# Metal Catalysis in Organic Reactions. Part 9.† Iron-induced Reaction of Organoaluminium Compounds with Aliphatic Alk-1-ynes

By Anna Maria Caporusso, Giampaolo Giacomelli, and Luciano Lardicci,\* Centro di Studio del C.N.R. 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 trialkylaluminium compounds and aliphatic alk-1-ynes in the presence of catalytic amounts of iron trichloride has been studied under various experimental conditions. The reaction affords a complex mixture of products, the main components being essentially 2-alkylalk-1-enes and trialkylbuta-1,3-dienes; linear oligomers and cyclo-trimers are also recovered under suitable experimental conditions. The use of (S)-3-methylpent-1-yne gives rise to optically active products in high optical yields. The mechanism of the reaction is discussed and tentatively interpreted in terms of alkyliron intermediates.

IN a previous paper,<sup>1</sup> a brief report was given on the reaction of hex-1-yne with tri-isobutylaluminium in the presence of iron trichloride. The preliminary results obtained have shown that the presence of catalytic amounts of FeCl<sub>3</sub> enhances the alkylative properties of the organoaluminium compound,<sup>2</sup> the alk-1-yne being completely converted into 2-methyl-4-methyleneoctane and 7-(2-methylpropyl)-5-methyleneundec-6-ene, together with small amounts of 1,3,5- and 1,2,4-tributyl-benzenes.<sup>1</sup> In continuing our researches on the catalysis of organic reactions by transition-metal complexes,<sup>3,4</sup> we have extended our studies on the dynamics of the reaction by using a series of terminal aliphatic alkynes and other organoaluminium compounds; in this context optically active alk-1-ynes have also been employed.

## RESULTS

Products of the Reaction.—The reaction of trialkylalanes with alk-1-ynes (1) in the presence of iron trichloride leads generally to the formation of a complex mixture of compounds (Scheme 1). The distribution of the products was determined by g.l.c. analysis, and all the components (1)— (9) were identified either by comparison of their retention times with those of authentic samples  $^{4,5}$  or by recovering them and evaluating their structures through chemical and spectroscopical techniques.

The stoicheiometric reaction of tri-isobutylaluminium with hex-1-yne (1a) in the presence of 1.6 mol % of iron trichloride affords, upon hydrolysis, 2-methyl-4-methylene-octane (3a) (28%), (Z)-7-(2-methylpropyl)-5-methylene-undec-6-ene (6a) (18%), and 1,3,5-tributylbenzene (8a) (17%), along with minor amounts of (E)-2-methylnon-4-ene (4a), (Z)-2-methyl-5-butyl-6-methylenedec-4-ene (5a), (4Z,6E)-2-methyl-5-butylundeca-4,6-diene (7a), 1,2,4-tributylbenzene (9a), and oligomers of formula  $C_{22}H_{40}$  and  $C_{28}H_{50}$  (Table 1, entry 9).

The reaction was generally carried out in pentane: care was taken in the preparation of the catalyst. Iron trichloride was added to a pentane solution of the trialkylalane maintained at -20 °C. To the suspension so obtained, compound (1) was added within a few minutes and the subsequent solution  $\ddagger$  thermostatted for the required time.

#### † Part 8, ref. 4.

t No reaction is observed when the iron salt is added to the pentane solution of the trialkylalanine; the iron trichloride dissolves and reacts rapidly when the alk-1-yne is added.

The data collected in Table 1 indicate that the course of the reaction between hex-1-yne and  $AlBu_{3}^{i}$  depends essentially on the temperature and the molar ratios [(1) : Al and (1) : Fe]. In fact, at molar ratio of (1) : Fe > 100 : 1, a minor conversion of compound (1a) is observed along with an increased yield of high-molecular-weight products (Table 1, entry 5). When the molar ratio (1) : Al is increased the formation of the vinylidene alkene (3a) and of



## TABLE 1

Reaction between tri-isobutylaluminium and hex-1-yne (1a) in the presence of iron trichloride a

