes have been greatly expanded. A number of exchange reactions of functional groups,[1] cyclization,[1a,2] reduction,[3] and oxidation[4] reactions catalyzed by ruthenium complexes have been reported. However, when attention is focussed on catalytic carbon–carbon bond formation reactions, the number of characteristic reactions of ruthenium is limited, e.g., carbonylation of olefins or acetylenes,[5] telomerization of olefins with alkyl halides,[6] polymerization and oligomerization of olefins[7] or acetylenes,[8] homologation of methyl acetates,[9] hydrogenation of carbon monoxide to ethylene glycol,[10] and [2 + 2] cross addition of norbornenes with acetylenes.[11] In the course of our study on characteristic carbon–carbon bond formation catalyzed by ruthenium complexes, the first selective linear codimerization of terminal acetylenes with 1,3-dienes catalyzed by dihydridotetrakis(trialkylphosphine)ruthe-

(1) For example: (a) Sasson, Y.; Rempel, G. L. *Tetrahedron Lett.* **1974**, 4133. (b) Watanabe, Y.; Tsuji, Y.; Ohsugi, Y. *Tetrahedron Lett.* **1981**, *22*, 2667. (c) Watanbe, Y.; Tsuji, Y.; Ohsugi, Y.; Shida, J. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 2452 and references cited therein. (d) Murahashi, S.-I.; Kondo, K.; Hakata, T. *Tetrahedron Lett.* **1982**, *23*, 229. (e) Suzuki, M.; Noyori, R.; Hamanaka, N. *J. Am. Chem. Soc.* **1982**, *104*, 2024. Cook, J.; Hamlin, J. E.; Nuton, A.; Maitlis, P. *J. Chem. Soc., Dalton Trans.* **1981**, 2342.

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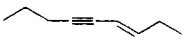
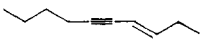
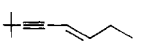
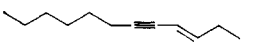
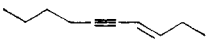
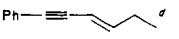
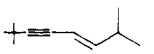
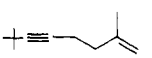
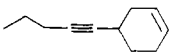
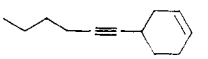
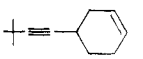
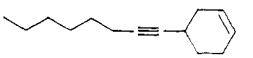
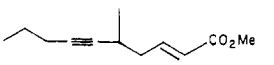
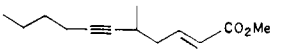
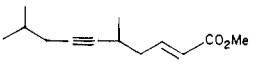
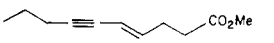
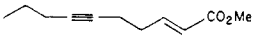
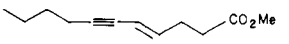
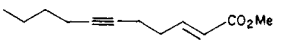
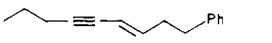
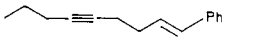
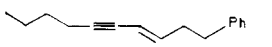
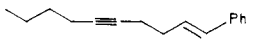
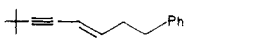
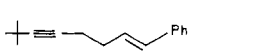
Table I. Linear Codimerization of Acetylenes and Dienes[a]

run	acetylene	no.	diene	catalyst,[c] mmol	temp, °C	time, h	product	no.	yield,[b] %
1	1-pentyne	1	1,3-butadiene	A 0.1	60	2		7	96 (67)
2	1-hexyne	2	1,3-butadiene	A 0.2	60	4		8	100
3	3,3-dimethyl-1-butyne	3	1,3-butadiene	A 0.2	60	4		9	100
4	1-octyne	4	1,3-butadiene	A 0.1	60	4		10	92
5	1-octyne	4	1,3-butadiene	A 0.1	80	2		10	99 (88)
6	1-octyne	4	1,3-butadiene	B 0.2	80	2		10	83
7	1-hexyne	2	1,3-butadiene	C 0.2	80	24		8	8
8	1-hexyne	2	1,3-butadiene	D 0.2	80	8		8	(73)
9	phenylacetylene	5	1,3-butadiene	A 0.2	80	4		11	31
10	3,3-dimethyl-1-butyne	3	isoprene	A 0.1	140	6		12a	
								12b	55, a/b = 85/15
11	1-pentyne	1	1,3-cyclohexadiene	A 0.1	80	4		13	39
12	1-hexyne	2	1,3-cyclohexadiene	A 0.1	80	4		14	20
13	3,3-dimethyl-1-butyne	3	1,3-cyclohexadiene	A 0.1	80	4		15	60
14	1-octyne	4	1,3-cyclohexadiene	A 0.1	80	4		16	48
15	1-pentyne	1	methyl (*E,E*)-2,4-hexadienoate	A 0.1	80	16		17	22
16	1-hexyne	2	methyl (*E,E*)-2,4-hexadienoate	A 0.1	80	8		18	86
17	4-methyl-1-pentyne	6	methyl (*E,E*)-2,4-hexadienoate	A 0.1	100	6		19	(68)
18	1-pentyne	1	methyl (*E*)-2,4-pentadienoate	A 0.1	60	10		20a	
								20b	(63), a/b = 60/40
19	1-hexyne	2	methyl (*E*)-2,4-pentadienoate	A 0.1	60	4		21a	
								21b	81, a/b = 62/38
20	1-pentyne	1	(*E*)-1-phenyl-1,3-butadiene	A 0.1	80	4		22a	
								22b	32, a/b = 63/37
21	1-hexyne	2	(*E*)-1-phenyl-1,3-butadiene	A 0.1	80	4		23a	
								23b	42, a/b = 62/38
22	3,3-dimethyl-1-butyne	3	(*E*)-1-phenyl-1,3-butadiene	A 0.1	80	4		24a	
								24b	39, a/b = 59/41

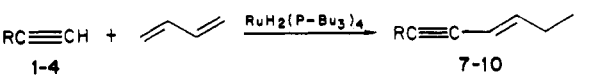
[a] Acetylene, 10 mmol; 1,3-butadiene, 20 mmol; other dienes, 10 mmol. [b] Determined by GLC based on the amount of acetylene. Isolated yields are given in parentheses. [c] Catalyst: A = $RuH_2(P\text{-}n\text{-}Bu_3)_4$, B = $RuH_2(PEt_3)_4$, C = Ru(COD)(COT), D = Ru(COD)(COT)-2P-*n*-Bu_3. [d] Homodimers of phenylacetylene and (*E*)- and (*Z*)-1,4-diphenyl-1-buten-3-yne, were formed in 64% yield (*E*/*Z* = 62/38).

nium was found and the result was briefly reported.[12] In this report, the scope and an application of this reaction are described.

Results and Discussion

Terminal aliphatic acetylenes readily reacted with 1,3-butadiene, 1,3-cyclohexadiene, (*E*)-1-phenyl-1,3-butadiene, methyl (*E*)-2,4-pentadienoate and methyl (*E,E*)-2,4-hexadienoate (methyl sorbate) in the presence of a catalytic amount of $RuH_2(P\text{-}n\text{-}Bu_3)_4$ or $RuH_2(PEt_3)_4$, in benzene at 60–100 °C to give the corresponding linear codimer selectively. The results are summarized in Table I.

The reactions of 1,3-butadienes with acetylenes **1–4** (Table I, runs 1–6) were highly chemo-, regio-, and stereoselective; the *E* isomers of the linear conjugated enynes **7–10** were produced almost quantitatively.



