91 (100). Anal. Calcd for $C_{15}H_{15}NO_3$: C, 70.02; H, 5.88; N, 5.44. Found: C, 70.14; H, 5.91; N, 5.44.

Reduction of 3,3′,4′,5,7-Pentamethyldihydroquercetin (15). Reduction of 700 mg (1.87 mmol) of pentamethyldihydroquercetin in 30 mL of liquid NH_3 using 200 mg (8.7 mmol) of Na as above gave a light brown oil. Chromatography of the oil on a silica gel column using 25% EtOAc–hexane as eluant afforded two major products. The first to elute, mp 125–126 °C (202 mg, 31%), was identical with the sample of dihydrochalcone **6** prepared previously. The second material was twice recrystallized from MeOH to afford 82 mg (12%) of **2-methoxy-1-(2,4-dimethoxy-6-hydroxyphenyl)-3-(3,4-dimethoxyphenyl)propanone (17):** mp 143.5–145 °C; NMR δ 2.8–3.1 (2 H, m, C_3H), 3.37 (3 H, s, OCH_3), 3.92 (12 H, s, OCH_3), 5.08 (1 H, q, C_2H), 6.15 (2 H, q, ArH), and 6.86 (3 H, br s, ArH); MS *m/e* (rel intensity) 376 (3), 344 (18), 181 (100), and 151 (39); IR (KBr) 1610, 1580, 1510, 1355, 1315, 1260, and 1210 cm^{-1}. Anal. Calcd for $C_{20}H_{24}O_7$: C, 63.82; H, 6.43. Found: C, 63.67; H, 6.64.

Reduction of 3′,4′,5,7-Tetramethyldihydroquercetin (16).[19] Reduction of 3′,4′,5,7-tetramethyldihydroquercetin (300 mg, 0.83 mmol) in 10 mL of NH_3 with 100 mg (4.35 mmol) of Na gave a complex mixture of products. The two major ones were isolated by preparative TLC on silica gel. Recrystallization from MeOH afforded 48 mg (16%) of dihydrochalcone 6, mp 125–126.5 °C, and 69 mg (23%) of α-hydroxydihydrochalcone 11, mp 116–117 °C.

Registry No.—**5**, 1247-97-8; **6**, 65236-01-3; **7**, 7245-02-5; **8**, 3516-95-8; **8** oxime, 69429-57-8; **9**, 69429-58-9; **10**, 1244-78-6; **11**, 65236-02-4; **12**, 577-85-5; **13**, 69429-59-0; **13** oxime, 69429-60-3; **14**, 4940-48-1; **15**, 20754-54-5; **16**, 20754-53-4; **17**, 69429-61-4.

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Metal Catalysis in Organic Reactions. 8. Alkylative Dimerization of 1-Alkynes Induced by Tris(acetylacetonato)manganese/Trialkylalane Systems

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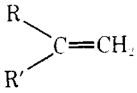
The reaction between trialkylalanes and terminal alkynes in the presence of manganese complexes has been investigated under various conditions. At room temperature, the $Mn(acac)_3$-catalyzed reaction between triisobutylaluminum and 1-alkynes affords (*E,E*)-1-isobutyl-2,4-dialkyl-1,3-butadienes, whose yields depend on the structure of the 1-alkyne used and on the experimental conditions. Using (*S*)-3-methyl-1-pentyne, the reaction was observed to occur without significant racemization. The preparative aspect of this manganese-induced process is discussed together with a mechanistic approach.

Recently we have reported that nickel-promoted dimerization of 1-alkynes provides a useful method for preparing dienes of particular structure.[1,2] In continuing our research, some interesting, although preliminary, results on the formation of (*E,E*)-2-methyl-5-butyl-4,6-undecadiene in a manganese-induced reaction of 1-hexyne with triisobutylaluminum have been described.[3] We have now extended our investigations to elucidate the potential synthetic use of the reaction between aliphatic 1-alkynes and trialkylalanes in the presence of tris(acetylacetonato)manganese(III) [$Mn(acac)_3$].[3] The present paper deals with the dynamics of the reaction along with an investigation on the stereospecificity of the process, carried out with chiral alkynes, and a mechanistic approach on the mode of acting of the catalytic system.

Results and Discussion

The stoichiometric reaction of trialkylalanes with 1-alkynes (**1**) in the presence of nickel complexes leads at room temperature to the formation of little amounts of the corresponding 1-alkenes (**2**), 2-alkyl-1-alkenes (**3**), and (*E*)-1-alkyl-1-alkenes (**4**), together with (*E*)-2,4-dialkyl-1,3-butadienes (**5**) as main product, and 1,3,5-trialkyl- and 1,2,4-trialkylbenzenes (**6** and **7**).[1-4] Using $Mn(acac)_3$ as catalyst under the same conditions, compound **9** is formed principally, along with a series of side products (Scheme I). Most of these products were identified by comparison of their GLC retention times with those of authentic samples,[1,5] while dienes **9** and **10** were isolated from the reaction mixtures and their structures assigned through chemical and spectroscopical techniques.