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Entry number	$\frac{[(1a)]}{[AlBu_{1}]}$	[(1a)] [FeCl.]	Temp. (°C)	Reaction time/h	(3a)	( <b>4</b> a)	(5a)	(6a)	(7a)	(8a)	(9a)	Trienes	Tetraenes
10	05	59	20	40	15	(10)	(00)	10	(14)	000	10		281150
1	0.0	00	-20	40	15	3	0	13	Э	20	10	13	7
2	0.5	58	0	40	36	<b>2</b>	3	<b>27</b>	<b>2</b>	10	<b>2</b>	10	7
3	0.5	61	<b>25</b>	0.5	42	1	1	27		9	2	9	6
4 °	0.5	148	25	0.5	29	2		21		16	5	8	6
5 d	0.5	340	<b>25</b>	0.5	16	1		21		30	8	9	7
6°.	0.5	59	65	0.5	53	1	1	<b>27</b>		4	4	8	2
7 °	0.5	54	98	0.5	51	1	1	26		5	5	9	
8 °	1.0	<b>58</b>	-20	40	10	4	7	5	8	<b>28</b>	12	12	7
9	1.0	61	<b>25</b>	0.5	<b>28</b>	1	2	18	3	17	5	13	9
10 •	1.0	55	65	0.5	36	1	1	<b>24</b>	1	9	10	11	3
115	4.0	56	-20	40	<b>2</b>	3	1	2	4	47	29		
12 "	4.0	90	<b>25</b>	40	4	2	1	4	<b>2</b>	37	36	6	$^{2}$
13 0,0	4.0	63	65	0.5	8	2	1	6	2	29	38	4	
14 °	12.0	77	25	20	1			2		41	52		

<sup>a</sup> Unless otherwise stated, all reactions were carried out in pentane. <sup>b</sup> Conversion 78%. <sup>c</sup> Conversion 70%. <sup>d</sup> Conversion 56%. <sup>e</sup> In heptane. <sup>f</sup> Conversion 34%. <sup>g</sup> Conversion 88%.

the diene (6a), together with the reaction conversion, are depressed, and aromatic products are formed prevalently (Table 1). At molar ratio (1): Al of 12.0: 1 the hex-1-yne (1a) is transformed only into the corresponding cyclotrimers (8a) and (9a) (Table 1, entry 14). It is noteworthy that, at temperatures above 25 °C and at molar ratios (1): Fe < 100: 1, the reaction is practically complete within 30 min.

As regards the influence of temperature, both the rate and the selectivity of the reaction are changed by varying the temperature. Above 25 °C, the reaction is rapid and selective for the formation of the olefin (3a) and, to a lesser extent, the diene (6a). Below 25 °C, the reaction rate decreases and the amounts of the alkene (4a) and the dienes (5a) and (7a) increase (Table 1, entries 1, 2, and 8); this phenomenon is even more noticeable at a molar ratio (1) : Al of 1.0:1. At low temperatures, the yields of the oligomers and of the aromatic products (8a) and (9a) are increased, as well as the selectivity of the cyclo-trimerization reaction.

The overall data of Table 1 indicate that the regioselectivity of the alkylation process and the selectivity of the reaction depend on the temperature: in particular, increasing the temperature increases the yields of the low molecular-weight products.

From these results, it appeared worthwhile to test the effect of the nature of the trialkylalane on the course of the reaction. The data summarized in Table 2 show that the distribution of the reaction products seems to depend on the organoaluminium compound, although the overall trend of the reaction is independent of the nature of the organometallic compound. Triethylaluminium favours the formation of the oligomerization products more than  $AlBu_{3}^{i}$ , and only at 65 °C are appreciable amounts of compounds (3h) and (6h) recovered. When the ratio (1a) : Al is very large, only cyclo-trimers are formed (Table 2, entry 17). Tris-(2-methylbutyl)aluminium gives lower yields of alkene (3i) and diene (6i) than does  $AlBu_{3}^{i}$ : this datum might be tentatively attributed to the greater steric hindrance of the alkyl group bound to the aluminium atom, which should hinder the alkylation processes. It is noteworthy that the use of trialkylaluminium-diethyl ether gives rise only to cyclo-trimers and polymeric products (Table 2, entry 19).

The structure of the acetylenic substrate is also important in determining the course of the reaction (Table 3). When 3-alkylalk-1-ynes are employed, low yields of the products corresponding to carbalumination and dimerization of the acetylenic substrate are observed. In particular, although with 3-methylpent-1-yne (1b) the course of the reaction does not change appreciably with respect to that observed with hex-l-yne (la), when 3,4-dimethyl- (lc) and 3,4,4trimethyl-pent-1-yne (1d) are used the yields of compounds (3) and (6), and of the linear oligomers, decrease noticeably with a concomitant increase in the yields of the metallation, reduction, and cyclo-trimerization products (Table 3). Moreover, increasing the size of the substituent alkyl group  $\alpha$  to the triple bond results in decreasing the selectivity of formation of compounds (3) and (4). However, the yields of (3) and (6) become satisfactory by using either straightchain alk-1-ynes (Table 3, entry 25) or  $\beta$ - or  $\gamma$ -substituted alkynes (entries 23 and 24).

