Metal Catalysis in Organic Reactions. Part 13.† The Reaction of 3-En-1-ynes with Trialkylalanes: Influence of Transition-metal Complexes

By Anna Maria Caporusso,* Giampaolo Giacomelli, and Luciano Lardicci, Centro di Studio del CNR per le Macromolecole Stereordinate ed Otticamente Attive, Istituto di Chimica Organica, Facoltà di Scienze M.F.N., Università di Pisa, 56100 Pisa, Italy

The reaction between trialkylalanes and 3-alkyl-, 4-alkyl-, or 3,4-dialkyl-but-3-en-1-ynes (1) leads to products which correspond to metallation, reduction, and carbalumination processes. The extent of such reactions, and the regio- and stereo-selectivity of the carbalumination, are dependent on the enyne used. A mechanism is proposed involving tautomeric equilibria among several α-unsaturated organoaluminium intermediates to explain the formation of the carbalumination products.

In the presence of catalytic amounts of nickel and manganese complexes, 3-en-1-ynes (1), by reacting with tri-isobutylaluminium, are dimerized selectively in a 'head-to-tail' fashion to conjugated tetraenes having different structures in relation to the different nature of the transition-metal complex. The preparative aspect of these induced reactions is discussed, and, in the light of previous reports, some mechanistic considerations are presented.

OUR recent studies on metal-promoted reactions of trialkylalanes with terminal acetylenes have led to synthetically useful methods for the preparation of dienes under mild conditions.[1-6] In particular the presence of small amounts of nickel complexes in the reaction between alk-1-ynes and tri-isobutylaluminium gives rise to the formation of (E)-2,4-dialkylbuta-1,3-dienes in satisfactory yields,[1-4] while using tris(acetylacetonato)manganese [Mn(acac)₃] as catalyst, the same reaction affords (EE)-1-isobutyl-2,4-dialkylbuta-1,3-dienes in high yields.[3,5]

We have now extended our researches to elucidate the synthetic utility of the reaction between aliphatic 3-en-1-ynes (1) and trialkylalanes in the presence of bis-(N-methylsalicylideneamine)nickel Ni(mesal)₂ and Mn(acac)₃, respectively, for preparing conjugated tetraenes having a defined structure and stereochemistry.
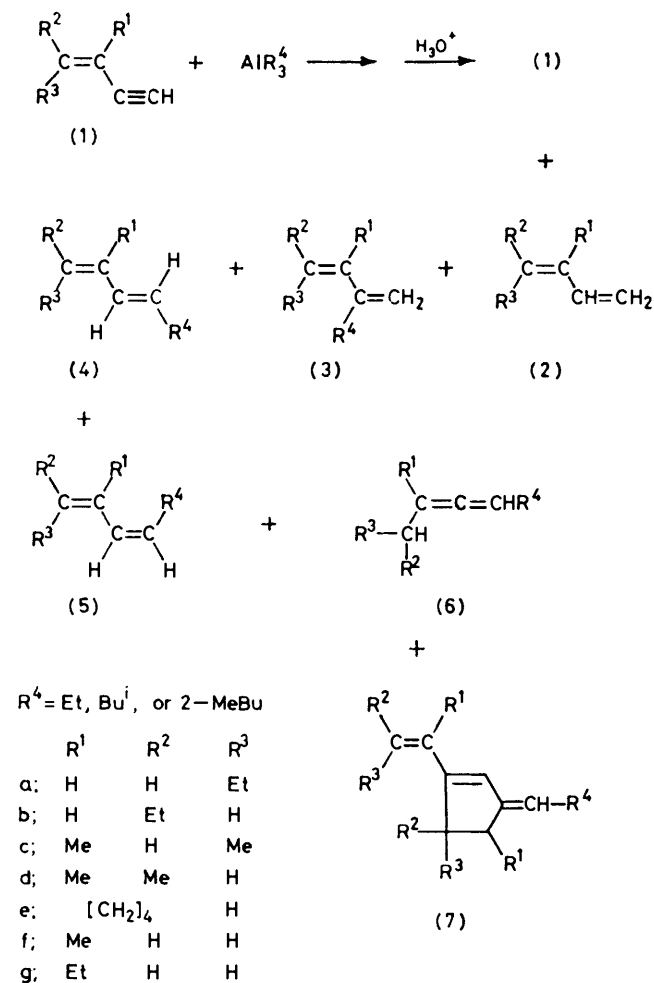
Previously we have reported that 1-alkenyl-3-alkylidene-4-alkylcyclopentenes can be synthesized via reaction of trialkylalanes with 3-alkylbut-3-en-1-ynes.[7] However, until now no systematic study has been carried out on the reaction between trialkylalanes and 3-en-1-ynes in the absence of any catalyst. Therefore we also report here an accurate investigation on the dynamics of this reaction.

RESULTS AND DISCUSSION

Reactions of Trialkylalanes with 3-En-1-ynes.—The stoicheiometric reaction of 3-en-1-ynes (1) with trialkylalanes, in pentane solution at 25 °C for 40 h, followed by hydrolysis with dilute sulphuric acid, affords products which correspond to metallation (1), reduction (2), carbalumination (3)—(6), and cyclic oligomerization (7) of the substrate (Scheme 1). The distribution of the products was determined by g.l.c. analyses and all the components (1)—(7) were identified either by comparison of their retention times with those of authentic samples, or on the basis of their spectroscopic properties (see Experimental section).

† Part 12, G. Giacomelli, L. Bertero, L. Lardicci, and R. Menicagli, *J. Org. Chem.*, in the press.

The data collected in Table 1 indicate that the course of the reaction depends essentially on the structure of the enyne (1) used. In particular, when 4-alkyl- and 3,4-dialkyl-but-3-en-1-ynes (1a—d) are employed, prevalent formation of the metallation product was observed,

	R¹	R²	R³
a;	H	H	Et
b;	H	Et	H
c;	Me	H	Me
d;	Me	Me	H
e;	[CH₂]₄		H
f;	Me	H	H
g;	Et	H	H

R⁴ = Et, Buⁱ, or 2—MeBu

SCHEME 1

along with small amounts of products corresponding to reduction and carbalumination of the triple bond of (1). All reactions are complete within 40 h as evidenced by the absence of unchanged compound (1) in the reaction mixtures before their hydrolysis. For example, the reaction of (Z)-hex-3-en-1-yne (1a) with tri-isobutyl-aluminium, under the above experimental conditions, afforded, upon hydrolysis, (1a) (83%), (Z)-hex-1,3-diene (2a) (13%), (Z)-7-methyl-5-methyleneoct-3-ene (3a; $R^4 = Bu^i$) (1%), and (3Z,5E)-8-methylnona-3,5-diene (4a; $R^4 = Bu^i$) (3%) (entry 1). On the other hand, the 3-alkylbut-3-en-1-ynes (1f and g) appear to follow considerably different reaction paths. In fact, appreciable