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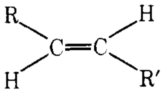

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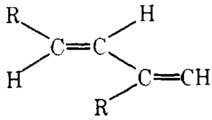

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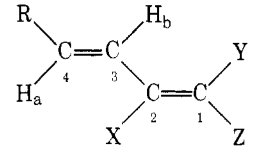
For example, the structure of diene **9a** was elucidated by partial ozonation of a sample, followed by treatment of the mixture of the ozonides with $LiAlH_4$ to afford 1-pentanol, 3-methyl-1-butanol, and two α,β-unsaturated carbinols of the

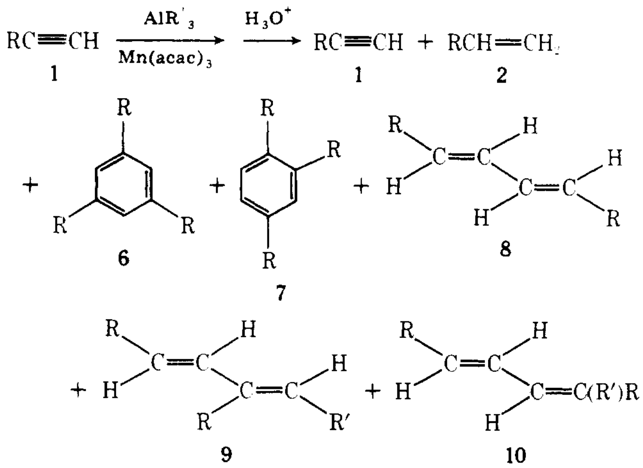
Table I. Comparative Spectral Data of Selected Dienes



compd, R	X	Y	Z	IR (neat), cm^{-1}	^{1}H NMR chemical shifts, δ^a (ppm)					coupling constants, J (Hz)				
					H_a	H_b	X	Y	Z	^2J	$^3J_{vic}$	^3J_t	^3J_s	^3J_c
5a, n-Bu^b	R	H	H	3090, 1610, 963, 882	5.57 (dt)	5.97 (d)		4.76 (m)	4.76		6.6	15.7		
5b, EtCH(Me)^{b,c}	R	H	H	3090, 1610, 965, 880	5.55 (dd)	6.00 (d)		4.90 (d)	4.77 (m)	1.5	7.5	15.7		
5c i-PrCH(Me)^b	R	H	H	3090, 1600, 965, 883	5.50 (dd)	5.93 (d)		4.90 (d)	4.73 (d)	1.6	7.1	15.5		
5d t-BuCH(Me)^{b,d}	R	H	H	3095, 1600, 965, 887	5.65 (m)	6.00 (d)		5.03 (m)	4.77 (m)	1.5	8.2	13.9		
8b, EtCH(Me)^e	H	H	R	985	5.56 (m)	5.93 (m)	5.93 (m)	5.56 (m)			7.9	14.9	10.7	
8d, t-BuCH(Me)^e	H	H	R	985	5.55 (m)	5.90 (m)	5.90 (m)	5.55 (m)			7.9	14.9	10.7	
9a, n-Bu	R	H	i-Bu	3020, 1085, 965	5.42 (dt)	5.84 (d)		5.22 (t)			6.5, 7.2	15.6		
9b, EtCH(Me)	R	H	i-Bu	3020, 965	5.54 (dd)	5.84 (d)		5.43 (t)			7.9, 7.4	15.5		
9c, i-PrCH(Me)	R	H	i-Bu	3020, 965	5.50 (dd)	5.87 (d)		5.37 (t)			6.5, 7.2	15.5		
9d, t-BuCH(Me)	R	H	i-Bu	3020, 965	5.55 (m)	5.98 (d)		5.44 (t)			7.6, 7.0	15.5		
9f, EtCH(Me)CH$_2$	R	H	i-Bu	3020, 963	5.40 (dt)	5.89 (d)		5.31 (t)			6.5, 7.3	15.6		
9g, EtCH(Me)(CH$_2$)$_2$	R	H	i-Bu		5.43 (dt)	5.93 (d)		5.27 (t)			6.3, 7.2	15.8		
9h, n-Bu(CH$_2$)$_2$	R	H	i-Bu		5.42 (dt)	5.88 (d)		5.25 (t)			6.5, 7.0	15.6		
10b, EtCH(Me)	H	R	i-Bu	3020, 960	5.34 (dd)	6.16 (dd)	5.75 (d)				7.8	14.9	10.6	
11, EtCH(Me)^e	H	R	H	980, 947, 747	5.51 (m)	6.27 (m)	5.90 (m)		5.05 (m)		7.5, 10.5	14.2	10.5	10.5
11, t-BuCH(Me)^e	H	R	H	980, 948, 770, 725	5.51 (m)	6.22 (m)	5.84 (m)		5.18 (m)		7.5, 10.5	14.2	10.5	10.5
12, n-Bu^f	R	i-Bu	H	3025, 965	5.52 (dt)	6.20 (d)			5.15 (t)		6.8, 7.4	15.5		

[a] In CCl$_4$, from Me$_4$Si. [b] Reference 1. [c] Reference 2. [d] Reference 4. [e] Reference 5. [f] Reference 7.

Scheme I



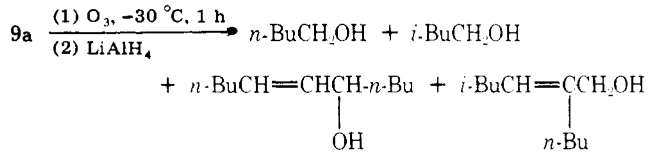
1–8: a, R = n-Bu
b, R = EtCH(Me)
c, R = i-PrCH(Me)
d, R = t-BuCH(Me)
e, R = t-Bu
f, R = EtCH(Me)CH$_2$
g, R = EtCH(Me)(CH$_2$)$_2$
h, R = n-Bu(CH$_2$)$_2$

9,10: a, R = n-Bu; R' = i-Bu
b, R = EtCH(Me); R' = i-Bu
c, R = i-PrCH(Me); R' = i-Bu
d, R = t-BuCH(Me); R' = i-Bu
e, R = t-Bu; R' = i-Bu
f, R = EtCH(Me)CH$_2$; R' = i-Bu
g, R = EtCH(Me)(CH$_2$)$_2$; R' = i-Bu
h, R = n-Bu(CH$_2$)$_2$; R' = i-Bu
i, R = n-Bu; R' = Et
j, R = n-Bu; R' = EtCH(Me)CH$_2$

formula $C_{11}H_{22}O$, having the structures shown in Scheme II.