Use of Optically Active Alk-1-ynes.—To elucidate some of mechanistic aspects of the reaction, and in particular to

Reaction between trialkylalanes  $AIR'_{a}$  and hex-l-yne (1a) in the presence of iron trichloride <sup>a</sup>

Entry		$[(\mathbf{la})]$	Temp	Products, yields % (by g.l.c.)									
number	R′	[AIR'3]	(°C)	(la) b	(2a)	(3)	(4)	(6)	(8a)	(9a)	Trienes	Tetraenes	
15	Et	0.5	25	5	5	12	2	13	18	12	15	12	
16 °	Et	0.5	65	2	7	35	<b>2</b>	20	8	7	8	7	
17 <sup>d</sup>	Et	12.0	<b>25</b>	19					20	47			
3	Bu <sup>i</sup>	0.5	<b>25</b>		1	<b>42</b>	1	27	9	2	9	6	
6	Bu <sup>i</sup>	0.5	65			53	1	<b>27</b>	4	4	8	2	
18 °	$EtCH(Me)CH_2$	0.5	65	10	16	<b>28</b>	<b>2</b>	13	10	11	5		
19 °	Bui	1.0	<b>25</b>	7					30	36			

<sup>a</sup> The reactions were carried out for 30 min in pentane: values of [(1a)]/[Fe] = 50-70. <sup>b</sup> Partially as alkynylalane. <sup>c</sup> In heptane. <sup>d</sup> Reaction time 20 h. <sup>e</sup> Reaction carried out with tri-isobutylaluminium-diethyl ether. Polyenes (27%) were also formed.

Reaction between tri-isobutylaluminium and alk-1-ynes R-C=CH (1) in the presence of iron trichloride a

Enter		Compounds, yields % (by g.l.c.)									
number	R	(1) *	(2)	(3)	(4)	(6)	(8)	(9)	Trienes	Tetraenes	
3	Bu <sup>n</sup>		1	42	1	27	9	2	9	6	
20	EtCH(Me)		<b>2</b>	33	2	31	8	2	16	5	
21	Pr <sup>i</sup> CH(Me)	2	10	19	4	9	40	5	9		
22 °	Bu <sup>t</sup> CH (Me)	39	<b>22</b>	10	4	2	]	12			
23	EtCH(Me)CH <sub>2</sub>		2	37	1	20	16	2	11	11	
24	EtCH(Me)CH <sub>2</sub> CH <sub>2</sub>		5	42	1	29	8	2	9	4	
<b>25</b>	Bu <sup>n</sup> CH <sub>2</sub> CH <sub>2</sub>		2	49	1	27	7	<b>2</b>	9	3	
(m)										· ·· · · · · ·	

<sup>a</sup> The reactions were carried out for 30 min in pentane at 25 °C: values of [(1)]/[Fe] = 50-70, and [(1)]/[Al] = 0.5. <sup>b</sup> Partially as alkynylalane. <sup>c</sup> In the reaction mixture 2,2,3-trimethylpentane (5%) was also detected.

verify if the carbon atom adjacent to the triple bond of compound (1) is directly involved in the reaction, we have investigated the stereochemistry of the reaction carried out with (S)-3-methylpent-1-yne (1b).

In the experimental conditions adopted [25 °C, (1) : Al = 0.5 : 1, (1) : Fe = 60 : 1 (Table 3, entry 20)], (S)-(1b),  $[\alpha]_{p}^{30}$  +41.58°, optical purity 89%, <sup>6</sup> afforded after 30 min a complex mixture of products, from which by preparative g.l.c., (S)-(3b),  $[\alpha]_{p}^{25}$  +18.97°, (3S,7S)-(6b),  $[\alpha]_{p}^{25}$  +51.24°, and 1,3,5-tris-[(S)-1-methylpropyl]benzene (8b),  $[\alpha]_{p}^{25}$  +60.1° (heptane), optical purity 87%, <sup>7</sup> were recovered (Scheme 2). Although the optical purity of the aromatic compound indicated that the reaction occurred with high stereospecificity, in order to accurately evaluate the extent of racemization during alkylation and dimerization, samples of (S)-(3b) and (3S,7S)-(6b) were converted, by ozonolysis, into (S)-2,5-dimethylheptan-4-one (10),<sup>8</sup> having respectively  $[\alpha]_{p}^{25}$  +21.56 and +21.36°. The optical purity of the two samples of (10) was evaluated by reduction of their tosylhydrazones, with NaBH<sub>4</sub> in diglyme,<sup>9</sup> into (S)-2,5-dimethylheptane (11),  $[\alpha]_{p}^{25}$  +9.85°, optical purity 92%,<sup>10</sup> and

 $+9.77^{\circ}$ , optical purity 91%,<sup>10</sup> respectively (Scheme 2). The data obtained confirm, within the accuracy limits, the complete stereospecificity of the process, also indicating that the carbon atom  $\alpha$  to the triple bond of compound (1) is not involved in the reaction.