(1)

1,7, R = *n*-Pr; **2,8**, R = *n*-Bu; **3,9**, R = *t*-Bu; **4,10**, R = *n*-hexyl

Phenylacetylene also gave the corresponding product **11** but in a yield of only 31% (run 9); the major product was a mixture of homodimers of phenylacetylene, (*E*)- and (*Z*)-1,4-diphenyl-1-buten-3-yne, in 64% yield (*E*/*Z* = 62:38).

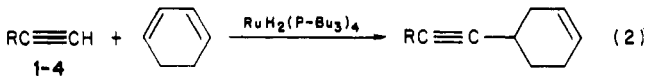
(12) Mitsudo, T.; Nakagawa, Y.; Watanabe, H.; Watanabe, K.; Misawa, H.; Watanabe, Y. *J. Chem. Soc., Chem. Commun.* **1981**, 496.
(13) Levison, J. J.; Robinson, S. D. *J. Chem. Soc. A* **1970**, 2974.

Table II. Oxidative Cocoupling of Acetylenes and 1,3-Butadiene Catalyzed by Ruthenium Complexes[a]

run	acetylene	no.	catalyst, mmol	temp, °C	time, h	product	no.	yield,[b] %
23	1-pentyne	1	$RuH_2(PPh_3)_4$, 0.6	80	24	(*E*)-1,3-nonadien-5-yne	**25**	14
24	1-hexyne	2	$RuH_2(PPh_3)_4$, 0.5	100	8	(*E*)-1,3-decadien-5-yne	**26**	14
25	1-octyne	4	$RuH_2(PPh_3)_4$, 0.2	80	8	(*E*)-1,3-dodecadien-5-yne	**27**	11
26[c]	1-octyne	4	$RuH_2(PPh_3)_4$, 0.2	80	8	(*E*)-1,3-dodecadien-5-yne	**27**	6
27[d]	1-octyne	4	$RuH_2(PPh_3)_4$, 0.2	80	8	(*E*)-1,3-dodecadien-5-yne	**27**	8
28[e]	1-octyne	4	$RuH_2(PPh_3)_4$, 0.5	80	24	(*E*)-1,3-dodecadien-5-yne	**27**	34
29	1-octyne	4	$RuH_2[P(p\text{-}PhOMe)_3]_4$, 0.2	80	8	(*E*)-1,3-dodecadien-5-yne	**27**	15
30	1-octyne	4	$RuH_2[P(p\text{-}PhMe)_3]_4$, 0.2	80	8	(*E*)-1,3-dodecadien-5-yne	**27**	4
31	1-octyne	4	$RuH_4(PPh_3)_3$, 0.2	80	8	(*E*)-1,3-dodecadien-5-yne	**27**	7
32	1-octyne	4	$RuH_2[PPh_2Me]_4$, 0.2	80	8	(*E*)-1,3-dodecadien-5-yne	**27**	4
33	1-octyne	4	$RuH_2[PPhMe_2]_4$, 0.2	80	8	(*E*)-1,3-dodecadien-5-yne	**27**	tr
34	phenylacetylene	5	$RuH_2(PPh_3)_4$, 0.2	80	8	(*E*)-1-phenyl-3-hexen-1-yne	**11**[f]	24
35	phenylacetylene	5	$RuH_2(PPh_3)_4$, 0.5	100	20	(*E*)-1-phenyl-3-hexen-1-yne	**11**	23

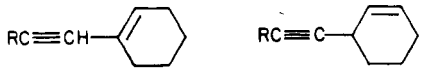
[a] Acetylene, 10 mmol; 1,3-butadiene, 20 mmol; benzene, 5 mL. [b] Determined by GLC based on the amount of acetylene. [c] 1-Octyne, 10 mmol; 1,3-butadiene, 40 mmol. [d] 1-Octyne, 10 mmol; 1,3-butadiene, 10 mmol. [e] Butenes (2.5 mmol) were also detected. [f] Only **11** was formed and the dienyne was not detected.

The reactions of 1,3-cyclohexadiene with acetylenes **1–4** gave the corresponding codimers **13–16** in 20–60% yields (runs 11–14). These products were the codimers derived



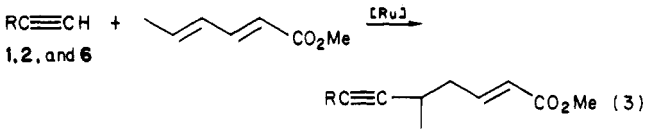
1-4 13-16

by the 1,2-addition of the acetylenes to 1,3-cyclohexadiene. In this case the conjugated enyne **28** and the allylacetylene **29** were not detected. Phenylacetylene did not react with 1,3-cyclohexadiene.



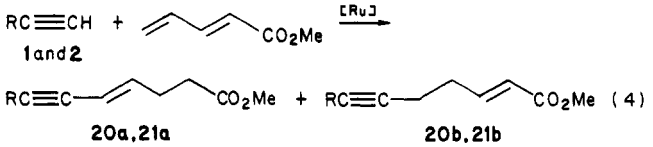
28 29

The reactions of methyl (*E,E*)-2,4-hexadienoate with acetylenes **1**, **2**, and **6** were highly regio- and stereoselective to give **17–19**, respectively, as a sole product in 86–22% yields (runs 15–17).



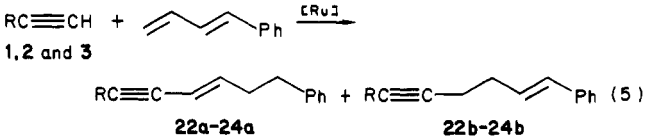
1, 2, and 6 17-19

On the other hand, the reactions of methyl (*E*)-2,4-pentadienoate with acetylenes **1** and **2** gave two isomers of the codimer, **20a**, **20b**, **21a**, and **21b**, respectively, in good yields (runs 18 and 19). The reactions were also regioselective and no other isomer was produced. The isomers **a** were the conjugated (*E*)-enynes and the isomers **b** were the (*E*)-α,β-unsaturated esters; the ratios of **a**/**b** were ca. 6/4 in both reactions.



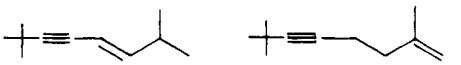
1 and 2 20a, 21a 20b, 21b

(*E*)-1-Phenyl-1,3-butadiene also reacted with acetylenes **1–3** to give two kinds of corresponding codimers **22a–24a** and **22b–24b** in total yields of 32–42%; the ratios of **a**/**b** were also ca. 6/4 (runs 20–22).



1, 2 and 3 22a-24a 22b-24b

Isoprene reacted with *tert*-butylacetylene at 140 °C giving two isomers of codimers **12a** and **12b** (**a**:**b** = 85:15) in a total yield of 55% accompanied by small amounts of three byproducts whose structures could not be determined (run 10). The reaction of (*E*)-1,3-pentadiene with *tert*-

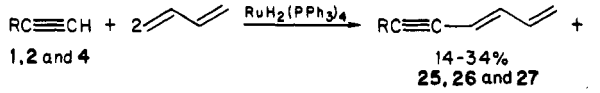


12a 12b

butylacetylene at 100 °C afforded more than six peaks in the GLC with low selectivity and low conversion; further investigation was not attempted. Reactions of 2,3-dimethyl-1,3-butadiene, 2,5-dimethyl-2,4-hexadiene, 1,3-butadienyl acetate, 1,3-cyclooctadiene, furan, and 1,2-propadiene with acetylenes were attempted but only the starting dienes were recovered. No codimer was obtained in the reactions of 1,3-butadiene with 3-hexyne, propargyl alcohol, propargyl acetate, and methyl acetylenecarboxylate.