In all cases, the E configuration of the double bonds of compounds **9** was established through the J_{HH} coupling constants and through correlation[6] of the chemical shifts of the appropriate alkenyl protons with those of dienes of defined structure.[1,5] As shown in Table I, which is a collection of some spectral properties of compounds **5, 8, 9,** and **10** together with spectral comparative data of selected dienes, the resonances of the H$_b$ protons bound to the 3 position of the unsaturated moiety of compounds **9** occur in fact at 5.84–5.98 ppm from Me$_4$Si, close to those of H$_b$ protons of diene **5**[1] and **8**,[5] which are characterized by similar chemical environments. The E configuration of the 1,2 double bond of dienes **9** is further confirmed by the observation that the H$_b$ proton of the configurational isomeric diene **12**[7] occurs at lower magnetic fields (6.20 ppm from Me$_4$Si), according to that observed in dienes **11** having the Z configuration for the 1,2 double bond.[5]

Scheme II



The reactions were generally carried out in pentane; care was taken in the preparation of the catalyst, which was obtained by adding Mn(acac)$_3$ to a pentane solution of the trialkylalane at −20 °C. The 1-alkyne **1** was added within 5 min, and the reaction mixtures were kept at a thermostatted temperature for the required time. When the catalyst was prepared at higher temperatures, no reproducible results were obtained. After the reaction was completed, the mixtures were hydrolyzed with dilute sulfuric acid and the organic phases were analyzed by GLC. The preliminary runs we have conducted have shown that, at least at temperatures higher than 0 °C, the reaction is practically complete within 5 h and that neither interconversion nor further transformation of the products occurs even when the reaction time is prolonged.

In order to provide more information on the dynamics of this manganese-induced reaction, we have explored the influence of some variables on the course of the reaction, such as the molar ratio 1/R'$_3$Al and the temperature. The results obtained in the reaction between triisobutylaluminum and 1-hexyne in the presence of Mn(acac)$_3$ (Table II) show that the molar ratio 1-hexyne (**1a**)/i-Bu$_3$Al is important in determining the course of the reaction. In fact, increasing the molar ratio from 0.5 to 4.0 (entries 2–4) has the effect of decreasing the yields of compound **9a**, while at high molar ratios of **1a**/i-Bu$_3$Al the yields of the cyclotrimers **6a** and **7a** are increased and these compounds become the main products (entry 4).

Table II. Reaction of 1-Alkynes (1a,b) with i-Bu$_3$Al in the Presence of Mn(acac)$_3$ at Various [1]/[i-Bu$_3$Al] Ratios and at Different Temperatures [a]

				products, % yields[b]						
entry	compd, R	[1]/[i-Bu$_3$Al]	temp, °C	1[c]	2	6	7	9	10	polyenes[d]
1[e]	**1a**, n-Bu	1.0	0	14	6	5	5	56		12
2	**1a**, n-Bu	0.5	25	11	7	7	6	67		
3	**1a**, n-Bu	1.0	25	6	4	10	9	69		traces
4[e]	**1a**, n-Bu	4.0	25	2	2	29	29	18		n.d.
5[f]	**1a**, n-Bu	0.5	65	3	3	8	8	75		
6[f]	**1a**, n-Bu	1.0	65			10	13	69		
7	**1b**, EtCH(Me)	0.5	25	9	6	6	13	55	4	
8	**1b**, EtCH(Me)	1.0	25	7	6	14	22	43	3	
9[f]	**1b**, EtCH(Me)	0.5	65	3	3	9	17	56	8	

[a] The reactions were carried out in pentane for 5 h: [1]/[Mn(acac)$_3$] = 40. [b] By GLC (SE 301) of the reaction mixtures upon hydrolysis, the other products being traces of compounds **3**, **4**, and **5**. [c] Present as alkynylalane before hydrolysis. [d] Based on methanol-insoluble polymer fraction. [e] Reaction time 40 h. [f] In heptane for 30 min.

Table III. Reaction between 1-Hexyne (1a) and R'$_3$Al in the Presence of MnX$_n$ [a]

			products, % yields[b]							
entry	R'$_3$Al	MnX$_n$	1[c]	2	3	4	6	7	9	polyenes[d]
3	i-Bu$_3$Al	Mn(acac)$_3$	6	4	traces		10	9	69	traces
10	i-Bu$_3$Al	Mn(acac)$_2$	12	10		1[l]	6	6	64	traces
11[e]	i-Bu$_3$Al	MnCl$_2$	38	56	1[j]	4				
12[f,g]	i-Bu$_3$Al	Mn$_2$(CO)$_{10}$	38	27	3	11	1	2		
13	Et$_3$Al	Mn(acac)$_3$	74	1	8[k]	7[m]	traces			11
14[g,h]	(EtCHMeCH$_2$)$_3$Al	Mn(acac)$_3$	11	9		1[n]	16	13	45	
15	i-Bu$_3$AlOEt$_2$	Mn(acac)$_3$					17[i]	16[i]		41

[a] The reactions were carried out in pentane at 25 °C for 40 h: [1a]/[i-Bu$_3$Al] = 1; [1a]/[MnX$_n$] = 40. [b] By GLC (SE 301). [c] Present as alkynylalane before hydrolysis. [d] Based on methanol-insoluble polymer fraction. [e] The mixture contained 1% of (Z)-9-methyl-6-butyl-5-methylene-6-decene. [f] In heptane at 65 °C for 2 h; the mixture contained 16% of (Z)-9-methyl-6-butyl-5-methylene-6-decene. [g] [1a]/[R'$_3$Al] = 0.5. [h] Reaction time 5 h. [i] Isolated yields. [j] Registry no. 52763-10-7. [k] Registry no. 1632-16-2. [l] Registry no. 28665-55-6. [m] Registry no. 14919-01-8. [n] Registry no. 69055-73-8.