## DISCUSSION

As regards the mechanism of the reaction, the results obtained indicate that the actual catalyst is formed by reaction of AlBu<sup>i</sup><sub>3</sub> with the iron salt. On the basis of previous results,<sup>11,12</sup> it seems likely that the catalyst contains the metal atom in a reduced state. The presence of small quantities of 2,5-dimethylhexane in the hydrolysed reaction mixtures suggests the formation of an alkyl–iron species.<sup>13</sup> It has been shown previously that reaction of an iron complex with organometallic compounds leads to alkyl–iron species,<sup>11,12,14</sup> which are catalytically active in the oligomerization of unsaturated substrates.<sup>15</sup> Since no reaction is observed when iron trichloride is treated at -20 °C with a pentane solution



of the trialkylalane, and a homogeneous red-brown solution is observed only when the alk-1-yne (1) is added, one may suppose that formation of the active species implies the co-ordination of molecules of (1) onto the metal atom too.

The possibility of formation of an alkynyliron hydride species is ruled out, since the acetylenic proton is not involved in the reaction. Thus, when the reaction is performed with  $[1-{}^{2}H_{1}]$ hex-1-yne, no transfer of deuterium atom is observed and upon hydrolysis all the products were recovered containing the original deuterium atom.

Deuteriolysis of the reaction mixtures revealed that compounds (3)—(7) and the linear oligomers contained a deuterium atom, *i.e.* they are present in the reaction

thermodynamically stable, has the organic ligands antiparallel to one another in order to minimize steric interactions, while (15) has much more steric strain and therefore should be more reactive. From the assumption that compounds (5)—(7) are derived from these intermediates (Scheme 3), the data of Table 1 indicate that intermediate (14) is in fact favoured by raising the temperature. The formation of the dienyl-aluminium compounds also depends on steric factors, since when  $\alpha$ -substituted alk-1-ynes (1) are used, compounds (5) and (7) do not form at all (Table 3). However, whatever the actual mechanism is, the formation of allene intermediates as precursors <sup>13</sup> is not possible, since the carbon atom  $\alpha$  to the triple bond is not involved, as demon-



mixture before hydrolysis as enyl-aluminium compounds. Therefore, taking into account that the reaction products arise formally from linear oligomerization and simultaneous alkylation processes, it seems likely that the mechanism is based on *cis*-insertion of (1) into the iron-carbon bond, followed by a fast exchange reaction with the excess of organoaluminium compound.

From these results, a possible mechanism is depicted in Scheme 3, where formation of the linear products is assumed to proceed *via* insertion mechanisms involving  $\pi$ -alkyne-iron complexes (13)--(15).<sup>16</sup> The prevailing formation of (3) rather than (4) is connected with steric and electronic factors favouring a *cis*-Markovnikoff addition of the alkyl group, bound to the iron atom in (13), to the triple bond of (1). According to this hypothesis, the dienyl-aluminium compounds might originate *via* the  $\pi$ -alkyne-iron species (14) and (15), which represent two geometrical extremes for the bis- $\pi$ -alkyne intermediates: complex (14), which is assumed to be strated from the stereospecificity of the reaction using optically active alk-1-ynes.

As regards the formation of the cyclo-trimers (8) and (9), the intervention of tris- $\pi$ -alkyne-iron intermediates can be proposed.<sup>17</sup> Taking into account the competitive alkylation processes, the cyclo-trimerization should be enhanced by steric hindrance in compound (1); in fact, for (1c) and (1d) the oligomerization reaction yields mainly cyclo-trimers (Table 3, entries 21 and 22).

The reaction between alk-1-ynes and organoaluminium compounds, catalysed by transition-metal complexes, can provide products having structures and stereochemistry not easily available *via* conventional methods, dependent on the nature of the transition-metal atom.<sup>1,3-5</sup> However, the present results indicate that the applicability of this iron-induced reaction is limited by the structure of the alk-1-yne (1) used, as  $\alpha$ -substituted substrates having bulky alkyl substituents do not give compounds (3) and (6).