(iii) For each of the reactions investigated the metallation and reduction of the triple bond of the enyne occurs with complete retention of configuration of the carbon–carbon double bond of the conjugated system, while the regio- and stereo-chemistry of the carbalumination processes vary depending on the starting materials. For example, by a cis-addition of the aluminium compound to the triple bond, the 4-alkylbut-3-en-1-ynes (1a) and (1b) give stereoselectively a mixture of the possible regioisomers (3) and (4) without involving the conjugated double bond. Moreover, the regioselectivity of this reaction is affected by the nature of the trialkylalane reagent, $AlBu^i_3$ favouring the formation of the 'anti-

TABLE 1

Reaction between trialkylalanes AlR^4_3 and 3-en-1-ynes (1)

Entry	3-En-1-yne (1)			AlR^4_3	Products, yields % (by g.l.c.)						
	R¹	R²	R³		(1)[b]	(2)	(3)	(4)	(5)	(6)	(7)
1	H	H	Et (1a)	$AlBu^i_3$	83	13	1	3			
2	H	H	Et (1a)	$AlEt_3$	96	2	1	1			
3	H	Et	H (1b)	$AlBu^i_3$	67	23	1	8			
4	H	Et	H (1b)	$AlEt_3$	89	5	3	3			
5	Me	H	Me (1c)	$AlBu^i_3$	79	20			1		
6	Me	H	Me (1c)	$AlEt_3$	95	4					
7	Me	Me	H (1d)	$AlBu^i_3$	73	23			1[c]		
8	[CH₂]₄		H (1e)	$AlBu^i_3$	37	52		9		2	
9[d]	Me	H	H (1f)	$AlBu^i_3$	27	18		3	8	5	37
10[d]	Me	H	H (1f)	$AlEt_3$	48	8		6	10	3	24
11[d]	Me	H	H (1f)	$Al(2\text{-}MeBu)_3$	40	18		2	6	3	31
12	Et	H	H (1g)	$AlBu^i_3$	45	37		1	6	2	6

[a] Unless otherwise stated, all reactions were carried out for 40 h, in pentane at 25°C: value of [(1)]/[Al] = 1.0. [b] From the metallation product. [c] The compound recovered is (5c). [d] In heptane.

amounts of 1-alkenyl-3-alkylidene-4-alkylcyclopentenes (7) were obtained, by an alkylative cyclodimerization process, together with 1,2-cis- (4), 1,2-trans- (5), and 1,4-addition products (6).

The reaction of 1-ethynylcyclohexene (1e) with tri-isobutylaluminium provides another interesting case (entry 8). This reaction shows high yields of the reduction product (2e) (52%) and affords 1,2-cis- and 1,4-addition products, (4e; $R^4 = Bu^i$) and (6e; $R^4 = Bu^i$), respectively.

Some other features of the data of Table 1 deserve comment. (i) The yields of the various products seem to depend, in general, on steric factors associated with the structure of the enyne. An increase in the steric hindrance of the alkenyl group bound to the triple bond substantially favours the metallation process at the expense of reduction and carbalumination reactions. Thus high percentages of (1) are observed when 4-alkyl- and 3,4-dialkyl-but-3-en-1-ynes and (Z)-hex-3-en-1-yne (1a), instead of the corresponding (E)-isomer (1b), are used. Moreover, in the case of 3-alkylbut-3-en-1-ynes, the yield of (1) increases when the alkyl group R¹ is changed from Me to Et, while the competitive formation of the cyclo-dimer (7) decreases drastically.

(ii) The distribution of the reaction products depends on the organoaluminium compound too, although the general trend of the reaction is independent of the structure of the alane reagent. Like the similar reactions with terminal alkynes,[8,9] triethylaluminium generally depresses the reduction and carbalumination processes with respect to $AlBu^i_3$.

Markovnikoff ' compound (4) (entries 1 and 3).[8,9] On the other hand, using the other 3-en-1-ynes (1c—g), the alkyl group R⁴ of the trialkylalane adds in a highly regiospecific manner to the terminal acetylenic carbon atom producing the dienes (4) and (5), and the allene (6), independently of the structure of the alane itself. In these cases, both the stereoselectivity and stereospecificity of the carbalumination reaction are very sensitive to the structure of (1), as indicated from the data in entries 5—12.*

On the basis of these results, it seems reasonable to assume that the formation of the reaction products (1)—(7) occurs via linked mechanistic pathways which should be controlled by both the different reactivity of the organoaluminium compound [10] and steric factors connected with the structure of (1).[4,8] However, any mechanistic scheme should involve the formation of an intermediate π-enyne-aluminium complex; in fact, when the reaction is carried out in the presence of co-ordinating solvents, such as diethyl ether, the conversion of the reaction drops down to ca. 5% (after 40 h).

In order to clarify the mechanism and, in particular, to gain further general information about the carbalumination processes, reaction mixtures from $AlBu^i_3$ and 3-methylbut-3-en-1-yne (1f) or [1-²H]-3-methylbut-3-en-1-yne were treated with deuterium oxide and water
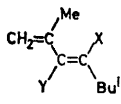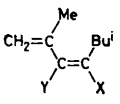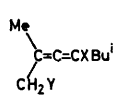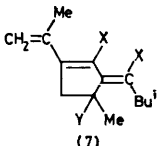
* Note that reaction of (1d) with $AlBu^i_3$ affords small amounts of (ZZ)-3,7-dimethylocta-2,4-diene (5c; $R^4 = Bu^i$) apparently arising from trans-addition of the aluminium–carbon bond to the triple bond of the enyne with inversion of configuration of the conjugated double bond (entry 7).

respectively, and the resulting products analysed by mass spectrometry. Table 2 shows that deuteriolysis of the reaction mixture from (1f) gives the diene (4f; R^4 = Bu^i) only 20% D-labelled, while compounds (5f; R^4 = Bu^i)—(7f; R^4 = Bu^i) do not contain deuterium atoms.* Moreover, the results obtained using [1-^{2}H]-3-methylbut-3-en-1-yne and subsequent treatment with H_2O (Table 2) indicate that compounds (4)—(7) are present in the reaction mixture before hydrolysis deriving from protonolysis of the corresponding aluminium derivatives by the excess of enyne.†