$RuH_2(PEt_3)_4$ was also an effective catalyst (run 6). Preparation of the complexes $RuH_2(P\text{-}n\text{-}Bu_3)_4$ and $RuH_2(PEt_3)_4$ has not previously been reported.[12] These complexes were prepared by the method similar to that for $RuH_2(PPh_3)_4$. Ruthenium(1,5-cyclooctadiene)(1,3,5-cyclooctatriene) [Ru^0(COD)(COT)] also catalyzed the reaction of 1-hexyne with 1,3-butadiene, however, the yield of **8** was low (run 7). Addition of 2 equiv. of tri-*n*-butylphosphine to Ru(COD)(COT) caused a dramatic increase in the catalytic activity, giving the codimer **8** in the yield of 73% (run 8). The following complexes were not effective: $RuH_2[P(OEt)_3]_4$, $RuH_2(Ph_2PCH_2CH_2PPh_2)_2$, ruthenium(benzene)(1,3-cyclohexadiene), $RuCl_3{\cdot}3H_2O$, $RuCl_2(PPh_3)_3$, $RuHCl(PPh_3)_4$, and $RhCl(PPh_3)_3$.

When $RuH_2(PPh_3)_4$ was used as a catalyst, the scope of the reaction of 1,3-butadiene with aliphatic acetylenes changed dramatically. The major product was the corresponding conjugated dienyne (eq 6) with a trace of the enyne. The oxidative cocoupling or the dehydro-



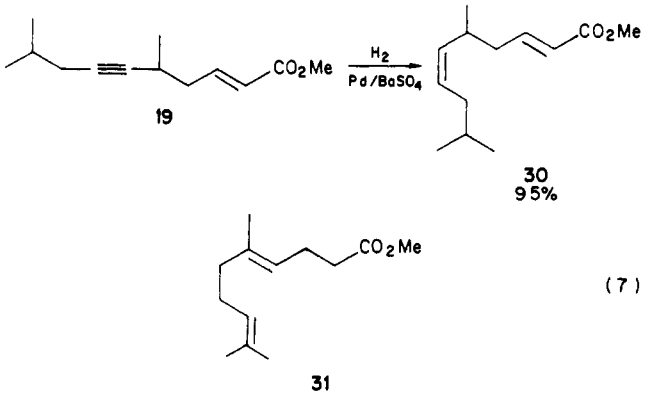
1, 2 and 4 14-34% 25, 26 and 27 butenes (6)

condensation of the acetylene and 1,3-butadiene was catalyzed by the ruthenium complex. The hydrogen was scavenged by the 1,3-butadiene giving the corresponding amount of butenes. The results are summarized in Table II. The yield of the products, however, was 34% even when the amount of the catalyst was increased to 5 mol%.

The optimum ratio of butadiene/acetylene was 2.0; both an excess (the ratio, 4.0) and an inadequate amount of butadiene (the ratio, 1.0) decreased the yield of the product (runs 26 and 27). The complexes $RuH_2[P(p\text{-}PhOMe)_3]_4$, $RuH_2[P(p\text{-}PhMe)_3]_4$, $RuH_4[PPh_3]_3$, $RuH_2[PPh_2Me]_4$, and $RuH_2[PPhMe_2]_4$ did not improve the yield. Addition of 2–4 mol/mol of Ru of tributyl- or triphenylphosphine to $RuH_2(PPh_3)_4$ had no influence on the yield of the product. Solvents such as toluene, diethyl ether, tetrahydrofuran, ethanol, and cyclohexene did not improve the yield. The reaction of phenylacetylene with 1,3-butadiene in the presence of $RuH_2(PPh_3)_4$ gave the codimer enyne **11** instead of the dienyne (runs 34 and 35).

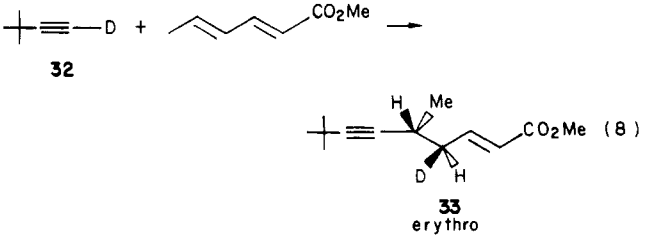
Although several examples of linear[14] or cyclic[15] cooligomerization of acetylenes and 1,3-butadiene are well-known, the present reactions are, to our knowledge, the first example of linear codimerization of acetylenes with 1,3-dienes. Except for compounds **9**[16] and **25–27**,[17] all products reported here are new.

The present reaction provides a novel route to the synthesis of terpenoids. For example, the cis hydrogenation of the triple bond of the codimer **19** by 5% Pd–$BaSO_4$ in methanol gave the previously unreported terpenoid **30** in a yield of 95% (eq 7). Compound **30** is the isomer of terpenoid **31** which is effective as an antispasmolytic.[18]

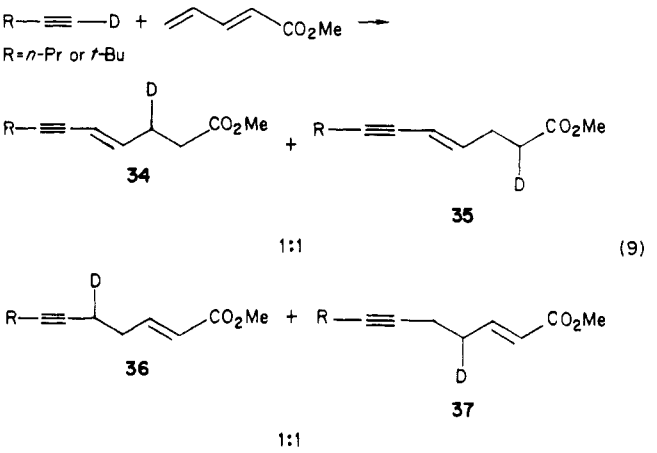


(7)

To elucidate the reaction mechanism of the codimerization, deuterium labeled acetylenes were allowed to react with methyl 2,4-hexadienoate and methyl 2,4-pentadienoate. The reaction of methyl (*E,E*)-2,4-hexadienoate with 3,3-dimethyl-1-butyne-*1-d* (**32**) selectively afforded erythro 4-deuterio isomer **33** as a sole product showing that the acetylene reacts with the dienoate by the cis addition (eq 8). The reaction of methyl 2,4-pentadienoate with 1-pentyne-*1-d* gave four kinds of the codimers, **34–37**. The ratio **(34 + 35)/(36 + 37)** was 6/4 and both ratios, **34/35** and **36/37**, were 1/1. It should be noted that no deuterium was introduced into the olefinic groups of the products. The reaction of **32** with methyl 2,4-pentadienoate also gave a result similar to that described above.



(8)

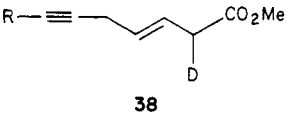


(9)

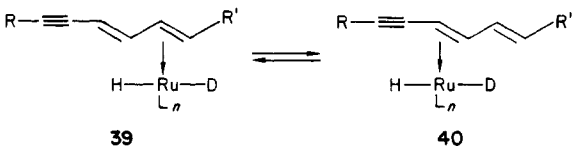
A characteristic feature of these reactions is the marked sensitiveness to the substituents on acetylenes, dienes, and phosphines. When an alkyl group in a terminal acetylene was changed to an aryl group, the main product was changed from the codimer to the homodimer of the acetylene. When the result shown in eq 9 is compared with that in eq 8, it looks that the methyl group on the diene in the sorbate controlled the regioselectivity of the olefinic group and the deuterium. A phenyl group and an alkyl group on the phosphine ligands in the catalyst also showed the discrepancy in the reaction products (eq 1 and 6).