## EXPERIMENTAL

Triethylaluminium, tri-isobutylaluminium (Fluka A.G. Co.), and tris-(2-methylbutyl)aluminium 18 were carefully redistilled under nitrogen and stored in sealed capillary glass vials, in weighed amounts. Hex-1-yne (1a) and oct-1-yne (1g) were commercial products (Fluka) which were purified by distillation before use. (S)-3-Methylpent-1-yne (1b)<sup>6</sup> and the other alk-1-ynes (1) employed were synthesized from the corresponding  $\alpha$ -olefins by published methods; <sup>6,19</sup> [1-2H1]hex-1-yne was obtained from hex-1-yne by a published procedure.<sup>20</sup> Commercial anhydrous iron trichloride was dried in vacuo and used without further purification. Solvents were commercial reagent-grade materials, purified by standard methods and redistilled under nitrogen from LiAlH<sub>4</sub> before using. G.l.c. analyses were performed on a Perkin-Elmer 3920 B instrument with flame-ionization detectors ( $200 \times 0.30$  cm columns), while preparative g.l.c. were carried out on a Perkin-Elmer F 21 chromatograph ( $300 \times 0.80$  cm columns). Optical rotations were measured with a Perkin-Elmer 142 automatic polarimeter; unless otherwise specified, rotations refer to pure liquid. <sup>1</sup>H N.m.r. spectra were obtained with a JEOL JNM-PS-100 spectrometer on CCl<sub>4</sub> solutions; chemical shifts are expressed on the  $\delta$  scale downfield from SiMe<sub>4</sub>. I.r. spectra were recorded on a Perkin-Elmer 225 spectrometer as liquid films. Mass spectra were taken at 70 eV on a Varian Mat CH-7 GC-MS spectrometer.

Iron Trichloride-catalysed Reactions. General Procedure. -All reaction were carried out at least in duplicate under a dry nitrogen atmosphere. In a typical small-scale reaction, three-necked 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 FeCl<sub>3</sub>. The vessel was charged with 2 ml of pentane and the required amount of the trialkylalane was added from a sealed capillary glass vial. The reaction flask, cooled to a -20 °C, was then inclined so that the iron salt dropped into the trialkylalane solution. After a 5-min agitation, the alk-1-yne (1) was injected by hypodermic syringe through the cap at the same temperature. The resulting red-brown mixture was then stirred, in a thermostatted bath at the appropriate temperature, for the desired time. Hydrolysis was carried out with dilute sulphuric acid and the organic phase extracted with diethyl ether. The combined extracts were washed with aqueous sodium bicarbonate 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 at 40-250 °C; nitrogen flow rate 10 ml min<sup>-1</sup>). All products were characterized by their mass spectra and most of them identified by comparison of their g.l.c. retention times with those of authentic samples.4,5 Compounds (3), (5), (6), and (7) were isolated, when possible, by preparative g.l.c. and their structures deduced by ozonolysis techniques and from spectral data; when necessary larger-scale reactions were used for these separations. The products actually isolated and purified are listed with spectroscopic data in Table 4. At 65 °C the experiments were carried out in heptane solutions. When [1-2H1]hex-1-yne was used, and in the deuteriolysis experiments, the reactions were carried out as above and the hydrolysis accomplished as previously reported.<sup>3</sup> All deuteriated compounds were identified by their mass spectra.

Reaction between Hex-1-yne (1a) and Tri-isobutylaluminium in the Presence of Iron Trichloride (Entry 9).-According to the general procedure tri-isobutylaluminium (31.5 g, 0.158 mol) was allowed to react with (1a) (13 g, 0.158 mol) in the presence of iron trichloride (0.357 g, 2.2 mmol). The crude products obtained upon hydrolysis were analysed by g.l.c. and fractionally distilled to give 2-methyl-4-methyleneoctane<sup>2</sup> (3a) ( $\geq 97\%$  pure; 5 g, 23\%) and a  $C_{16}$  fraction (3.1 g, 18%) containing (Z)-7-(2-methylpropyl)-5-methyleneundec-6-ene (6a) as the main product with minor amounts of (Z)-2-methyl-5-butyl-6-methylenedec-4ene<sup>2,3</sup> (5a) and (Z,E)-2-methyl-5-butylundeca-4,6-diene (7a). The mixture was separated by preparative g.l.c.  $(8\% \text{ Carbowax } 20 \text{ M} + 2\% \text{ KOH}; 125 ^{\circ}\text{C})$  to yield the three products, which were distilled before final spectroscopic analysis (Table 4).