There is no doubt that these protonolysis processes must play an important role in determining the course of

the corresponding dienyl-aluminium compounds (8) and (9).[4,8] On the other hand, the allene (6) might arise from the organoaluminium derivative (10), obtained through a regiospecific conjugated addition. The preferred mode of addition should be defined by the structure of the enyne substrate, and in particular by the steric environment around the double bond of the unsaturated systems. Thus, the lack of steric hindrance at C-4 might be the cause of appreciable allene formation when the 3-alkylbut-3-en-1-ynes are used. However, independently of the initial mode of addition, a 1,3-aluminium shift causes the interconversion of the intermediates (9) and (10); [7,11] an analogous tautomeric

TABLE 2

Reaction between CH_2=CMe-C≡C-X and $AlBu^i_3$ *

X	Hydrolysis with	(4)		(5)		(6)		(7)	
		Y(%)		Y(%)		Y(%)		Y(%)	
H	D_2O	H	80	H	93	H	100	H	100
		D	20	D	7	D	0	D	0
D	H_2O	H	40	H	22	H	18	H	7
		D	60	D	78	D	82	D	93

* The reactions were carried out in heptane at 25 °C for 40 h, under the usual experimental conditions.

the reaction between the 3-en-1-yne and the trialkylalane; the high isotope effect, observed when [1-^{2}H]-3-methylbut-3-en-1-yne is reacted with $AlBu^i_3$ under the usual experimental conditions, provides clear evidence for the above assumption. In this case [1',2,4-^{2}H$_3$]-1-isopropenyl-3-(3'-methylbutylidene)-4-methylcyclopentene, whose structure was determined by n.m.r. spectroscopy,[7] is obtained in 70% yield (cf. Table 1, entry 9).

With these overall results in mind, the formation of the metallation and reduction products should follow mechanistic schemes analogous to those previously proposed for alk-1-ynes,[4,8] i.e. direct reaction of AlR^4_3 with the acidic hydrogen of (1) and, at least partially, protonolysis by (1) of dienylaluminium species formed to achieve the metallation derivative, and migration of a hydride ion of the AlR^4_3 β-carbon atom to the triple bond to give rise to the reduction product. On the contrary, we now suggest that the formation of the carbalumination products occurs via the mechanism shown in Scheme 2. The initial step might involve 1,2-cis- or 1,4-addition of an aluminium–carbon bond to the conjugated system. The cis-addition to the acetylene moiety gives rise to the regioisomers (3) and (4), through
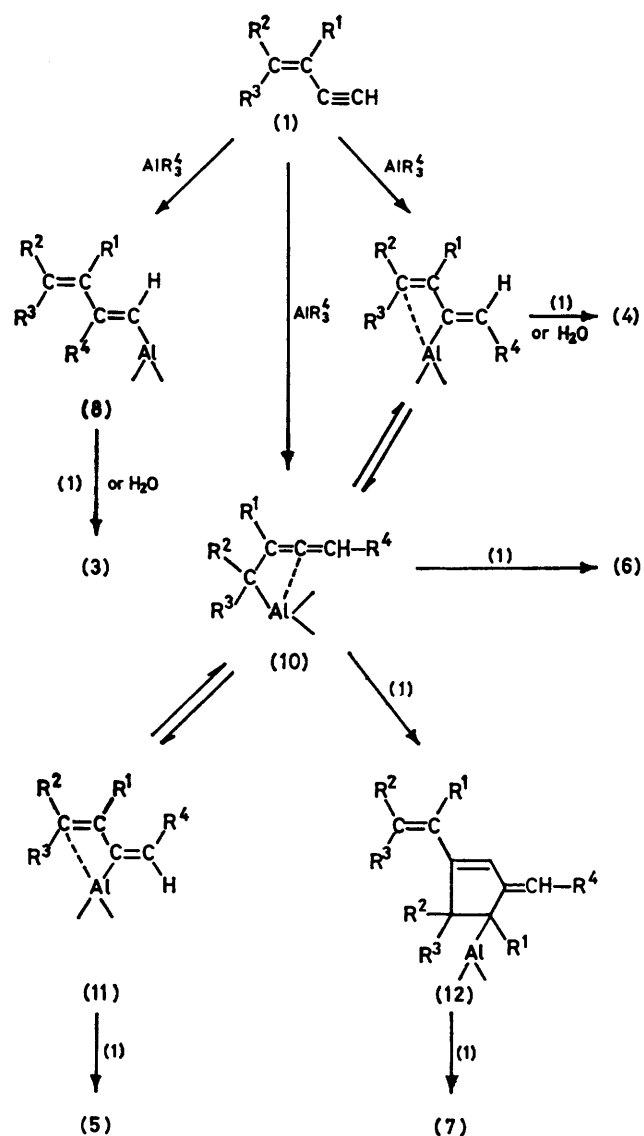
equilibrium should also permit the transformation of (10) into the dienylaluminium (11).‡ It is thus possible to rationalize the formation of the diene (5) which apparently results from a 1,2-trans-addition.

In this context, the formation of the cyclopentene (7) is also explicable.[7] This compound arises from an irreversible cyclization step involving the allenic derivative (10) and the enyne (1); the aluminium intermediate (12) is in turn protonolyzed in the reaction mixture.[7]

Reaction of Tri-isobutylaluminium with 3-En-1-ynes in the Presence of Nickel or Manganese Complexes.—As expected, the stoicheiometric reaction of 3-en-1-ynes (1) with tri-isobutylaluminium takes an entirely different course when carried out in the presence of catalytic amounts of $Ni(mesal)_2$ or $Mn(acac)_3$. As in the analogous reactions with aliphatic alk-1-ynes,[1-5] ' head-to-tail ' dimers, (13) and (14), are formed as main products along with cyclo-trimers (15), and also products which are formed even in the absence of any transition-metal complex (Scheme 3).

The aromatic compounds (15) were characterized by mass spectrometry while the tetraenes (13) and (14) were isolated from the reaction mixtures by preparative g.l.c. and their structures assigned by spectroscopic techniques (see Experimental section). In particular, the stereochemical configuration of the double bonds was estab-

* Analogously, upon deuteriolysis the diene (3a; R^4 = Bu^i) from $AlBu^i_3$ and (1a) is recovered only 40% D-labelled, while the regioisomer (4a; R^4 = Bu^i) is not D-labelled. Deuteriolysis of the reaction mixture from $AlBu^i_3$ and (1c) also gives unlabelled (5c; R = Bu^i).