Although it is very hard to propose a reaction mechanism which explains these complicated observations completely at the present time, the results obtained are suggesting much information on the mechanism.

The fact that no deuterium is introduced into the olefinic groups in **34–37** shows that these products are not produced by the isomerization of deuterated codimers such as **35**, **37**, or **38**. If the products are formed by the isomerization, the deuterium should be introduced into the olefinic groups of **34–37**.



A possible reaction intermediates which could explain this observation and the ratios of **34/35** and **36/37**, both of which are 1/1, would be hydridodeuterido(dienyne)ruthenium complexes **39** and **40** which would be in an equilibrium. The intermediate **39** or **40** has futher advantages that could explain the formation of dienyne **25–27**, i.e., the larger cone angle of triarylphosphines[19] may cause the dissociation of the dieneynes prior to the hydrogenation. However, the mechanism of the formation of **39** or **40** would be rather unusual.



Although it is reported that zerovalent complexes are formed by the reaction of $RuH_2(PR_3)_4$ with olefins[20,21] and

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the fact that a zerovalent complex $Ru^0(COD)(COT)-PR_3$ is an active catalyst suggests that a zerovalent complex is playing an important role in the present catalytic reactions, the real catalytic cycle is still unclear, and further studies are required to give an unequivocal mechanism for these complicated and sensitive reactions.

Conclusion

The first catalytic and selective linear codimerization of terminal acetylenes with 1,3-dienes was achieved by dihydridotetrakis(trialkylphosphine)ruthenium complexes. The reaction provides a novel tool for construction of carbon skeletons with acetylenic and olefinic groups.

Experimental Section

All boiling points were uncorrected. Infrared spectra were recorded on a Hitachi Model 215 spectrometer either as films or in potassium bromide disks. Proton nuclear magnetic resonance spectra were obtained on a JNM-FX-100 or NICOLET NT-300NB spectrometer as 5–20% solutions with tetramethylsilane as an internal reference. Carbon-13 nuclear magnetic resonance spectra were obtained on a JNM-FX-100 spectrometer as 5–30% 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 Pharmacentical Science at Kyoto University. Gas chromatographic analysis (GLC) were carried out on a 1.5 m × 3 mm diameter column with OV 17 or a 45 m × 0.25 mm diameter column with OV 101. 1-Pentyne, 1-hexyne, 1-octyne, phenylacetylene, 1,3-butadiene, 1,3-cyclohexadiene, methyl (*E*,*E*)-2,4-hexadienoate, ethanol, and benzene were commercial samples and were purified by distillation under an atmosphere of argon before use. 3,3-Dimethyl-1-butyne,[22] 4-methyl-1-pentyne,[23] (*E*)-1-phenyl-1,3-butadiene,[24] methyl (*E*)-2,4-pentadienoate,[25] 3,3-dimethyl-1-butyne-*1-d*[26] and 1-pentyne-*1-d*[26] were prepared by the methods described in the literature. The complexes $RuH_2(PPh_3)_4$,[9] $RuH_2[P(p\text{-}PhOMe)_3]_4$,[13] $RuH_2[P(p\text{-}PhMe)_3]_4$,[13] $RuH_2[PPh_2Me]_4$,[13] $RuH_2[PPhMe_2]_4$,[13] $RuH_4(PPh_3)_3$,[13] and Ru(COD)(COT)[27] were prepared by the reported methods. All the catalytic reactions were carried out under an atmosphere of argon.

Dihydridotetrakis(tri-*n*-butylphosphine)ruthenium was prepared by adding a solution of $NaBH_4$ (42.0 mmol) in ethanol (40 mL) to a mixture of $RuCl_3{\cdot}nH_2O$ (3.8 mmol, Mitsuwa Co.) and P-*n*-Bu_3 (31 mmol) in ethanol (40 mL) at 70 °C. After 1 h, the reaction solution was cooled to 20 °C and concentrated to about 40 mL. The product was recrystallized from benzene and the colorless crystals collected (1.12 g, yield 32%): 87 °C dec; IR (KBr) 1910 cm^{-1} (br); ^1H NMR (100 MHz, benzene-d_6) δ −11.51 (m, 2 H, RuH).[28] Anal. Calcd for $C_{48}H_{110}P_4Ru$: C, 63.19; H, 12.15. Found: C, 62.44; H, 12.28.

Dihydridotetrakis(triethylphosphine)ruthenium was prepared in a similar manner (yield, 44%): 83 °C dec; IR (KBr) 1900 cm^{-1} (br); ^1H NMR (100 MHz, benzene-d_6) δ −11.49 (m, 2 H, RuH).[28] Anal. Calcd for $C_{24}H_{62}P_4Ru$: C, 50.11; H, 10.89. Found: C, 49.65; H, 10.99.

General Reaction Procedure. The reaction of 1-octyne with 1,3-butadiene is representative. A mixture of 1-octyne (1.10 g, 10 mmol), 1,3-butadiene (20 mmol), $RuH_2(P\text{-}n\text{-}Bu_3)_4$ (0.091 g, 0.1 mmol), and benzene (5.0 mL) was heated in a heavy walled sealed tube at 60 °C for 2 h. Careful vacuum distillation of the reaction mixture afforded 1.44 g (yield 88%) of (*E*)-3-dodecen-5-yne **10**. Other reactions were carried out in a similar manner. The catalysts used were cited in Tables I and II.

(*E*)-3-Nonen-5-yne (7): colorless liquid; bp 30 °C (40 torr); IR (neat) 2217, 955 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.10 (dt, J = 15.7, 6.4 Hz, 1 H olefinic), 5.44 (dtt, J = 15.7, 2.0, 1.6 Hz, 1 H olefinic), 2.26 (td, J = 7.0, 2.0 Hz, 2 H), 2.1 (qdd, J = 7.3, 6.4, 1.6 Hz, 2 H), 1.54 (qt, J = 7.6, 7.0 Hz, 2 H), 0.99 (t, J = 7.6 Hz, 3 H), 0.96 (t, J = 7.3 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 144.3 (d, olefinic), 109.4 (d, olefinic), 88.4 (s, acetylenic), 79.5 (s, acetylenic), 26.2 (t), 22.5 (t), 21.5 (t), 13.6 (q), 13.2 (q); MS, m/e 122. Anal. Calcd for C_9H_{14}: C, 88.45; H, 11.55. Found: C, 88.17; H, 11.70.

(*E*)-3-Decen-5-yne (8): colorless liquid; bp 59 °C (4.8 torr); IR (neat) 2220, 955 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.03 (dt, J = 15.9, 6.4 Hz, 1 H), 5.44 (dtt, J = 15.9, 2.1, 1.6 Hz, 1 H), 2.27 (td, J = 7.0, 2.1 Hz, 2 H), 2.09 (qdd, J = 7.6, 6.4, 1.6 Hz, 2 H), 1.47 (m, 2 H), 1.43 (m, 2 H), 0.99 (t, J = 7.6 Hz, 3 H), 0.91 (t, J = 7.6 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 144.4 (d), 109.2 (d), 88.6 (s), 79.2 (s), 31.1 (t), 26.1 (t), 22.1 (t), 19.1 (t), 13.6 (q), 13.2 (q); MS, m/e 136. Anal. Calcd for $C_{10}H_{16}$: C, 88.16; H, 11.84. Found: C, 88.03; H, 11.90.