Table IV. Reaction of 1-Alkynes (1) with i-Bu$_3$Al in the Presence of Mn(acac)$_3$ [a]

		products, % yields[b]						
entry	compd, R	1[c]	2	6	7	8	9	10
2	**1a**, n-Bu	11	7	7	6		67	
7	**1b**, EtCH(Me)	9	6	6	13	3	55	4
16	**1c**, i-PrCH(Me)	25	13	3	2	2	49	4
17[d]	**1c**, i-PrCH(Me)	8	2	5	4	3	73	4
18[e]	**1d**, t-BuCH(Me)	53	14	2	1	2	23	3
19[d,e]	**1d**, t-BuCH(Me)	32	6	3	2	3	45	6
20[d]	**1e**, t-Bu	22	27	traces		12	18	14
21	**1f**, EtCH(Me)CH$_2$	24	14	2	3		55	
22	**1g**, EtCH(Me)(CH$_2$)$_2$	19	18	5	5		49	
23	**1h**, n-Bu(CH$_2$)$_2$	17	14	3	3		53	

[a] The reactions were carried out in pentane at 25 °C for 5 h: [1]/[i-Bu$_3$Al] = 0.5; [1]/[Mn(acac)$_3$] = 40. [b] By GLC (SE 301) of the reaction mixtures upon hydrolysis, the other products being traces of compounds **3**, **4**, and **5**. [c] Present as alkynylalane before hydrolysis. [d] [1]/[Mn(acac)$_3$] = 20. [e] The mixture contained 1% of 2,3,3-trimethylpentane.

Variation of the reaction temperature has little effect on the yields of the products; an increase of temperature seems to favor slightly the dimerization and cyclotrimerization processes over those leading to the low molecular weight products (entries 2,5 and 3,6). At last, it is noteworthy that when carrying out the reaction at 0 °C, noticeable amounts of polyenes are formed, at least when **1a** is used.

A similar trend is observed when 3-methyl-1-pentyne (**1b**) is used as substrate (entries 7–9). In this case, the dimerization is less selective; the isomer diene **10b** is also formed, and its formation seems to be improved by an increase of temperature (entries 7 and 9).

To obtain further information on the preparative aspects of this reaction,[4] we have tested the possibility of using other organometallic systems, changing both the nature of the trialkylalanes and of manganese complex. The runs were carried out at 25 °C for 40 h in order to compare the results obtained (Table III) with those related to the uncatalyzed reaction.[8] The data show that bis(acetylacetonato)manganese has a behavior similar to that of Mn(acac)$_3$ (entries 3 and 10), whereas MnCl$_2$ and a zerovalent manganese complex, Mn$_2$(CO)$_{10}$, do not have any catalytic action on the reaction for only slight deviations in yields were observed compared with the products of the uncatalyzed reaction[8] (entries 11 and 12).

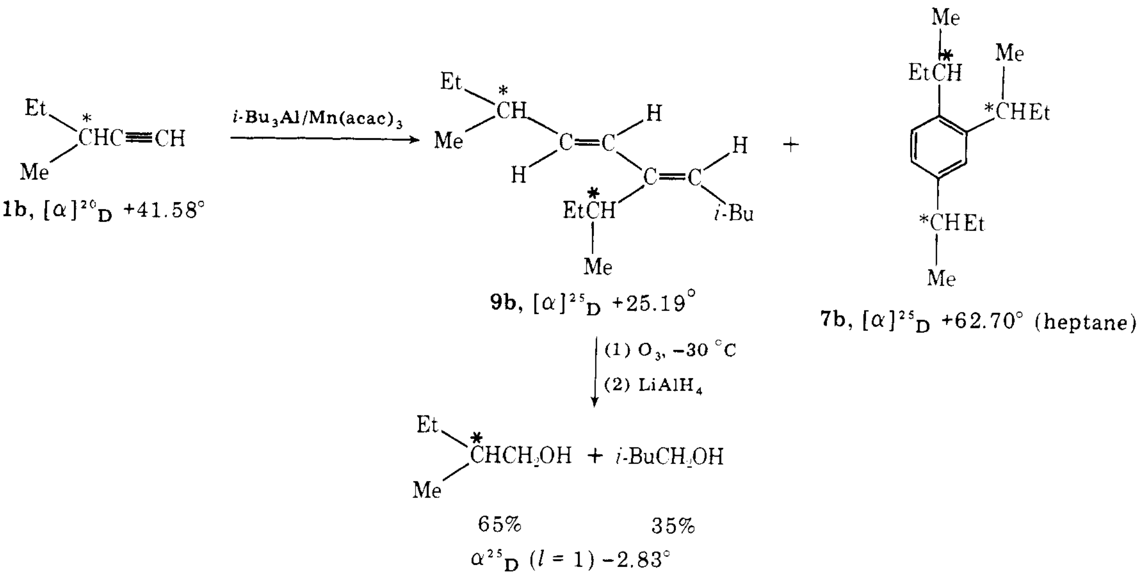
The course of the reaction is noticeably affected by the nature of the trialkylalanes used; in fact, while triethylaluminum does not give rise to the formation of diene **9i** (entry 13), tris(2-methylbutyl)aluminum, whose structure resembles that of i-Bu$_3$Al, provides **9j** even if to a less extent (entry 14).

In this context, it can be observed that the presence of diethyl ether as a ligand on i-Bu$_3$Al prevents the formation of the alkylation and dimerization products **3a**, **4a**, and **9a**, whereas cyclotrimerization and oligomerization processes are improved.

Although these last data have indicated that the capability of this reaction to synthesize compounds of general formula **9** is limited by the structure of the trialkylalane used, the results obtained with i-Bu$_3$Al[4] prompted us to explore the synthetic value of this reaction for preparing (E,E)-1-isobutyl-2,4-dialkyl-1,3-butadienes (**9a–h**). For this purpose, some 3-alkyl-, 4-alkyl-, and 5-alkyl-1-alkynes were used as substrates. Inspection of Table IV shows that the yields of diene **9** are depressed when the 1-alkyne **1** used is sterically hindered, as in the case of 3-alkyl-1-alkynes.