† The reduction product (2f) cannot be taken off from the mixture before hydrolysis; the rate of protonolysis of the dienylalanes by (1) might be therefore related to the structures of the unsaturated organoaluminium compounds.[4]

‡ This equilibrium should be influenced by the steric requirements of the intermediates (9), (10), and (11) as well as by their rate of protonolysis by the excess of enyne during the course of the reaction.[4]

reacting the trialkylalane with Ni(mesal)$_2$ (at 0 °C) or Mn(acac)$_3$ (at —20 °C), as already described.[1,5] The distribution of the products was determined by g.l.c. analysis.

Initial experiments were carried out on the reaction of (Z)-hex-3-en-1-yne (1a) with AlBu$^i_3$ in the presence of Ni-(mesal)$_2$. The results obtained (Table 3) show that the nickel complex noticeably increases the reaction rate,

SCHEME 2

(1)

R^2 R^1
C=C
R^3 C≡CH

AlR$^4_3$ / AlR$^4_3$ / AlR$^4_3$

(8)

(10)

(3)

(4)

(6)

(11)

(12)

(5)

(7)

R^4 = Et, Bu^i, or 2—MeBu

	R^1	R^2	R^3
a;	H	H	Et
b;	H	Et	H
c;	Me	H	Me
d;	Me	Me	H
e;	[CH$_2$]$_4$		H
f;	Me	H	H
g;	Et	H	H

SCHEME 3

(1)

(1) Mn (acac)$_3$ (1) Ni (mesal)$_2$
(2) H$_3$O$^+$ (2) H$_3$O$^+$
          +
        AlBu$^i_3$

(14)

(13)

(15)

(14)

(15)

	R^1	R^2	R^3
a;	H	H	Et
b;	H	Et	H
c;	Me	H	Me
d;	Me	Me	H
e;	[CH$_2$]$_4$		H
f;	Me	H	H
g;	Et	H	H

with respect to the uncatalysed reaction, and favours the formation of (3Z,6E,8Z)-5-methyleneundeca-3,6,8-triene (13a) together with small amounts of (3Z,6E,8Z)-5-isopentylideneundeca-3,6,8-triene (14a). However, both metallation and reduction of the triple bond of the unsaturated system are competitive with the metal-promoted dimerization processes, depending on the molar ratio (1a) : Ni. Thus when decreasing the ratio from 200 : 1 to 25 : 1 (entries 13—16), the yields of the tetraenes are increased. In particular, at a molar ratio of (1a) : Ni ≤ 50 : 1, compound (13a) is obtained with
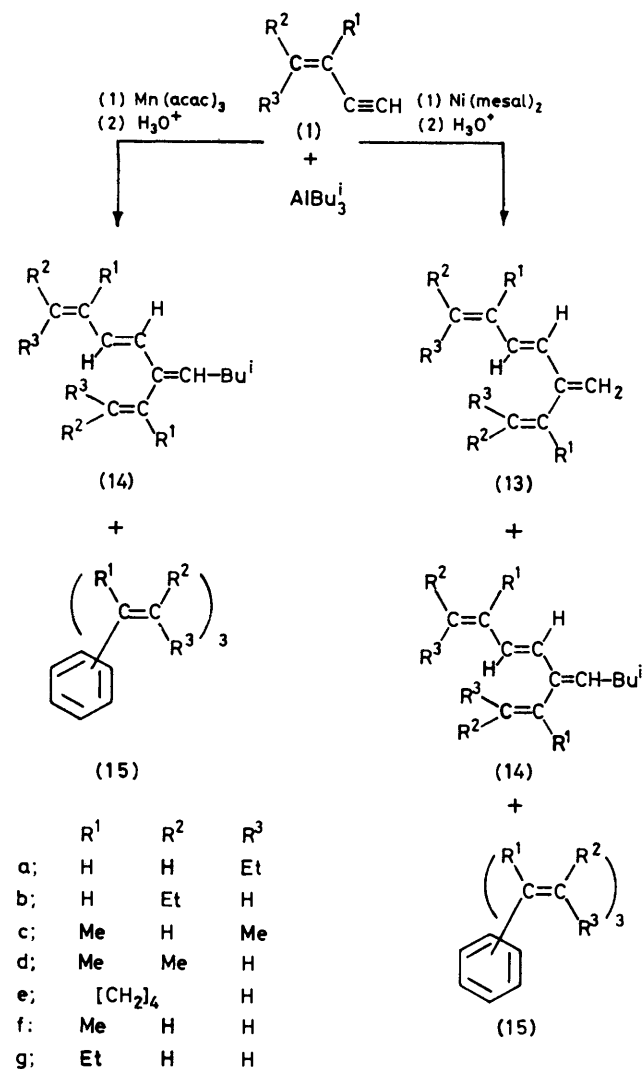
lished by means of the J_{HH} coupling constants (¹H n.m.r.) and/or correlation of the chemical shifts of the appropriate unsaturated protons with those of compounds of defined structure.[5]

The reactions were generally carried out in hydrocarbon solvents at 25 °C; the catalyst was obtained by

high selectivity and in good yields (60—65%).* It is also noteworthy that the dimerization processes occur with complete retention of configuration of the enyne double bond.

These results have encouraged us to explore the synthetic value of the nickel-catalysed reaction for preparing compounds of general formula (13). For this purpose, 4-alkyl-, 3,4-dialkyl-, and 3-alkyl-but-3-en-1-ynes (1b—g) were used as substrates.

Unfortunately, the course of the reaction is strictly dependent on the nature of the enyne (1) and changes appreciably even when (1b), the (E)-isomer of (1a), is employed. Thus at a molar ratio (1b) : Ni of 50 : 1,

in terms of simple steric and electronic effects related to the nature of (1), it is evident that subtle differences in the steric requirements of the alkenyl group bound to the triple bond should be important in determining the reaction pathways. Such assumption results from the following considerations: (i) the (Z)-isomers (1a and c) afford compounds (13) in yields higher than the corresponding (E)-isomers (1b and d); (ii) the yield of (13) decreases from 60 to 16% when the alkyl group R^1 in the 3-alkylbut-3-en-1-yne substrate is changed from Me to Et.