(*E*)-7,7-Dimethyl-3-octen-5-yne (9): colorless liquid; bp 84 °C (4 torr); IR (neat) 2220, 957 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.05 (dt, J = 15.7, 6.5 Hz, 1 H), 5.46 (dt, J = 15.7, 1.6 Hz, 1 H), 2.09 (qdd, J = 7.6, 6.5, 1.6 Hz, 2 H), 1.23 (s, 9 H), 0.99 (t, J = 7.6 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 144.1 (d), 109.2 (d), 96.7 (s), 77.7 (s), 31.1 (q), 27.9 (s), 26.0 (t), 13.1 (q); MS, m/e 136. Anal. Calcd for $C_{10}H_{16}$: C, 88.16; H, 11.84. Found: C, 87.88; H, 11.78.

(*E*)-3-Dodecen-5-yne (10): colorless liquid; bp 68.5 °C (1.8 torr); IR (neat) 2230, 1470, 960 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.07 (dt, J = 15, 8, 6.5 Hz, 1 H), 5.44 (dtt, J = 15.8, 2.2, 1.6 Hz, 1 H), 2.27 (td, J = 7.0, 2.2 Hz, 2 H), 2.10 (qdd, J = 7.6, 6.5, 1.6 Hz, 2 H), 1.3–1.6 (m, 8 H), 0.99 (t, J = 7.6 Hz, 3 H), 0.89 (t, J = 7.6 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 144.3 (d), 109.2 (d), 88.6 (s), 79.2 (s), 31.5 (t), 28.9 (t), 28.7 (t), 22.7 (t, 2C), 19.4 (t), 14.1 (q), 13.1 (q); MS, m/e 164. Anal. Calcd for $C_{12}H_{20}$: C, 87.73; H, 12.27. Found: C, 87.83; H, 12.17.

(*E*)-1-Phenyl-3-hexen-1-yne (11): colorless liquid; bp 68 °C (0.45 torr); IR (neat) 2200, 1595, 955 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.3 (m, 5 H, Ph), 6.3 (dt, J = 15.8, 6.4 Hz, 1 H), 5.6 (dt, J = 15.8, 1.5 Hz, 1 H), 2.1 (qdd, J = 7.3, 6.4, 1.5 Hz, 2 H), 1.0 (t, J = 7.3 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 146.3 (d, olefinic), 131.3 (d), 128.1 (d), 127.7 (d), 123.6 (s), 108.6 (d, olefinic), 88.2 (s), 87.9 (s), 26.2 (t), 12.9 (q); MS, m/e 156. Anal. Calcd for $C_{12}H_{12}$: C, 92.26; H, 7.74. Found: C, 92.20; H, 7.80.

Reaction of Isoprene with *tert*-Butylacetylene. A mixture of 91 mg (0.1 mmol) of $RuH_2(P\text{-}n\text{-}Bu_3)_4$, 1.2 mL (10 mmol) of 3,3-dimethyl-1-butyne, 2.0 mL (20 mmol) of isoprene, and 5.0 mL of benzene was heated in a sealed tube at 140 °C for 10 h. The distillation of the reaction mixture gave 1.1 g of colorless liquid (bp 45–48 °C (6 torr)) which was revealed to be a mixture of (*E*)-2,7,7-trimethyl-3-octen-5-yne (**12a**, yield 48% based on the acetylene), 2,7,7-trimethyl-1-octen-5-yne (**12b**, yield 7%), and small amounts of three other products whose structures were not examined further. Although **12a** and **12b** could not be isolated in analitically pure form even by a preparative GLC, the structures were determined by their ^1H NMR spectra.

(*E*)-2,7,7-Trimethyl-3-octen-5-yne (12a): ^1H NMR ($CDCl_3$) δ 6.03 (dd, J = 16.0, 6.7 Hz, 1 H), 5.42 (dd, J = 16.0, 1.2 Hz, 1 H), 2.28 (hepdd, J = 6.8, 6.7, 1.2 Hz, 1 H), 1.23 (s, 9 H), 0.99 (d, J = 6.8 Hz, 6 H).

2,7,7-Trimethyl-1-octen-5-yne (12b): ^1H NMR ($CDCl_3$) δ 4.71 (m, 2 H), 2.19–2.27 (m, 4 H), 1.73 (s, 3 H), 1.19 (s, 9 H).

4-(1-Pentynyl)-1-cyclohexene (13): colorless liquid; bp 104 °C (34 torr); IR (neat) 1650 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.61 (tm, 2 H, olefinic), 2.52 (m, 1 H), 2.25 (dm, 1 H), 2.12 (td, J = 7.2, 2.1 Hz, 2 H), 1.98–2.10 (m, 3 H), 1.86 (m, 1 H), 1.60 (m, 1 H), 1.48 (tq, J = 7.2, 7.2 Hz, 2 H), 0.96 (t, J = 7.2 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 126.5, 125.2, 84.2, 79.6, 32.0, 29.0, 25.7, 24.2, 22.5, 20.7, 13.3; MS, m/e 148. Anal. Calcd for $C_{11}H_{16}$: C, 89.12; H, 10.88. Found: C, 89.23; H, 11.09.

4-(1-Hexynyl)-1-cyclohexene (14): colorless liquid; bp 98 °C (15 torr); IR (neat) 1645 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.63

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4-(3,3-Dimethyl-1-butynyl)-1-cyclohexene (15): colorless liquid; bp 78 °C (19 torr); IR (neat) 1645 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.62 (tm, 2 H), 2.50 (m, 1 H), 2.25 (dm, 1 H), 1.92–2.18 (m, 3 H), 1.86 (m, 1 H), 1.57 (m, 1 H), 1.19 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 126.6 (d), 125.4 (d), 88.7 (s), 82.4 (s), 32.2 (t), 31.5 (q), 29.2 (t), 27.2 (s), 25.6 (d), 24.3 (t); MS, m/e 162. Anal. Calcd for $C_{12}H_{18}$: C, 88.82; H, 11.18. Found: C, 88.55; H, 11.35.

4-(1-Octynyl)-1-cyclohexene (16): colorless liquid; bp 116 °C (6 torr); IR (neat) 1650 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.62 (tm, 2 H), 2.53 (m, 1 H), 2.26 (dm, 1 H), 2.14 (td, J = 6.9, 2.1 Hz, 2 H), 1.91–2.11 (m, 3 H), 1.86 (m, 1 H), 1.60 (m, 1 H), 1.23–1.52 (m, 8 H), 0.88 (t, J = 6.8 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 126.7 (d), 125.4 (d), 84.2 (s), 80.1 (s), 32.2 (t), 31.5 (t), 29.2 (t), 29.2 (t), 28.6 (t), 25.8 (d), 24.3 (t), 22.7 (t), 18.9 (t), 14.1 (q); MS, m/e 190. Anal. Calcd for $C_{14}H_{22}$: C, 88.35; H, 11.65. Found: C, 88.07; H, 11.93.

Methyl (*E*)-5-methyl-2-decen-6-ynoate (17): colorless liquid; bp 103 °C (6 torr); IR (neat) 1650, 1720 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.00 (dt, J = 15.6, 7.2 Hz, 1 H), 5.88 (dt, J = 15.6, 1.2 Hz, 1 H), 3.73 (s, 3 H), 2.3–2.6 (m, 3 H), 2.12 (td, J = 6.9, 2.1 Hz, 2 H), 1.49 (tq, J = 7.2, 7.2 Hz, 2 H), 1.16 (d, J = 6.9 Hz, 3 H), 0.96 (t, J = 7.2 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 166.8 (s), 146.7 (d), 122.6 (d), 83.3 (s), 81.4 (s), 51.4 (q), 39.8 (t), 25.3 (d), 22.5 (t), 21.2 (q), 20.7 (t), 13.4 (q); MS, m/e 194. Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 73.97; H, 9.57.