The conversion of compound **1** into the dimer **9** does in fact decrease with increasing size of the substituent alkyl group

Scheme III



on the triple bond of **1**, from 3-methyl-1-pentyne (**1b**) to 3,3-dimethylbutyne (**1e**). However, the yields of diene **9** become satisfactory by using linear 1-alkynes (entries 2 and 23) and β- or γ-branched terminal substrates (entries 21 and 22).

These findings would seem to indicate that all of the processes that do not require catalytic action of the manganese complex are competitive with the metal-promoted pathways. This competition seems to be dependent on the structure of **1** and undoubtedly on the molar ratio **1**/Mn(acac)$_3$; in fact, by decreasing such a ratio both the conversion of the acetylenic substrate **1** and the yields of diene **9** are again increased (entries 17 and 19). The structure of **1** seems to be important also in determining the formation of some byproducts, such as compounds **8** and **10**, which are formed only with α-branched 1-alkynes. Compounds **8** and **10**, derived from head-to-head dimerization processes, are particularly improved in the case of **1e**. Moreover, it is interesting to note that the cyclotrimerization process is not selective, with the exception of **1b** (entry 7).

The overall results have pointed out that under mild conditions aliphatic 1-alkynes and *i*-Bu$_3$Al react in the presence of catalytic amounts of Mn(acac)$_3$ to afford (*E*,*E*)-1-isobutyl-2,4-dialkyl-1,3-butadienes **9a–h** in satisfactory yields.

Therefore, since compounds **9** cannot be prepared easily through conventional methods, the value of synthesis is clear. In order to establish also the possibility of preparing chiral dienes of general formula **9**, a sample of (*S*)-3-methyl-1-pentyne, optical purity 89%,[9] was treated with 2 equiv of *i*-Bu$_3$Al in the presence of Mn(acac)$_3$ (molar ratio **1b**/Mn = 40:1) in pentane at 25 °C for 5 h (Scheme III). The reaction mixture, after hydrolysis, contained mostly the diene **9b** and the trialkylbenzene **7b** (entry 7). Distillative workup gave (*E*,*E*)-(1′*S*,8*S*)-2,8-dimethyl-5-(1′-methylpropyl)-4,6-decadiene (44% yield) and 1,2,4-tris[(*S*)-1-methylpropyl]benzene, optical purity 85%.[2] For evaluating the stereospecificity of the dimerization process, a sample of compound **9b** was converted into (*S*)-2-methyl-1-butanol, optical purity 89%,[10] through reductive ozonolysis (Scheme III).

These results show that all of the processes occur without racemization; thus, the synthesis of optically active dienes of general formula **9** can be conveniently performed from chiral 1-alkynes **1** via this manganese-induced reaction.

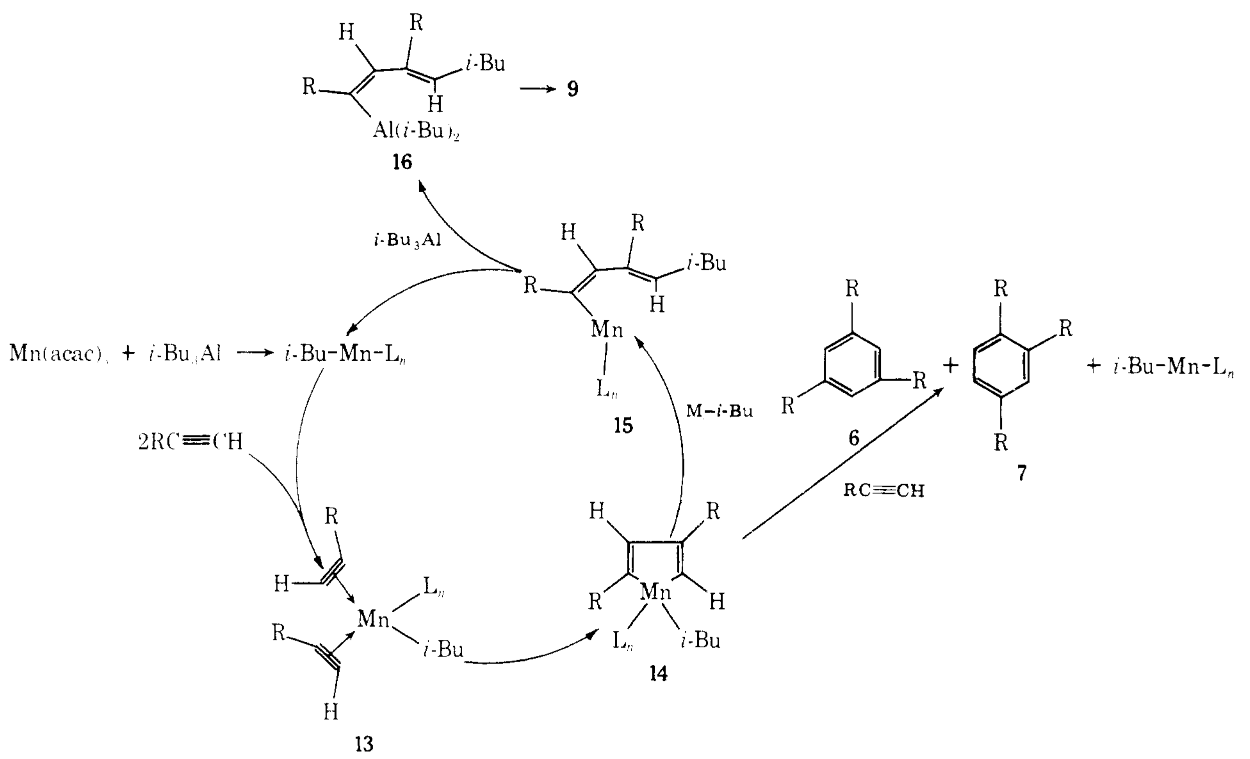
Regarding the mechanism of the reaction, the results obtained indicate that the actual catalyst is formed by reaction of *i*-Bu$_3$Al with the manganese complex. On the basis of literature[11] and considering also that Mn(acac)$_2$ has the same catalytic activity as Mn(acac)$_3$ (entries 3 and 10), it seems likely that the catalyst might contain the metal atom in a reduced state. The presence of small quantities of 2,5-dimethylhexane in the hydrolyzed reaction mixtures suggests the formation of alkylmanganese species, containing at least partially the ligand group and presumably stabilized by coordination with molecules of **1**.[12]

During the reaction fast alkyl exchange processes[13] must occur between the catalytic species and the excess *i*-Bu$_3$Al; in fact, when the reaction is carried out in the presence of coordinating solvents, only those products whose formation does not require exchange reactions, such as cyclotrimers and polyenes, are formed (entry 15).