When Mn(acac)₃ is used as catalyst, the stoicheiometric reaction of (Z)-hex-3-en-1-yne (1a) with AlBu$^i_3$ proceeds rapidly and affords, with high selectivity, (3Z,-

TABLE 3

Reaction between tri-isobutylaluminium and 3-en-1-ynes (1) in the presence of bis-(N-methylsalicylideneamine) nickel [a]

	3-En-1-yne (1)			[(1)]/[Ni(mesal)₂]	Products, yields % (by g.l.c.)				
Entry	R¹	R²	R³		(1) [b]	(2)	(13)	(14)	(15)
1 [c]	H	H	Et (1a)		83	13			
13 [d]	H	H	Et (1a)	200	51	28	15	1	
14 [d]	H	H	Et (1a)	100	40	28	25	2	
15	H	H	Et (1a)	50	9	20	60	6	
16	H	H	Et (1a)	25		18	65	9	traces
17	H	Et	H (1b)	50	11	29	27	15	
18 [c]	H	Et	H (1b)	25		20	26	25	
19	Me	H	Me(1c)	50	16	14	56		13
20	Me	Me	H (1d)	50	35	32	27	1	
21	[CH₂]₄		H (1e)	50	38	35	18		
22 [f]	Me	H	H (1f)	50	9	7	60	1	8
23	Et	H	H (1g)	50	41	18	16	traces	10

[a] Unless otherwise stated, all reactions were carried out for 15 h in pentane at 25°C: value of [(1)]/[Al] = 1.0. [b] From the metallation product. [c] Reaction time 40 h. [d] Reaction time 25 h. [e] The mixture contained 10% of a diene having molecular formula $C_{14}H_{26}$, m/e 194 (M^+). [f] In heptane.

compound (13b) is obtained in only 27% yield along with significant amounts of (2b) (29%) and (14b) (15%) (entry 17). Addition of increasing amounts of Ni(mesal)₂ to the reaction mixture has little effect on the yield of (13b) while favouring slightly the formation of (14b), as well as that of by-products involving alkylative processes (entry 18). Moreover, further attempts to obtain (13b) selectively by using either a two-fold molar excess of AlBu$^i_3$ [1] or reaction temperatures higher than 25 °C were unsuccessful.†

On the other hand, comparison of these results with those of entries 19—23 (Table 3) confirms that the yields of the tetraene (13) are determined mainly by the nature and structure of the enyne substrate. Thus the yields of (13) are satisfactory (60%) when (Z)-3-methylpent-3-en-1-yne (1c) (entry 19) and 3-methylbut-3-en-1-yne (1f) (entry 22) are used, but yields drop to ca. 20% when (1d), (1e), and (1g) are employed. In addition, significant amounts of cyclo-trimerization products (15) are detected only in the reaction mixtures from (1c), (1f), and (1g).

Although it seems difficult to rationalize these findings

* The use of both higher nickel concentrations and an excess of organoaluminium compound [molar ratio (1a):Al of 1:2] affect smoothly the yields of the reaction products.

† When the reaction of (1b) with AlBu$^i_3$ is carried out at 25 °C using molar ratios (1b):Ni of 50:1 and (1b):Al of 1:2, compounds (13b) and (14b) are obtained in 25 and 14% yields, respectively. At 65 °C [molar ratios (1b):Ni of 50:1 and (1b):Al of 1:1] the reaction affords (2b) as the main product (62% yield).

6E,8Z)-5-isopentylideneundeca-3,6,8-triene (14a), which formally arises from a ' head-to-tail ' alkylative dimerization process; minor amounts of cyclo-trimers (15a) are also detected in the reaction mixture.[5] As shown in Table 4 a satisfactory yield of (14a) is achieved in the presence of 5 mol % of the catalyst; in fact at molar ratios (1a) : Mn > 20 : 1, the metallation and reduction of the triple bond of the substrate are competitive (entries 24 and 25). Contrary to previous results for the analogous reactions with aliphatic alk-1-ynes,[5] the use of a two-fold molar excess of AlBu$^i_3$ does not increase the yields of the dimerization product. A comparison of entries 25 and 26 shows that an excess of organoaluminium compound favours substantially the metallation process.

Table 4 also provides data that demonstrate the capability of this manganese-catalysed reaction to synthesize tetraenes of general formula (14). When the reaction is carried out under optimum experimental conditions (Table 4), such compounds are in general obtained in good yields independently of the structure of the enyne (1) employed. An exception is the reaction of AlBu$^i_3$ with 1-ethynylcyclohexene (1e), which affords (14e) in only 19% yield, presumably because of steric reasons (entry 30).[5] Steric factors related to the structure of (1) should influence the course of the manganese-catalysed reaction, even if to a lesser extent with respect to that observed for the nickel-catalysed reaction; the

small differences in the yields of (14) (Table 4) may be justified in this way.

The above results from the nickel- and manganese-catalysed reactions of 3-en-1-ynes with AlBu$^i_3$ agree fairly well with those already published for similar reactions with alk-1-ynes.[1-5] It seems therefore reasonable to suppose that the formation of tetraenes (13) and (14) may follow, in at least certain major details, the mechanistic pathways previously described for the

3-en-1-ynes (1) employed were synthesized according to literature methods;[17] [1-^{2}H]-3-methylbut-3-en-1-yne was obtained from 3-methylbut-3-en-1-yne by a published procedure.[18] Solvents were commercial reagent-grade materials, purified by standard methods and re-distilled under nitrogen from LiAlH$_4$ before use. G.l.c. analyses were performed on a Perkin-Elmer 3920 B instrument with flame-ionization detectors (200 × 0.30 cm columns), while preparative g.l.c. was carried out on a Perkin-Elmer F 21 chromatograph (300 × 0.80 cm columns). I.r. spectra were

TABLE 4

Reaction between tri-isobutylaluminium and 3-en-1-ynes (1) in the presence of tris(acetylacetonato)manganese [a]

	3-En-1-yne (1)			[(1)]	[(1)]	Product, yields (%) (by g.l.c.)			
Entry	R^1	R^2	R^3	[Mn(acac)$_3$]	[AlBu$^i_3$]	(1) [b]	(2)	(14)	(15)
1 [c]	H	H	Et (1a)	—	1	83	13		
24	H	H	Et (1a)	40	1	55	23	17	3
25	H	H	Et (1a)	20	1	20	3	60	12
26	H	H	Et (1a)	20	0.5	40	11	46	3
27	H	Et	H (1b)	20	1	28	7	62	traces
28	Me	H	Me (1c)	20	1	1	1	55	25
29	Me	Me	H (1d)	20	1	36	18	43	traces
30	[CH$_2$]$_4$		H (1e)	20	1	36	40	19	
31 [d]	Me	H	H (1f)	20	1	7	4	64	9
32	Et	H	H (1g)	20	1	22	4	52	10