A sample of the diene (6a) (0.50 g, 2.3 mmol) in pentane (20 ml) was treated with ozonized oxygen at -70 °C for 1 h. The crude reaction mixture was decomposed in ethereal solution with LiAlH<sub>4</sub> according to the procedure described elsewhere.<sup>21</sup> G.l.c. analysis (8% Carbowax 20 M + 2% KOH on 80—100 mesh Chromosorb W at 150 °C; nitrogen flow rate 15 ml min<sup>-1</sup>) of the ether layer showed the presence of 2-methyloctan-4-ol <sup>22</sup> together with minor amounts of an  $\alpha,\beta$ -unsaturated alcohol of molecular formula C<sub>15</sub>H<sub>30</sub>O, *m/e* 226 (*M*<sup>+</sup>), 225, 208 (20%), 169 (100), 151 (34), 123 (26), 113 (97), 109 (43), 95 (89), 81 (46), 69 (51), 67 (48), 57 (64), and 55 (48).

Reaction between (S)-3-Methylpent-1-yne (1b) and Tri-isobutylaluminium in the Presence of Iron Trichloride.---As previously described, a pentane solution (30 ml) of tri-isobutylaluminium (33.8 g, 0.170 mol) was allowed to react, at 25 °C for 30 min, with (S)-(1b) (7 g, 0.085 mol),  $[\alpha]_{\rm p}^{20}$  $+41.58^{\circ}$ ,<sup>6</sup> in the presence of the iron salt (0.227 g, 1.4 mmol). The mixture was hydrolysed and extracted with ether as above. Fractional distillation gave a sample of (S)-2,5-dimethyl-4-methyleneheptane (3b) ( $\geq 96\%$  pure, 3.2 g, 26%) which, further purified by preparative g.l.c. (25%, 3,3'-oxydipropionitrile; 80 °C), had b.p. 80 °C at 80 mmHg;  $n_{\rm D}^{25}$  1.421 1;  $d_4^{25}$  0.743 2;  $[\alpha]_{\rm D}^{25}$  +18.97°; and a fraction (2.8 g) containing (E)-(35,75)-3,7-dimethyl-6-(2-methylpropyl)-4-methylenenon-5-ene (6b) (85%). The crude diene was purified by preparative g.l.c. (2.5% Silicone E 301; 150 °C), b.p. 55 °C at 0.3 mmHg;  $n_{\rm D}^{25}$  1.456 0;  $d_4^{25}$  0.801 6;  $[\alpha]_{D}^{25}$  +51.24°. Preparative g.l.c. (8%) Carbowax + 2% KOH; 175 °C) afforded also a sample of pure 1,3,5-tris-[(S)-1-methylpropyl]benzene (8b),  $[\alpha]_{n}^{25}$  $+60.1^{\circ}$  (c 2.23 in n-heptane).<sup>7</sup>

(S)-2,5-Dimethylheptan-4-one (10).<sup>8</sup>—An ethereal solution of isobutylmagnesium chloride (0.250 mol) was treated, at 0 °C, with anhydrous cadmium chloride (24.7 g, 0.135 mol), and the reaction mixture was refluxed for 30 min. Diethyl ether was removed by distillation, dry benzene was added (80 ml) and the resulting dark mixture was heated to reflux for 3 h. To the crude di-isobutylcadmium obtained, (S)-2methylbutyryl chloride (24 g, 0.20 mol) {b.p. 72 °C at 160 mmHg;  $\alpha_{\rm D}^{25}$  (l = 1) +18.02°; from (S)-2-methylbutanoic acid,  $[\alpha]_{\rm D}^{25}$  +19.47°} <sup>23</sup> was added rapidly while the reaction temperature was kept below 15 °C. The mixture was stirred for 20 min, then hydrolysed with ice and dilute sulphuric acid. After the usual work-up, distillation gave (10) (16 g, 56%), b.p. 63 °C at 17 mmHg;  $n_{\rm D}^{25}$  1.413 3;  $d_4^{25}$  0.811 6;  $[\alpha]_{\rm D}^{25}$  +22.46°.

In order to determine its optical purity, according to a

## TABLE 4

Spectral data for products of iron trichloride-catalysed reactions

<sup>1</sup>H N.m.r. (δ)