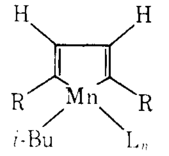
Although no totally satisfactory mechanism can be formulated, a possible picture that accounts for the results is suggested in Scheme IV, where the formation of the reaction products is assumed to proceed via coordination of two molecules of the alkyne **1** on the alkylmanganese species (**13**). Subsequent intermolecular oxidative coupling of the two acetylene moieties should give the metallocyclic manganese derivative **14**.[4,14,15] Under this assumption, the metallocycle **14** could give rise to the dienylmanganese complex **15** and hence to the dienylaluminum compound **16**[16] through a migration of an isobutyl group to the hydrogen-bearing α position. Based on the structure of diene **9**, such a process should take place by inverting the configuration at the terminal carbon atom. Since a reductive elimination occurs generally with retention of configuration at least in the cases reported up to date, this experimental finding seems to be best supported by assuming that the pathway leading to **15** may involve an intermolecular attack of an isobutyl group on the intermediate **14** (Scheme IV).[17] Moreover, although a "zipper" mechanism in which three molecules of the 1-alkyne **1** cyclize in the coordinative sphere of the metal atom[18] cannot be ruled out, the intermediate **14** could be responsible for the trialkylbenzene formation as well.[4]

When α-branched acetylenic compounds **1** are used, small amounts of byproducts are formed together with diene **9**, relative yields increasing with increasing steric hindrance of **1** (Table IV). Even the formation of these products might be rationalized with the mechanism of Scheme IV, the crucial feature being the intermediacy of complexes, like **13**, in which steric hindrance is minimized before the metallocycle-forming

Scheme IV



step. In particular, the formation of the isomeric diene **10** should be related to a different steric arrangement (head-to-head) of the acetylenic units in the reaction intermediate **13**. Thus, a metallocyclic manganese cyclopentadiene **17** that



17

gives rise to the dienylmanganese compound, precursor of **10**, should be formed. The formation of diene **8** should be attributed to the same intermediate **17**, steric hindrance preventing alkyl migration to the α position of the metallocycle **17**. Subsequent exchange reaction with i-Bu$_3$Al should afford **8** upon hydrolysis.[19]

Experimental Section

General. Triethylaluminum, triisobutylaluminum (Fluka A. G. Co., Buchs), and tris(2-methylbutyl)aluminum, prepared as previously reported,[20] were carefully redistilled under nitrogen and stored in sealed capillary glass vials in weighed amounts. Triisobutylaluminum diethyl etherate was prepared by adding diethyl ether to trialkylalane and removing the excess of the former under vacuum, manganese pentacarbonyl dimer [Mn$_2$(CO)$_{10}$] was a commercial product (Strem Chemicals, U.S.A), and anhydrous MnCl$_2$ was obtained from its tetrahydrate by treating at 150 °C for 50 h in vacuo, while Mn(acac)$_2$ and Mn(acac)$_3$ were prepared and purified by known procedures.[21,22] 1-Hexyne, 1-octyne, and 3,3-dimethylbutyne were commercial products (Fluka), which were carefully distilled before use. (S)-3-Methyl-1-pentyne ($[\alpha]^{20}{}_{\mathrm{D}}$ +41.58°)[9] and other 1-alkynes (**1**) employed were synthesized from the corresponding α-olefins by published methods;[9,23] 1-hexyne-*1-d* was obtained from 1-hexyne by a described procedure.[24] Solvents were commercial reagent grade materials, purified by standard methods and redistilled under nitrogen from LiAlH$_4$ before use. All air-sensitive compounds were handled in a glovebox filled with nitrogen. GLC analyses were performed on Perkin-Elmer F-30 and 3920 B instruments with flame ionization detectors (200 × 0.30 cm columns), while preparative GLC was carried out on a Perkin-Elmer F21 chromatograph (300 × 0.80 cm columns).

Optical rotations were measured with a Perkin-Elmer 142 polarimeter; unless otherwise specified, rotations refer to pure liquid. NMR spectra were obtained with a Jeol JNM PS-100 spectrometer on CCl$_4$ solutions; all chemical shifts are reported in δ (ppm) with Me$_4$Si as an internal standard. Splitting patterns were designated as follows: s, singlet; d, doublet; t, triplet; dd, doublet of doublet; dt, doublet of triplet; and m, multiplet. IR spectra were recorded on a Perkin-Elmer 225 spectrometer as liquid films. Mass spectra were taken at 70 eV on a Varian Mat CH7 GC-MS spectrometer.