Methyl (*E*)-5-methyl-2-undecen-6-ynoate (18): colorless liquid; bp 43 °C (0.4 torr); IR (neat) 1650, 1720 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.00 (dt, J = 15.7, 6.9 Hz, 1 H), 5.87 (dt, J = 15.7, 1.5 Hz, 1 H), 3.73 (s, 3 H), 2.3–2.6 (m, 7 H), 1.40 (m, 2 H), 1.16 (d, J = 6.6 Hz, 3 H), 0.90 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ 166.7 (s), 146.6 (d), 122.5 (d), 83.0 (s), 81.5 (s), 51.2 (q), 39.7 (t), 31.1 (t), 25.4 (d), 21.8 (t), 21.1 (q), 18.3 (t), 13.5 (q); MS, m/e 208. Anal. Calcd for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68. Found: C, 75.01; H, 9.59.

Methyl (*E*)-5,9-dimethyl-2-decen-6-ynoate (19): colorless liquid; bp 85 °C (3 torr); IR (neat) 1655, 1725 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.01 (dt, J = 15.9, 7.2 Hz, 1 H), 5.88 (d, J = 15.9 Hz, 1 H), 3.72 (s, 3 H), 2.58 (m, 1 H), 2.31 (dd, J = 7.2, 7.2 Hz, 2 H), 2.03 (dd, J = 6.6, 2.0 Hz, 2 H), 1.75 (dq, J = 6.6, 6.6 Hz, 1 H), 1.17 (d, J = 6.9 Hz, 3 H), 0.95 (d, J = 6.6 Hz, 6 H); ^{13}C NMR ($CDCl_3$) δ 166.7 (s), 146.7 (d), 122.6 (d), 84.0 (s), 80.4 (s), 51.3 (q), 39.9 (t), 28.2 (d), 28.0 (t), 25.5 (d), 21.9 (q), 21.3 (q); MS, m/e 208. Anal. Calcd for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68. Found: C, 75.31; H, 10.11.

In the reactions of methyl (*E*)-2,4-pentadienoate or (*E*)-1-phenyl-1,3-butadiene with acetylenes **1–3**, the distillation of the reaction mixtures gave the products as a mixture of two isomers. The boiling points of the mixtures are as follows: **20a**, **20b** 125 °C (12 torr); **21a**, **21b** 90 °C (0.1 torr); **22a**, **22b** 106 °C (4 torr); **23a**, **23b** 118 °C (4 torr); **24a**, **24b** 118 °C (5 torr). The mass spectral data and elemental analyses given for **20a–24a** were taken on the isomer mixtures. **20a**, **21a**, **21b**, and **24a** were isolated by preparative GLC (Apiezon).

Methyl (*E*)-4-decen-6-ynoate (20a): colorless liquid; IR (neat) 1650, 1735, 2220 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.02 (dm, J = 15.6 Hz, 1 H), 5.52 (dm, J = 15.6 Hz, 1 H), 3.67 (s, 3 H), 2.39–2.43 (m, 4 H), 2.26 (td, J = 7.2, 2.1 Hz, 2 H), 1.54 (tq, J = 7.2, 7.2 Hz, 2 H), 0.98 (t, J = 7.2 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 173.0 (s), 140.3 (d), 111.3 (d), 89.5 (s), 78.8 (s), 51.6 (q), 33.3 (t), 28.1 (t), 22.2 (t), 21.3 (t), 13.5 (q); MS, m/e 180. Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 73.48; H, 8.98.

Methyl (*E*)-2-decen-6-ynoate (20b): colorless liquid; ^{1}H NMR ($CDCl_3$) δ 7.00 (dt, J = 15.6, 6.6 Hz, 1 H), 5.88 (dt, J = 15.6, 1.5 Hz, 1 H), 3.73 (s, 3 H), 2.22–2.44 (m, 4 H), 2.12 (tt, J = 7.2, 2.1 Hz, 2 H), 1.49 (tq, J = 7.2, 7.2 Hz, 2 H), 0.96 (t, J = 7.2 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 166.8, 147.4, 121.8, 81.4 (2C), 51.4, 31.8, 22.4, 20.7, 17.8, 13.4.

The reaction of 1-pentyne-*1-d* (10 mmol) with (*E*)-2,4-pentadienoate (10 mmol) was carried out similarly. Distillation of the reaction mixture gave a mixture of **34**, **35**, **36**, and **37** (0.5 g, 28%, 112 °C (8 torr)). GLC analysis and the NMR spectra showed that the ratios of (**34** + **35**)/(**36** + **37**), **34**/**35**, and **36**/**37** were 6/4, 1/1, and 1/1, respectively.

Methyl (*E*)-4-Decen-6-ynoate-*3-d* (34). Spectral data were the same as those of **20a** except for the following signals: ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.02 (d(br), J = 15.6 Hz, 1 H), 5.52 (d, J = 15.6 Hz, 1 H), 2.39–2.43 (m, 3 H); ^{13}C NMR ($CDCl_3$) (^{1}H decoupled) δ 27.8 (t, J_{C-D} = 20 Hz) in the place of the signal 28.1 (t) in **20a**.

Methyl (*E*)-4-Decen-6-ynoate-*2-d* (35). Spectral data were the same as those of **20a** except for the following signals: ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.39–2.43 (m, 3 H); ^{13}C NMR ($CDCl_3$) (^{1}H decoupled) δ 33.0 (t, J_{C-D} = 20 Hz) in the place of the signal 33.3 (t) in **20a**.

Methyl (*E*)-2-Decen-6-ynoate-*5-d* (36). Spectral data were the same as those of **20b** except for the following signals: ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.12 (t, J = 6.9 Hz, 1 H); ^{13}C NMR ($CDCl_3$) (^{1}H decoupled) δ 17.6 (t, J_{C-D} = 20 Hz) in the place of the signal 17.8 (t) in **20b**.

Methyl (*E*)-2-Decen-6-ynoate-*4-d* (37). Spectral data were the same as those of **20b** except for the following signals: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.00 (d(br), J = 15.6 Hz, 1 H), 5.88 (d, J = 15.6 Hz, 1 H); ^{13}C NMR ($CDCl_3$) (^{1}H decoupled) δ 31.8 (t, J_{C-D} = 20 Hz) in the place of the signal 31.8 (t) in **20b**.

Methyl (*E*)-4-undecen-6-ynoate (21a): colorless liquid; IR (neat) 1620, 1720, 2200 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.99 (dt, J = 15.6, 6.7 Hz, 1 H), 5.87 (dt, J = 15.6, 1.4 Hz, 1 H), 3.73 (s, 3 H), 1.0–2.5 (comp, 13 H); ^{13}C NMR ($CDCl_3$) δ 172.9 (s), 140.2 (d), 111.3 (d), 89.6 (s), 78.7 (s), 51.6 (q), 33.3 (t), 30.8 (t), 28.1 (t), 22.0 (t), 19.0 (t), 13.6 (q); MS, m/e 194. Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.35; H, 9.49.

Methyl (*E*)-2-undecen-6-ynoate (21b): colorless liquid; ^{1}H NMR ($CDCl_3$) δ 6.03 (dt, J = 15.7, 6.7 Hz, 1 H), 5.49 (d, J = 15.7 Hz, 1 H), 3.67 (s, 3 H), 1.0–2.5 (comp, 13 H); ^{13}C NMR ($CDCl_3$) δ 166.8 (s), 147.4 (d), 121.8 (d), 81.5 (s), 81.5 (s), 51.4 (q), 31.8 (t), 31.1 (t), 21.9 (t), 18.4 (t), 17.8 (t), 13.6 (q).