[a] Unless otherwise stated, all reactions were carried out for 10 h in pentane at 25°C. [b] From the metallation product. [c] Reaction time 40 h. [d] In heptane.

conversion of terminal alkynes into (E)-2,4-dialkylbuta-1,3-dienes[4] and (EE)-1-isobutyl-2,4-dialkylbuta-1,3-dienes.[5]

Presumably the actual catalyst is formed by reaction of AlBu$^i_3$ with the transition-metal complex, and contains the transition-metal atom in a reduced state,[4,5] and probably the aluminium atom too.[12] Thus, the active species, which should be stabilized via co-ordination with molecules of the substrate,[5] are responsible for the formation of the dimerization products via catalytic cycles involving insertion or oxidative addition processes followed by reductive elimination and/or alkyl exchange reactions with the excess of organoaluminium compound.[4,5]

Apart from the precise mechanism, the results of this work indicate that the reaction between 3-en-1-ynes and trialkylalanes, catalysed by transition-metal complexes, provides a stereoselective route to conjugated tetraenes having different structures depending on the transition-metal atom. This new development, along with other related reactions,[1-6,12,13] demonstrates the highly efficient and selective nature of the organo-aluminium routes to certain molecules of defined stereochemistry.

EXPERIMENTAL

Triethylaluminium, tri-isobutylaluminium (Fluka A.G. Co), and tris-(2-methylbutyl)aluminium[14] were re-distilled under nitrogen and stored in sealed capillary glass vials, in weighed amounts. Bis-(N-methylsalicylideneamine)nickel [Ni(mesal)$_2$] and tris(acetylacetonato)manganese [Mn(acac)$_3$] were prepared and purified by known procedures.[15,16] 3-Methylbut-3-en-1-yne (1f) was a commercial sample (Fluka) which was purified by distillation before use. The other

recorded on a Perkin-Elmer 225 spectrophotometer for liquid films, and u.v. spectra on a Cary 14 spectrometer for heptane solutions. ^{1}H N.m.r. spectra (100 MHz) and ^{13}C n.m.r. Fourier-transform spectra (25.2 MHz) were obtained with a Varian XL-100 spectrometer on CDCl$_3$ solutions; chemical shifts are reported as δ values with SiMe$_4$ as internal reference. Mass spectra were taken at 70 eV on a Varian Mat CH-7 GC-MS spectrometer.

General Procedure.—All reactions were carried out at least in duplicate under dry nitrogen. In a typical small-scale uncatalysed reaction a weighed amount of the trialkylalane (10 mmol) was transferred from the sealed capillary glass vial to a two-necked 25 ml round-bottom flask equipped with a magnetic stirrer, a Versilic silicone cap, and a glass stopcock. The vessel, cooled at 0 °C, was charged with dry pentane (2 ml) and the required amount of the 3-en-1-yne (1) was syringed through the cap. The resulting mixture was then stirred, in a thermostatted bath at 25 °C, for the desired time.

General experimental details for the nickel- and manganese-catalysed reactions were as specified in Parts 7[4] and 8[5] respectively. In all cases the hydrolysis was carried out with dilute sulphuric acid and the organic phase extracted with pentane. The combined extracts were washed with aqueous sodium hydrogencarbonate then dried over anhydrous sodium sulphate; quantitative analyses (by the internal standard method) of the reaction products were performed by g.l.c. on the crude mixture (2.5% Silicone gum rubber E 301 on 80—100 mesh Chromosorb W and/or 8% Carbowax 20M + 2% KOH on 80—100 mesh Chromosorb W at 40—200 °C; nitrogen flow rate, 10 ml min⁻¹). The products were characterized by their mass spectra and most of them identified by chromatographic comparison; all unknown compounds were isolated and had spectral data in accord with the structures assigned, but full data are only reported in selected cases (Tables 5 and 6).

It should be noted that the tetraenes (13) and (14) poly-

TABLE 5

Spectroscopic data for products of the uncatalysed reactions.