General Procedure. All reactions were carried out at least in duplicate under a dry nitrogen atmosphere. In a typical small-scale reaction, a three-neck, 25-mL, round-bottom flask was fitted with a stirring bar, a glass stopcock, a Versilic silicone cap, and a sealed angular piece of glass tubing containing 0.3 mmol of the solid manganese compound. The vessel was charged with 2 mL of pentane, and the required amount of trialkylalane was added from the sealed capillary glass vial. The reaction flask, cooled with a −20 °C cold bath, was then turned so that the manganese compound dropped into the trialkylalane solution. After a 5-min agitation, the 1-alkyne (**1**) was injected by hypodermic syringe through the cap at the same temperature (−20 °C). The resulting mixture was stirred in a thermostatted bath, at the appropriate temperature, for the desired time of aging. Hydrolysis was carried out with dilute sulfuric acid, and the organic phase was extracted with ether. The combined extracts were washed with aqueous sodium bicarbonate and then dried over anhydrous sodium sulfate; quantitative (by internal standard method) and qualitative analyses of the reaction products were performed by GLC on the crude mixture (2.5% silicone gum rubber E 301 on 80–100 mesh Chromosorb W at 40–250 °C, N$_2$ flow rate 10 mL min^{-1}). All unknown oligomers were isolated by preparative GLC, and their structures were deduced by ozonolysis techniques and from IR, ^{1}H NMR, and mass spectra; when necessary, larger scale reactions were used for these separations. After the gas chromatographic measurements, any polymer fraction was precipitated by methanol from the ethereal solution, isolated by filtration, and dried under vacuum.

At 65 °C the experiments were carried out in n-heptane solutions.

When -1-hexyne-*1-d* was used and in the deuteriolysis experiments, the reactions were carried out as above, taking care that all glassware used was carefully dried. In these cases, the hydrolysis was accomplished with water or deuterium oxide (>99.5% pure). The suspension obtained was added with 10 mL of dry pentane, stirred under nitrogen for 24 h, filtered, and washed with dry pentane. All deuterated compounds were identified through their mass spectra.

Several experiments are described below.

Reaction between 1-Hexyne (1a) and i-Bu$_3$Al in the Presence

of Mn(acac)$_3$ (Entry 3). According to the general procedure, Mn(acac)$_3$ (0.540 g, 1.53 mmol) was allowed to react at −20 °C in a three-neck, 250-mL, round-bottom flask with *i*-Bu$_3$Al (12 g, 61 mmol) in pentane (20 mL) to give an orange-yellow solution. To this solution, at the same temperature (−20 °C), was added **1a** (5 g, 61 mmol), and the resulting mixture, the color of which changed to red-brown within a few minutes, was stirred at 25 °C for 5 h.

The crude products obtained upon hydrolysis were analyzed by GLC and fractionally distilled to yield 3.3 g (48% yield) of **9a** (≥99% pure): bp 94 °C (0.8 mmHg); mass spectrum, *m/e* 222 (M^+, 23%), 207 (3), 193 (15), 179 (42), 165 (21), 151 (8), 137 (6), 124 (76), 123 (39), 109 (45), 95 (51), 81 (76), 67 (96), 55 (58), 43 (82), 41 (100); IR 3020, 1085, 965 cm^{-1}; NMR δ 0.93 (12 H, m, CH$_3$), 1.23–1.47 (8 H, m, CH$_2$), 1.47–1.76 (1 H, m, CH), 1.91–2.27 (6 H, m, CH$_2$C=), 5.22 (1 H, t, J = 7.2 Hz, =CH–), 5.42 (1 H, dt, J = 15.6 and 6.5 Hz, =CH–), 5.84 (1 H, d, J = 15.6 Hz, =CH–).

In this run, only traces of methanol-insoluble poly(1-hexyne) were obtained: IR (polymer film) 1680, 1623, 935, 640, 625 cm^{-1}.[25]

A sample of the diene **9a** (1.5 g, 6.8 mmol) in pentane solution (50 mL) was treated with ozonized oxygen at −30 °C for 2 h. The crude reaction mixture was decomposed in ethereal solution with LiAlH$_4$, according to a procedure elsewhere described.[2] GLC analysis (8% Carbowax 20M +2% KOH on 80–100 mesh Chromosorb W at 80 °C, N$_2$ flow rate 15 mL min^{-1}) of the ether layer showed the presence of 1-pentanol and 3-methyl-1-butanol, together with minor amounts of two α,β-unsaturated carbinols of the formula $C_{11}H_{22}O$: mass spectra, *m/e* 170 (M^+, 3%), 152 (6), 113 (100), 95 (59), 69 (39), 67 (29), 57 (96), 55 (38), 43 (32), 41 (52), 28 (54), and *m/e* 170 (M^+, 34%), 152 (6), 113 (61), 109 (39), 95 (72), 71 (77), 69 (67), 67 (54), 57 (100), 55 (75), 43 (57), 41 (87).