(*E*)-1-Phenyl-3-nonen-5-yne (22a): colorless liquid; IR (neat) 1595, 2210 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.10–7.35 (m, 5 H), 6.06 (dt, J = 15.9, 6.9 Hz, 1 H), 5.45 (dt, J = 15.9, 2.1 Hz, 1 H), 2.66 (t, J = 7.8 Hz, 2 H), 2.34–2.44 (m, 2 H), 2.24 (td, J = 7.2, 2.1 Hz, 2 H), 1.52 (tq, J = 7.2, 7.2 Hz, 2 H), 0.97 (t, J = 7.2 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 141.7 (d), 141.3 (s), 128.3 (d), 128.3 (d), 126.0 (d), 110.7 (d), 88.9 (s), 79.2 (s), 35.3 (t), 34.7 (t), 22.3 (t), 21.4 (t), 13.5 (q); MS, m/e 198. Anal. Calcd for $C_{15}H_{18}$: C, 90.85; H, 9.15. Found: C, 90.69; H, 9.31.

(*E*)-1-Phenyl-1-nonen-5-yne (22b): colorless liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.10–7.35 (m, 5 H), 6.41 (d, J = 15.9 Hz, 1 H), 6.25 (dt, J = 15.9, 6.5 Hz, 1 H), 2.33–2.44 (m, 2 H), 2.32 (m, 2 H), 2.12 (tt, J = 6.9, 2.4 Hz, 2 H), 1.49 (tq, J = 6.9, 7.2 Hz, 2 H), 0.96 (t, J = 7.2 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 137.6 (s), 130.8 (d), 129.0 (d), 128.4 (d), 126.9 (d), 125.9 (d), 80.7 (s), 79.5 (s), 32.8 (t), 22.6 (t), 20.8 (t), 19.2 (t), 13.5 (q).

(*E*)-1-Phenyl-3-decen-5-yne (23a): colorless liquid; IR (neat) 1660, 2220 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.06–7.32 (m, 5 H), 6.03 (dt, J = 15.6, 7.2 Hz, 1 H), 5.46 (dt, J = 15.6, 1.8 Hz, 1 H), 2.62 (t, J = 7.7 Hz, 2 H), 2.33 (m, 2 H), 2.24 (td, J = 6.9, 2.1 Hz, 2 H), 1.26–1.58 (m, 4 H), 0.88 (t, J = 7.2 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 141.6 (d), 141.3 (s), 128.3 (d), 128.3 (d), 126.1 (d, olefinic), 110.9 (d, olefinic), 88.9 (s, acetylenic), 79.1 (s, acetylenic), 35.3 (t), 34.8 (t), 31.1 (t), 22.0 (t), 19.1 (t), 13.6 (q); MS, m/e 212. Anal. Calcd for $C_{16}H_{20}$: C, 90.51; H, 9.49. Found: C, 90.25; H, 9.31.

(*E*)-1-Phenyl-1-decen-5-yne (23b): colorless liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.06–7.32 (m, 5 H), 6.38 (d, J = 15.6 Hz, 1 H), 6.22 (dt, J = 15.6, 6.6 Hz, 1 H), 2.27–2.38 (m, 4 H), 2.13 (tt, J = 6.9, 2.1 Hz, 2 H), 1.26–1.58 (m, 4 H), 0.87 (t, J = 7.2 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 137.6 (s), 130.9 (d), 129.0 (d), 128.3 (d), 126.9 (d), 125.9 (d), 80.8 (s), 79.2 (s), 32.8 (t), 31.3 (t), 22.0 (t), 19.1 (t), 18.6 (t), 13.6 (q).

(*E*)-1-Phenyl-7,7-dimethyl-3-octen-5-yne (24a): colorless liquid; IR (neat) 1595, 2210 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.14–7.38 (m, 5 H), 6.07 (dt, J = 15.9, 6.9 Hz, 1 H), 5.51 (d, J = 15.9 Hz, 1 H), 2.70 (t, J = 8.0 Hz, 2 H), 2.34–2.45 (m, 2 H), 1.12 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 142.0 (d), 141.9 (s), 128.7 (d), 128.7 (d), 126.2 (d, olefinic), 110.9 (d, olefinic), 97.6 (s), 77.7 (s), 35.5 (t), 35.0 (t), 31.1 (q), 28.1 (s); MS, m/e 212. Anal. Calcd for $C_{16}H_{20}$: C, 90.51; H, 9.49. Found: C, 90.46; H, 9.54.

(*E*)-1-Phenyl-7,7-dimethyl-1-octen-5-yne (24b): colorless

liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.14–7.38 (m, 5 H), 6,44 (d, J = 15.9 Hz, 1 H), 6.26 (dt, J = 15.9, 6.6 Hz, 1 H), 2.34–2.45 (m, 2 H), 2.30 (t, J = 6.6 Hz, 2 H), 1.11 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 137.6 (s), 130.7 (d), 129.0 (d), 128.3 (d), 126.8 (d), 125.9 (d), 89.7 (s), 77.6 (s), 32.8 (t), 31.3 (q), 27.3 (s), 19.0 (t).

(*E*)-1,3-Nonadien-5-yne (25): colorless liquid; bp 49 °C (8 torr); IR (neat) 1630, 2230 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.5–6.1 (m, 2 H), 5.6 (dt, J = 15.0, 2.5 Hz, 1 H), 5.2 (d, J = 15.5 Hz, 1 H), 4.9 (d, J = 9.3 Hz, 1 H), 2.3 (td, J = 7.1, 2.5 Hz, 2 H), 1.5 (m, 2 H), 1.0 (t, 3 H); ^{13}C NMR ($CDCl_3$) δ 140.8 (d), 136.2 (d), 118.4 (t), 112.6 (d), 93.3 (s), 79.6 (s), 22.1 (t), 21.5 (t), 13.4 (q); MS, m/e 120. Anal. Calcd for C_9H_{12}: C, 89.94; H, 10.06. Found: C, 89,61; H, 10.39.

(*E*)-1,3-Decadien-5-yne (26): colorless liquid; bp 81 °C (18 torr); IR (neat) 1625, 2220 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.5–6.1 (m, 2 H), 5.6 (dt, J = 15, 2.5 Hz, 1 H), 5.3 (d, J = 15.3 Hz, 1 H), 5.1 (d, J = 8.0 Hz, 1 H), 2.3 (td, J = 7.1, 2.5 Hz, 2 H), 1.5 (m, 4 H), 0.9 (t, 3 H); ^{13}C NMR ($CDCl_3$) δ 140.8 (d), 136.3 (d), 118.3 (t), 112.7 (d), 93.4 (s), 79.5 (s), 30.8 (t), 22.0 (t), 19.3 (t), 13.5 (q); MS, m/e 134. Anal. Calcd for $C_{10}H_{14}$: C, 89.49; H, 10.51. Found: C, 89.06; H, 10.94.

(*E*)-1,3-Dodecadien-5-yne (27): colorless liquid; bp 65 °C (2.0 torr); IR (neat) 1630, 2230 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.5–6.1 (m, 2 H), 5.6 (dt, J = 15.0, 2.5 Hz, 1 H), 5.2 (d, J = 15.2 Hz, 1 H), 5.1 (d, J = 9.3 Hz, 1 H), 2.3 (td, J = 7.1, 2.5 Hz, 2 H), 1.4 (m, 8 H), 0.9 (t, 3 H); ^{13}C NMR ($CDCl_3$) δ 140.8 (d), 136.2 (d), 118.4 (t), 112.6 (d), 93.6 (s), 79.4 (s), 31.3 (t), 28.7 (t), 28.6 (t), 22.5 (t), 19.6 (t), 14.0 (q); MS, m/e 162. Anal. Calcd for $C_{12}H_{18}$: C, 88.82; H, 11.18. Found: C, 88.67; H, 11.33.