- (3a) <sup>b</sup> 0.85-1.80 (14 H, m, aliphatic), 1.92 (14 H, m, allylic) 4.61 (1 H, d, J 2.3 Hz, =CH<sub>2</sub>), 4.65 (1 H, d, J 2.3 Hz, = $CH_2$ )
- (5a) 0.85-1.78 (21 H, m, aliphatic), 2.02 (6 H, m, allylic) 4.62 (1 H, m, J 2.6 and 0.5 Hz, =CH<sub>2</sub>), 4.92 (1 H, m, J 2.6 and 1.5 Hz, =CH<sub>2</sub>) 5.19 (1 H, t of t, J 7.0 and 1.2 Hz, -CH=)
- and 1.2 Hz,  $\Box_{1-j}$  (6 H, m, aliphatic), 2.04 (6 H, m, allylic) 4.66 (1 H, m, J 2.4 Hz. =CH<sub>2</sub>), 4.81 (1 H, m, J 2.4 and 1.2 Hz, =CH<sub>2</sub>) 5.57 (1 H, s, -CH=) (6a)
- (7a)  $^{\circ}$  0.86–1.83 (21 H, m, aliphatic), 2.07 (6 H, m, allylic) 5.17 (1 H, t, J 7.4 Hz, -CH=), 5.57 (1 H, d of t, J 15.5 and 6.8 Hz, -CH=) 6.20 (1 H, d, J 15.5 Hz -CH=)
- 0.81–1.72 (15 H, m, aliphatic), 1.77–2.12 (3 H, m, allylic) 4.67 (1 H, m, =CH<sub>2</sub>), 4.73 (1 H, m, =CH<sub>2</sub>) (3b)
- (6b) 0.80-1.75 (23 H, m, aliphatic), 2.07 (4 H, m, allylic) 4.73 (1 H, m, f 2.4 and 1.5 Hz, =CH<sub>2</sub>), 4.89 (1 H, d, f 2.4 Hz, =CH<sub>2</sub>) 5.64 (1 H. s. -CH=)
- (3c)
- (3d)
- 0.80-1.67 (16 H, m, aliphatic), 1.85 (4 H, m, allylic) (3e) 4.68 (2 H, s, =CH<sub>2</sub>)
- 0.83-1.73 (25 H, m, aliphatic), 2.04 (6 H, m, allylic) (6e) 4.79 (1 H, m, =CH<sub>2</sub>), 4.85 (1 H, m, =CH<sub>2</sub>), 5.60 (1
- H, s, -CH=) 0.82-1.77 (18 H, m, aliphatic), 1.88 (4 H, m, allylic) (3f) 4.64 (1 H, m, =CH<sub>2</sub>), 4.69 (1 H, m, =CH<sub>2</sub>)
- -1.80 (29 H, m, aliphatic), 2.04 (6 H, m, allylic) (6f) 0.84 -4.68 (1 H, m, =CH<sub>2</sub>), 4.85 (1 H, m, =CH<sub>2</sub>) 5.63 (1 H, s, -CH=)
- 0.82-1.77 (18 H, m, aliphatic), 1.90 (4 H, m, allylic) (3g)4.64 (1 H, m,  $=CH_2$ ), 4.69 (1 H, m,  $=CH_2$ )
- 0.84-1.76 (29 H, m, aliphatic), 2.04 (6 H, m, allylic) (6g) 4.70 (1 H, m, =CH<sub>2</sub>), 4.86 (1 H, m, =CH<sub>2</sub>), 5.62 (1 H, s, -CH=)
- 0.83-1.53 (17 H, m, aliphatic), 2.06 (6 H, m, allylic) (6h) 4.67 (1 H, m, J 2.5 Hz, =CH<sub>2</sub>), 4.81 (1 H, m, J 2.5 Hz, =CH<sub>2</sub>) 5.47 (1 H, s, -CH=)