Reaction between (*S*)-3-Methyl-1-pentyne [(*S*)-1b] and *i*-Bu$_3$Al in the Presence of Mn(acac)$_3$ (Entry 7). As previously described, a pentane solution of *i*-Bu$_3$Al (38.6 g, 195 mmol, 30 mL) was allowed to react at 25 °C for 5 h with (*S*)-**1b** (8 g, 97 mmol), $[\alpha]^{20}{}_D$ +41.58°, in the presence of Mn(acac)$_3$ (0.858 g, 2.4 mmol). The resulting mixture was hydrolyzed and analyzed by GLC as above. Careful distillation of the crude products gave a fraction (5.6 g) containing dienes **9b** (85%) and **10b** (15%). The mixture was separated by preparative GLC (8% Carbowax 20M + 2% KOH on 80–100 mesh Chromosorb W at 130 °C, N$_2$ flow rate 130 mL min^{-1}) to yield pure (*E*,*E*)-(1′*S*,8*S*)-2,8-dimethyl-5-(1′-methylpropyl)-4,6-decadiene [bp 68 °C (0.4 mmHg); $n^{25}{}_D$ 1.4569; $d^{25}{}_4$ 0.7918; $[\alpha]^{25}{}_D$ +25.19°; mass spectrum, *m/e* 222 (M^+, 10%), 193 (6), 179 (9), 165 (12), 151 (7), 137 (30), 123 (41), 109 (66), 95 (45), 81 (69), 67 (45), 57 (48), 55 (57), 43 (44), 41 (100); IR 3020, 965, 920, 840 cm^{-1}; NMR δ 0.78–1.03 (18 H, m, CH$_3$), 1.25–1.44 (4 H, m, CH$_2$), 1.56–1.68 (1 H, m, CH), 1.95 (2 H, m, CH$_2$C=), 2.02 (1 H, m, CHC=), 2.53 (1 H, m, CHC=), 5.43 (1 H, t, J = 7.4 Hz, =CH–), 5.54 (1 H, dd, J = 15.5 and 7.9 Hz, =CH–), 5.84 (1 H, d, J = 15.5 Hz, =CH–) ppm] and pure **10b** [mass spectrum, *m/e* 222 (M^+, 17%), 193 (19), 165 (22), 151 (9), 137 (69), 123 (37), 109 (100), 95 (75), 81 (91), 69 (28), 67 (37), 57 (56), 55 (56), 43 (56), 41 (75); IR 3020, 1010, 960, 890 cm^{-1}; NMR δ 0.76–1.03 (18 H, m, CH$_3$), 1.20–1.52 (4 H, m, CH$_2$), 1.55–1.76 (1 H, m, CH), 1.79–2.20 (4 H, m, CH$_2$C= and CHC=), 5.34 (1 H, dd, J = 14.9 and 7.8 Hz, =CH–), 5.75 (1 H, d, J = 10.6 Hz, =CH–), 6.16 (1 H, m, J = 14.9, 10.6, and 0.9 Hz, =CH–) ppm].

Preparative GLC (8% Carbowax 20M +2% KOH at 175 °C, N$_2$ flow rate 100 mL min^{-1}) afforded also a sample of pure 1,2,4-tris[(*S*)-1-methylpropyl]benzene, $[\alpha]^{25}{}_D$ +62.70° (*c* 5.35, heptane).[2]

Ozonolysis of (*E*,*E*)-(1′*S*,8*S*)-2,8-Dimethyl-5-(1′-methylpropyl)-4,6-decadiene. Ozonized oxygen was passed through a solution of the diene (1.5 g, 6.8 mmol), $[\alpha]^{25}{}_D$ +25.19°, in pentane (50 mL) at −30 °C for 8 h. The crude ozonide was decomposed in ethereal solution (50 mL) with LiAlH$_4$ (2 g).[2] After hydrolysis, preparative GLC (8% Carbowax 20M + 2% KOH at 100 °C, N$_2$ flow rate 150 mL min^{-1}) gave a mixture, $\alpha^{25}{}_D$ (l = 1) −2.83°,[10] containing (*S*)-2-methyl-1-butanol (65%) and 3-methyl-1-butanol (35%) (by GLC analysis, 15% (+)-diethyl tartrate on 30–50 mesh Celite C$_{22}$-AW[26] at 80 °C, N$_2$ flow rate 15 mL min^{-1}).

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Registry No.—**1a**, 693-02-7; **1b**, 2868-07-7; **1c**, 61064-08-2; **1d**, 52763-16-3; **1e**, 917-92-0; **1f**, 52713-81-2; **1g**, 61064-09-3; **1h**, 628-71-7; **2a**, 592-41-6; **2b**, 760-20-3; **2c**, 7385-78-6; **2d**, 564-03-4; **2e**, 558-37-2; **2f**, 3769-23-1; **2g**, 13151-04-7; **2h**, 111-66-0; **5a**, 61063-95-4; **5b**, 61063-96-5; **5c**, 61063-97-6; **5d**, 61063-98-7; **6a**, 841-07-6; **6b**, 64282-70-8; **6c**, 61064-01-5; **6d**, 61064-02-6; **6f**, 61064-03-7; **6g**, 61064-04-8; **6h**, 29536-28-5; **7a**, 4800-16-9; **7b**, 64282-71-9; **7c**, 61139-52-4; **7d**, 68986-03-8; **7f**, 61064-06-0; **7g**, 61064-07-1; **7h**, 10069-28-0; **8b**, 68986-09-4; **8c**, 68986-04-9; **8d**, 65604-62-8; **8e**, 22430-49-5; **9a**, 68986-10-7; **9b**, 68986-1-8; **9c**, 68986-12-9; **9d**, 68986-13-0; **9e**, 68986-05-0; **9f**, 68986-14-1; **9g**, 68986-15-2; **9h**, 9027-51-6; **10b**, 68986-16-3; **10c**, 68986-06-1; **10d**, 68986-07-2; **10e**, 68986-08-3; 11 [R = EtCH(Me)], 68986-09-4; 11 [R = *t*-BuCH(Me)], 65604-62-8; **12**, 68986-17-4; Et$_3$Al, 97-93-8; (EtCHMeCH$_2$)$_3$Al, 20663-73-4; *i*-Bu$_3$-AlOEt$_2$, 14263-25-3; *i*-Bu$_3$Al, 100-99-2; Mn(acac)$_2$, 14024-58-9; Mn(acac)$_3$, 14284-89-0; MnCl$_2$, 7773-01-5; Mn$_2$(CO)$_{10}$, 10170-69-1; 1-pentanol, 71-41-0; 3-methyl-1-butanol, 123-51-3; (*S*)-2-methyl-1-butanol, 1565-80-6.

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(16) Compound **9** can be obtained only upon hydrolysis; deuteriolysis of the reaction mixture gave, in fact, compound **9** completely D-labeled at C(4). The use of 1-hexyne-*1-d,* followed by H$_2$O-hydrolytic workup, results in the formation of 100% 1,3-D labeled **9.**

(17) Theoretically, an alternative mechanism might be assumed that proceeds from **14** through its interconversion into a π-cyclobutadienemanganese complex[14a] which should originate compound **15** via either an isobutyl group migration to the cyclobutadiene moiety or cis carbalumination of the ring followed by conrotatory ring opening, according to a referee's suggestion.

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