	^{1}H N.m.r. (δ, J/Hz)	$\nu_{max.}$/cm^{-1}	M^+	Base peak
(3a; $R^4 = Bu^i$)	0.82—1.80 (10 H, m, aliphatic), 1.80—2.50 (4 H, m, allylic), 4.93 (2 H, m, =CH$_2$), 5.47 (1 H, dt, J 6.5 and 11.0, −CH=), 5.78 (1 H, d, J 11.0, −CH=)	3080, 890, 760	138	41
(3a; $R^4 = Et$)		3080, 890, 760	110	41
(3b; $R^4 = Bu^i$)		3090, 1610, 963, 882	138	81
(3b; $R^4 = Et$)		3080, 1610, 965, 880	110	81
(4a; $R^4 = Bu^i$)	0.87—1.83 (10 H, m, aliphatic), 1.86—2.24 (4 H, m, allylic), 5.16 (1 H, dt, J 7.5 and 10.5, −CH=), 5.50 (1 H, dt, J 6.4 and 15.0, −CH=), 5.82 (1 H, t, J 10.5, −CH=), 6.15 (1 H, dd, J 10.5 and 15.0, −CH=)	3020, 1650, 982, 948, 725	138	95
(4a; $R^4 = Et$)		3020, 1650, 980, 947, 725	110	95
(4b; $R^4 = Bu^i$)	0.84—1.77 (10 H, m, aliphatic), 1.80—2.25 (4 H, m, allylic), 5.18—5.59 (2 H, m, CH=C−C=CH), 5.70—6.19 (2 H, m, C=CH−CH=C).	3010, 985	138	95
(4b; $R^4 = Et$)		3010, 985	110	95
(4e; $R^4 = Bu^i$)	0.84—1.80 (11 H, m, aliphatic), 1.83—2.15 (6 H, m, allylic), 5.34 (1 H, dt, J 7.1 and 15.8, −CH=), 5.45 (1 H, m, −CH=), 5.86 (1 H, d, J 15.8, −CH=)		164	79
(4f; $R^4 = Bu^i$)	0.85—1.80 (7 H, m, aliphatic), 1.82—2.13 (5 H, m, allylic), 4.83 (2 H, m, =CH$_2$), 5.60 (1 H, dt, J 7.0 and 15.0, −CH=), 6.13 (1 H, d, J 15.0, −CH=)		124	68
(4f; $R^4 = Et$) [a]	1.0 (3 H, t, Me), 1.77—2.22 (5 H, m, allylic), 4.77 (2 H, m, =CH$_2$), 5.57 (1 H, dt, J 6.0 and 15.4, −CH=), 6.08 (1 H, d, J 15.4, −CH=)		96	81
(4g; $R^4 = Bu^i$)	0.85—1.80 (10 H, m, aliphatic), 1.80—2.37 (4 H, m, allylic), 4.80 (2 H, s, =CH$_2$), 5.57 (1 H, dt, J 6.0 and 15.6, −CH=), 6.05 (1 H, d, J 15.6, −CH=)		138	67
(5c; $R^4 = Bu^i$)	0.87—1.77 (7 H, m, aliphatic), 1.65—2.18 (8 H, m, allylic), 5.18 (1 H, dt, J 7.1 and 11.6, −CH=), 5.30 (1 H, q, J 6.4, −CH=), 5.75 (1 H, d, J 11.6, −CH=)	1640, 840, 725	138	95
(5f; $R^4 = Bu^i$)	0.87—1.77 (7 H, m, aliphatic), 1.86—2.25 (5 H, m, allylic), 4.82 (1 H, m, =CH$_2$), 4.92 (1 H, m, =CH$_2$), 5.37 (1 H, dt, J 6.5 and 12.0, −CH=), 5.88 (1 H, d, J 12.0, −CH=)	3080, 1635, 890, 760	124	109
(5f; $R^4 = Et$) [a]	1.0 (3 H, t, Me), 1.80—2.34 (5 H, m, allylic), 4.83 (1 H, m, =CH$_2$), 4.93 (1 H, m, =CH$_2$), 5.35 (1 H, dt, J 7.1 and 11.6, −CH=), 5.80 (1 H, d, J 11.6, −CH=)	3080, 3010, 1640, 890, 760	96	81
(5g; $R^4 = Bu^i$)	0.87—1.83 (10 H, m, aliphatic), 1.83—2.28 (4 H, m, allylic), 4.77 (1 H, m, =CH$_2$), 4.93 (1 H, m, =CH$_2$), 5.43 (1 H, dt, J 6.5 and 12.0, −CH=), 5.83 (1 H, d, J 12.0, −CH=)		138	67
(6e; $R^4 = Bu^i$)	0.82—2.17 (19 H, m, aliphatic and allylic), 4.83 (1 H, m, J 3.0, CH=C=C)	1960	164	107
(6f; $R^4 = Bu^i$)	0.87—1.92 (15 H, m, aliphatic and allylic), 4.85 (1 H, m, J 3.0, CH=C=C)	1968	124	67
(6f; $R^4 = Et$) [a]		1960	96	67
(6g; $R^4 = Bu^i$)	0.87—2.12 (17 H, m, aliphatic and allylic), 4.93 (1 H, m, J 3.0, CH=C=C)	1965	138	81
(7f; $R^4 = Bu^i$) [b]	0.87—1.82 (10 H, m, aliphatic), 1.89—2.88 (8 H, m, allylic), 4.83 (2 H, m, =CH$_2$), 4.98 (1 H, t, −CH=), 6.19 (1 H, s, cyclic −CH=)	3090, 3065, 1610, 1570, 1380, 1365, 885, 875, 850	190	147
(7f; $R^4 = Et$)	0.92—1.11 (6 H, m, aliphatic), 1.92—2.85 (8 H, m, allylic), 4.83 (2H, m, =CH$_2$), 4.93 (1 H, t, −CH=), 6.16 (1 H, s, cyclic −CH=)	3090, 3063, 1610, 1570, 885, 875, 833	162	147
(7g; $R^4 = Bu^i$)	0.87—1.85 (15 H, m, aliphatic), 1.92—2.95 (7 H, m, allylic), 4.87 (2H, m, =CH$_2$), 4.98 (1 H, t, −CH=), 6.21 (1 H, s, cyclic −CH=)	3080, 3060, 1605, 1563, 1378, 1360, 882, 870, 847	218	175

[a] D. J. Pasto, R. H. Shults, J. A. McGrath, and A. Waterhouse, *J. Org. Chem.*, 1978, **43**, 1382.　　[b] See ref. 7.

merize readily, even under nitrogen, to white solids insoluble in ordinary organic solvents; it is therefore necessary to handle these compounds as dilute pentane solutions, with exclusion of daylight and in the presence of 2,6-di-t-butyl-*p*-cresol.

When [1-^{2}H]-3-methylbut-3-en-1-yne was used, and in the deuteriolysis experiments, the reactions were carried out as above and the hydrolysis accomplished as previously reported.[4,5] All deuteriated compounds were identified by mass-spectrometry.

Representative experiments are described below.

Reaction between 3-Methylbut-3-en-1-yne (1f) *and Tri-isobutylaluminium* (*Entry* 9).—According to the general procedure, a heptane solution (20 ml) of tri-isobutylaluminium (21.2 g, 0.107 mol) was allowed to react, at 25 °C for

40 h, with (1f) (7.1 g, 0.107 mol). The crude products obtained upon hydrolysis were analysed by g.l.c. and fractionally distilled to give a sample of 1-isopropenyl-3-iso-pentylidene-4-methylcyclopentene[7] (7f; $R^4 = Bu^i$) (>97% pure) (3.15 g, 31%), b.p. 60 °C at 0.01 mmHg; and a C_9 fraction (2.0 g) containing (*E*)-2,6-dimethylhepta-1,3-diene (4f; $R^4 = Bu^i$), (*Z*)-2,6-dimethylhepta-1,3-diene (5f; $R^4 = Bu^i$), and 2,6-dimethylhepta-2,3-diene (6f; $R^4 = Bu^i$). The mixture was separated by preparative g.l.c. (25%, 3,3′-oxydipropionitrile; 60 °C) to yield the three products, which were distilled before final spectroscopic analysis (Table 5).