Mass spectrum  $(m/e)^{a}$  $\nu_{\rm max}/{\rm cm}^{-1}$ 3 075, 3 068, 1 645, 1 383, 140 (10%,  $M^+$ ), 83 (19%), 70 (23%), 1 168, 920, 890, 822, 735 **69** (12%), **57** (20%), **56** (100%)  $\begin{array}{c} 222\ (57\%,\ M^+),\ 179\ (41\%),\ 165\ (100\%),\\ 124\ (39\%),\ 123\ (73\%),\ 109\ (85\%),\\ 95\ (66\%),\ 81\ (68\%),\ 67\ (41\%) \end{array}$ 3 080, 1 630, 1 380, 1 365, 1 168, 895, 728 222 (7%,  $M^+$ ), 165 (100%), 123 (36%),  $\begin{array}{c} 109 \ (46\%), \ 95 \ (40\%), \ 81 \ (52\%), \\ 67 \ (42\%) \end{array}$  $\begin{array}{c} 222 (25\%, \ M^+), \ 179 \ (47\%), \ 124 \ (70\%), \\ 123 \ (44\%), \ 109 \ (44\%), \ 95 \ (49\%), \\ 81 \ (76\%), \ 79 \ (38\%), \ 67 \ (100\%) \end{array}$ 140 (13%,  $M^+$ ), 83 (37%), 70 (48%), 69 (100%), 57 (17%), 56 (28%) 222 (6%,  $M^+$ ), 165 (100%), 137 (32%),  $\begin{array}{c} 123 (42\%), 109 (90\%), 95 (38\%), \\ 81 (32\%), 57 (34\%) \\ 154 (7\%, M^+), 112 (35\%), 83 (30\%), \\ 70 (82\%), 69 (100\%) \\ 168 (2\%, M^+), 112 (30\%), 83 (14\%), \\ 70 (22\%), 69 (100\%) \\ \end{array}$ 70 (33%), 69 (18%), 57 (100%) 154 (8%,  $M^+$ ), 83 (19%), 70 (28%). 69 (16%), 57 (64%), 56 (100%) 250 (8%,  $M^+$ ), 179 (100%), 137 (26%), 123 (67%), 109 (70%), 95 (56%), 81 (49%), 57 (61%) 168 (18%,  $M^+$ ), 83 (31%). 70 (76%), 69 (29%), 57 (45%), 56 (100%) 278 (1%,  $M^+$ ), 193 (71%), 138 (61%), 123 (100%), 109 (49%), 96 (57%) 95 (98%), 81 (50%), 69 (32%), 57 (33%) 168 (24%,  $M^+$ ), 83 (53%), 70 (47%), 69 (37%), 57 (36%), 56 (100%) 278 (7%,  $M^+$ ), 193 (100%), 123 (18%). 109 (18%), 95 (20%), 81 (21%) 1 168, 920, 895, 725 **194** (31%,  $M^+$ ), **165** (38%), **137** (85%) **123** (91%), **110** (65%), **109** (69%), **05** (0100), **010** (0100), **05** (0100 95 (91%), 81 (81%), 67 (55%), 41 (100%)

• Only parent and important fragmentation peaks are reported. • See ref. 2. • See ref. 4.

literature method,<sup>9</sup> a sample of (10) ( $[\alpha]_D^{25} + 22.46^\circ$ ) (6 g, 42 mmol) was converted into the corresponding tosylhydrazone, which was reduced with sodium borohydride in diglyme to yield (S)-2,5-dimethylheptane (11)  $^{10}$  (2 g, 37%) which was purified by preparative g.l.c. (20% Carbowax 20 M; 80 °C),  $[\alpha]_{D^{25}} + 10.27^{\circ}$  (c 8.37 in n-heptane). A sample of (11),  $[\alpha]_{p}^{25} + 9.65^{\circ}$  (ref. 10) showed  $[\alpha]_{p}^{25} + 10.15^{\circ}$  (c 8.77 in n-heptane).

Ozonolysis of (S)-(3b).-The olefin (2.1 g, 15 mmol),  $[\alpha]_{D}^{25}$  +18.97°, was ozonized, at -30 °C, in methanol solution (15 ml), and the crude ozonide was treated with dimethyl sulphide according to the described procedure.24 After work-up, distillation afforded (10) (1.12 g, 53%),  $[\alpha]_{D}^{25} + 21.56^{\circ}$ 

Ozonolysis of (3S,7S)-(6b).—As described above, the diene (1.6 g, 7.3 mmol),  $[\alpha]_{D}^{25}$  +51.24°, gave (10) (0.52 g, 50%),  $[\alpha]_{p}^{25} + 21.36^{\circ}$ , by the ozonolysis procedure.

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3 078, 1 628, 1 380, 1 365, 1 167, 893, 740, 730 3 025, 1 380, 1 365, 1 168, 963, 860, 730 3 080, 3075, 3 065, 1 640, 1 380, 1 365, 1 165, 920, 890, 825, 760 3 080, 1 628, 1 380, 1 365, 1 168, 1 020, 920, 898, 775 3 080, 1 640, 1 380, 1 365, 1 165, 920, 890 3 080, 1 640, 1 635, 1 393, 1 385, 1 372, 1 365, 1 260, 1 230, 1 223, 1 168, 898 3 080, 3 070, 1 640, 1 378, 1 365, 1 165, 920, 890,

820, 770 3 080, 1 628, 1 378, 1 368, 1 165, 920, 895, 770

3 072, 3 063, 1 640, 1 378, 1 365, 1 165, 920, 888, 823, 770 3 080, 1 628, 1 378, 1 367, 1 168, 920, 893, 772

3 065, 3 070, 1 645, 1 383, 1 368, 1 167, 920, 890, 823, 725 3 080, 1 628, 1 380, 1 368,

3 080, 1 630, 1 380, 893, 743, 730

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