Methyl (*E*,*Z*)-5,9-Dimethyl-2,6-decadienoate (30). Methyl (*E*)-5,9-dimethyl-2-decen-6-ynoate (**19**) (0.53 g), 75 mg of 5% Pd–$BaSO_4$, ca. 20 mg of quinoline, and 3 mL of methanol were placed in a 50-cm^3 flask which had been flushed with hydrogen and the mixture was stirred at 25 °C for 72 h. Vacuum distillation of the reaction mixture gave **30** (0.50 g, yield 95%): colorless liquid; bp 80 °C (2 torr); ^{1}H NMR ($CDCl_3$) δ 6.90 (dt, J = 15.6, 7.0 Hz, 1 H), 5.73 (d, J = 15.6 Hz, 1 H), 5.29 (dt, J = 10.0, 6.5 Hz, 1 H), 5.10 (dd, J = 10.0, 7.9 Hz, 1 H), 3.70 (s, 3 H), 2.57 (m, 1 H), 2.13 (dd, J = 7.0, 6.5 Hz, 2 H), 1.89 (dd, J = 6.4, 6.0 Hz, 2 H), 1.50 (m, 1 H), 0.95 (d, J = 7.0 Hz, 3 H), 0.90 (d, J = 6.7 Hz, 6 H); MS, m/e 210. Anal. Calcd for $C_{13}H_{22}O_2$: C, 74.24; H, 10.54. Found: C, 73.97; H, 10.51.

Methyl *erythro*-5,8,8-trimethyl-2-nonen-6-ynoate-*4*-*d* (33): Colorless liquid; bp 98 °C (6 torr); IR (neat) 1650, 1720, 2150 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.99 (dd, J = 15.6, 7.5 Hz, 1 H), 5.87 (dd, J = 15.6, 1.2 Hz, 1 H), 3.73 (s, 3 H), 2.54 (dq, J = 6.9, 6.9 Hz, 1 H), 2.28 (m, 1 H), 1.18 (s, 9 H), 1.14 (d, J = 6.9 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 166.9 (s), 146.8 (d), 122.5 (d), 90.4 (s), 81.5 (s), 51.4 (q), 39.5 (td, J_{C-D} = 20 Hz), 31.4 (q), 27.3 (s), 25.3 (d), 21.2 (q); MS, m/e 209. Anal. Calcd for $C_{13}H_{19}DO_2$: C, 74.60; H, 10.11. Found: C, 74.08; H, 9.85.

Registry No. **1**, 827-19-0; **2**, 693-02-7; **3**, 917-92-0; **4**, 629-05-0; **5**, 536-74-3; **6**, 7154-75-8; **7**, 79159-62-9; **8**, 79159-61-8; **9**, 70600-70-3; **10**, 79159-60-7; **11**, 79159-59-4; **12a**, 94426-44-5; **12b**, 94426-45-6; **13**, 94426-46-7; **14**, 82315-94-4; **15**, 94426-47-8; **16**, 94426-48-9; **17**, 94426-49-0; **18**, 94426-50-3; **19**, 94426-51-4; **20a**, 94426-52-5; **20b**, 94426-53-6; **21a**, 94426-54-7; **21b**, 94426-55-8; **22a**, 94426-56-9; **22b**, 94426-57-0; **23a**, 94426-58-1; **23b**, 94426-59-2; **24a**, 94426-60-5; **24b**, 94426-61-6; **25**, 66426-76-4; **26**, 66426-78-6; **27**, 66426-80-0; **30**, 94426-62-7; **32**, 6833-44-9; **33**, 94458-39-6; **34** (R = *n*-Pr), 94426-63-8; **35** (R = *n*-Pr), 94426-64-9; **36** (R = *n*-Pr), 94426-65-0; **37** (R = *n*-Pr), 94426-66-1; A, 79169-54-3; B, 79169-53-2; C, 42516-72-3; $RuH_2(PPh_3)_4$, 19529-00-1; $RuH_2[P(p\text{-}PhOMe)_3]_4$, 94458-40-9; $RuH_2[P(p\text{-}PhMe)_3]_4$, 94458-41-0; $RuH_4(PPh_3)_3$, 31275-06-6; $RuH_2[PPh_2Me]_4$, 23940-61-6; $RuH_2[PPhMe_2]_4$, 54831-65-1; CH_2=CHCH=CH_2, 106-99-0; CH_2=$C(CH_3)$CH=CH_2, 78-79-5; (*E*,*E*)-$CH_3(CH$=$CH)_2CO_2Me$, 689-89-4; (*E*)-CH_2=CHCH=$CHCO_2Me$, 2409-87-2; (*E*)-CH_2=CHCH=CHPh, 16939-57-4; (*E*)-PhC≡CCH=CHPh, 13343-79-8; (*Z*)-PhC≡CCH=CHPh, 13343-78-7; CH_2=$C(CH_3)C(CH_3)$=CH_2, 513-81-5; $(CH_3)_2$C=CHCH=$C(CH_3)_2$, 764-13-6; CH_2=CHCH=CHOAc, 1515-76-0; CH_2=C=CH_2, 463-49-0; *n*-PrC≡CD, 7299-47-0; $RuCl_3$, 10049-08-8; $NaBH_4$, 16940-66-2; P(*n*-Bu)$_3$, 998-40-3; PEt_3, 554-70-1; 1,3-cyclohexadiene, 592-57-4; 1,3-cyclooctadiene, 1700-10-3; furan, 110-00-9.

Hydrolysis of *N*-(Sulfonatooxy)-*p*-acetotoluidide: Solution Chemistry of Models for Carcinogenic Metabolites of Aromatic Amides

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The hydrolysis reactions of the title compound, a model for the carcinogenic metabolites of polycyclic aromatic amides, were investigated over the pH range 1.0–8.0 by UV spectroscopic methods, product analyses, HPLC, and ^{1}H NMR. This compound is unique among the *N*-(sulfonatooxy)acetanilides that have been studied to date in that over most of the pH range examined it exhibits non-first-order reaction kinetics. Product analyses indicate that, like the other *N*-(sulfonatooxy)acetanilides, the hydrolysis of this compound involves N–O bond cleavage, and the kinetics of the N–O bond cleavage process are consistent with a mechanism that includes generation of nitrenium ion–sulfate ion pairs. Four transient species, **9**–**12**, were generated in sufficient quantity to be detected during the hydrolysis reaction. On the basis of isolated decomposition products and kinetic and spectral data obtained during the course of the hydrolysis reaction, the intermediate **9** was identified as 4-hydroxy-4-methylcyclohexa-2,5-dien-1-one *N*-acetylimine, while **10** and **11** were identified as the isomeric *cis*- and *trans*-*N*-acetyl-2-amino-5,6-dihydroxy-5-methylcyclohexa-1,3-dienes. These species are analogous to materials isolated by Gassman and Granrud from the methanolysis reactions of the methanesulfonate ester of *N*-hydroxy-*p*-acetotoluidide. The fourth intermediate, **12**, has been tentatively identified as 4-(sulfonatooxy)-4-methylcyclohexa-2,5-dien-1-one. The pH dependence of the hydrolysis reactions of **9** and **10** have also been thoroughly investigated. Both are subject to acid catalysis of hydrolysis and give rise to a number of products.

There is considerable evidence that several carcinogenic aromatic amides such as *N*-acetyl-2-aminofluorene (AAF) are metabolically activated by *N*-hydroxylation followed by esterification.[1,2] The sulfuric acid esters appear to be

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