Reaction between (*Z*)-3-*Methylpent-3-en-1-yne* (1c) *and Tri-isobutylaluminium in the Presence of* Ni(mesal)$_2$ (*Entry* 19).—As described above,[1,4] tri-isobutylaluminium (12.4 g, 62.4 mmol) was reacted with the nickel complex (0.340 g,

TABLE 6

Spectroscopic data for selected tetraenes (13) and (14)

	^{1}H N.m.r. (δ, J/Hz)	^{13}C N.m.r. (δ) *	$\nu_{max.}$/cm^{-1}	$\lambda_{max.}$/nm (ε)	M^+	Base peak
(13a)	0.95 (3 H, t, Me), 0.98 (3 H, t, Me), 2.12 (4 H, m, allylic), 4.86 (1 H, d, =CH$_2$), 5.09 (1 H, d, =CH$_2$), 5.33 (1 H, dt, J 7.0 and 11.0, -CH=), 5.55 (1 H, dt, J 7.0 and 11.0, -CH=), 5.90 (1 H, d, J 11.0, -CH=; 1 H, t, J 11.0, -CH=), 6.11 (1 H, d, J 15.0, -CH=), 6.39 (1 H, dd, J 11.0 and 15.0, -CH=)	14.2(q), 14.4(q), 21.3(t), 22.1(t), 116.7(t), 125.6(d), 125.8(d), 127.9(d), 134.1(d), 134.5(d), 135.4(d), 142.8(s)		280 (28 600) 269 (36 400) 261 (27 400), 250 sh	162	105
(13c)	1.42—1.88 (12 H, m, allylic), 4.88 (1 H, d, J 2.0, =CH$_2$), 5.16 (1 H, d, =CH$_2$), 5.47 (2 H, m, J 6.8, -CH=), 6.20 (1 H, d, J 16.0, -CH=), 6.60 (1 H, d, J 16.0, -CH=)	19.5 (q), 21.1 (q), 26.8 (q), 31.0(q), 121.6(t), 127.9(d), 131.8(d), 133.6(d) 134.6(d), 139.1(s), 142.1(s), 155.3(s)	3080, 1603, 1583, 1450, 1430, 1370, 960, 885, 824, 809, 796	282 (28 400) 271 (33 400) 262 (24 400) 250sh	162	105
(13d)	1.60—1.80 (12 H, m, allylic), 4.93 (1 H, d, J 2.0, =CH$_2$), 5.03 (1 H, d, =CH$_2$), 5.60 (2 H, m, -CH=), 6.10 (1 H, d, J 16.0, -CH=), 6.40 (1 H, d, J 16.0, -CH=)				162	105
(13f)	1.92 (6 H, m, allylic), 4.98 (4 H, s, =CH$_2$), 5.05 (2 H, d, =CH$_2$), 6.11 (1 H, d, J 16.0, -CH=), 6.42 (1 H, d, J 16.0, -CH=)		3080, 3020, 1635, 1603, 1583, 1450, 1435, 1373, 965, 885		134	91
(14a)	0.84—1.82 (13 H, m, aliphatic), 1.82—2.33 (6 H, m, allylic), 5.37 (1 H, dt, J 7.0 and 10.0, -CH=), 5.57 (1 H, t, J 7.0, -CH=), 5.64 (1 H, dt, J 7.0 and 10.0, -CH=), 5.84 (1 H, d, J 10.0, -CH=), 6.00 (1 H, t, J 10.0, -CH=), 6.18 (1 H, d, J 15.0, -CH=), 6.41 (1 H, dd, J 15.0 and 10.0, -CH=)	13.7(q), 14.3(q), 21.3(t), 22.3(t), 22.5(q), 28.7(d), 38.5(t), 123.5(d), 123.9(d), 128.3(d), 132.4(d), 133.1(d), 135.2(d), 135.5(d), 137.0(s)	1385, 1367, 983, 945, 910, 736		218	91
(14c)	0.87—1.80 (7 H, m, aliphatic), 1.37—2.00 (14 H, m, allylic), 5.39 (1H, m, J 6.8, -CH=), 5.55 (1 H, t, J 7.0, -CH=), 5.54 (1 H, m, J 6.8 and 1.3, -CH=), 6.16 (1 H, d, J 16.0, -CH=), 6.47 (1 H, d, J 16.0, -CH=)	13.1(q), 14.5(q), 20.5(q), 22.6(q), 23.4(q), 28.6(d), 38.2(t), 122.0(d), 123.9(d), 124.4(d), 129.4(d), 130.6(d), 132.9(s), 133.4(s), 141.5(s)	1383, 1370, 960, 820, 809, 785		218	119
(14f)	0.89—1.82 (7 H, m, aliphatic), 1.83—2.16 (8 H, m, allylic), 4.78 (1 H, m, =CH$_2$), 5.02 (2 H, s, =CH$_2$), 5.23 (1 H, m, =CH$_2$), 5.57 (1 H, t, -CH=), 6.27 (2 H, s, trans -CH=CH-)	18.7(q), 22.5(q), 23.3(q), 28.9(d), 38.2(t), 114.9(t), 115.7(t), 130.7(d), 130.9(d), 131.1(d), 136.8(s), 142.1(s), 143.4(s)	3080, 3020, 1640, 1618, 1590, 1450, 1435, 1380, 1372, 1365, 962, 897, 880		190	105

* The multiplicities observed on off-resonance decoupling are noted.

1.04 mmol) at 0 °C; a pentane solution (10 ml) of (1c) (5.0 g, 62.4 mmol) was immediately added to the brownish homogeneous mixture, which was then heated at 25 °C for 15 h. The mixture was cautiously hydrolysed with dilute sulphuric acid and extracted with pentane. G.l.c. analysis of the pentane solution showed the presence of (2Z,5E,7Z)-3,7-dimethyl-4-methylenenona-2,5,7-triene (13c) as the major product with small amounts of cyclo-trimers, m/e 240 (M^+). After removal of the solvent in vacuo (35 °C at 20 mmHg), preparative g.l.c. (2.5% Silicone E 301; 80 °C) gave pure (13c) (2.1 g, 42%), b.p. 32 °C at 0.01 mmHg.

Compounds (13a), b.p. 42 °C at 0.01 mmHg, and (13f), b.p. 30 °C at 0.01 mmHg, were recovered in an analogous manner.

Reaction between (Z)-3-*Methylpent*-3-*en*-1-*yne* (1c) *and Tri-isobutylaluminium in the Presence of* Mn(acac)$_3$ (*Entry* 28).—As previously reported,[5] Mn(acac)$_3$ (1.060 g, 3.0 mmol) was allowed to react at − 20 °C with tri-isobutylaluminium (11.9 g, 60 mmol) in pentane (10 ml) to give an orange-yellow solution. To this solution, at the same temperature (− 20 °C), was then added (1c) (4.8 g, 60 mmol) and the resulting mixture was stirred at 25 °C for 10 h. After the usual work-up and removal of the solvent in vacuo (35 °C at 20 mmHg), preparative g.l.c. (8% Carbowax 20M + 2% KOH, 140 °C) gave pure (2Z,5E,7Z)-3,7-dimethyl-4-isopentylidenenona-2,5,7-triene (14c) (2.9 g, 45%), b.p. 63 °C at 0.01 mmHg.

Compounds (14a), b.p. 65 °C at 0.01 mmHg, and (14f), b.p. 57 °C at 0.01 mmHg, were recovered in an analogous manner.

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