

TABLE 1

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

Entry number	[(1a)]		Temp. (°C)	Reaction time/h	Products, yields % (by g.l.c.)							Trienes C ₂₂ H ₄₀	Tetraenes C ₂₈ H ₅₀
	[AlBu ⁱ ₃]	[FeCl ₃]			(3a)	(4a)	(5a)	(6a)	(7a)	(8a)	(9a)		
1 ^b	0.5	58	-20	40	15	3	6	13	5	25	10	13	7
2	0.5	58	0	40	36	2	3	27	2	10	2	10	7
3	0.5	61	25	0.5	42	1	1	27		9	2	9	6
4 ^c	0.5	148	25	0.5	29	2		21		16	5	8	6
5 ^d	0.5	340	25	0.5	16	1		21		30	8	9	7
6 ^e	0.5	59	65	0.5	53	1	1	27		4	4	8	2
7 ^e	0.5	54	98	0.5	51	1	1	26		5	5	9	
8 ^e	1.0	58	-20	40	10	4	7	5	8	28	12	12	7
9	1.0	61	25	0.5	28	1	2	18	3	17	5	13	9
10 ^e	1.0	55	65	0.5	36	1	1	24	1	9	10	11	3
11 ^f	4.0	56	-20	40	2	3	1	2	4	47	29		
12 ^g	4.0	90	25	40	4	2	1	4	2	37	36	6	2
13 ^{c,e}	4.0	63	65	0.5	8	2	1	6	2	29	38	4	
14 ^e	12.0	77	25	20	1			2		41	52		

^a Unless otherwise stated, all reactions were carried out in pentane. ^b Conversion 78%. ^c Conversion 70%. ^d Conversion 56%. ^e In heptane. ^f Conversion 34%. ^g 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 cyclo-trimers (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 AlBuⁱ₃, 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 AlBuⁱ₃: 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-yne 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-1-yne (1a), when 3,4-dimethyl- (1c) and 3,4,4-trimethyl-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 α 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 straight-chain alk-1-yne (Table 3, entry 25) or β - or γ -substituted alkynes (entries 23 and 24).

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

TABLE 2

Reaction between trialkylalanes AlR'₃ and hex-1-yne (1a) in the presence of iron trichloride ^a

Entry number	R'	[(1a)]		Temp. (°C)	Products, yields % (by g.l.c.)							Trienes	Tetraenes
		[AlR' ₃]	[FeCl ₃]		(1a) ^b	(2a)	(3)	(4)	(6)	(8a)	(9a)		
15	Et	0.5	58	25	5	5	12	2	13	18	12	15	12
16 ^c	Et	0.5	65	65	2	7	35	2	20	8	7	8	7
17 ^d	Et	12.0	25	25	19					20	47		
3	Bu ⁱ	0.5	25	25		1	42	1	27	9	2	9	6
6	Bu ⁱ	0.5	65	65			53	1	27	4	4	8	2
18 ^e	EtCH(Me)CH ₂	0.5	65	65	10	16	28	2	13	10	11	5	
19 ^e	Bu ⁱ	1.0	25	25	7					30	36		

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

TABLE 3

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

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

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

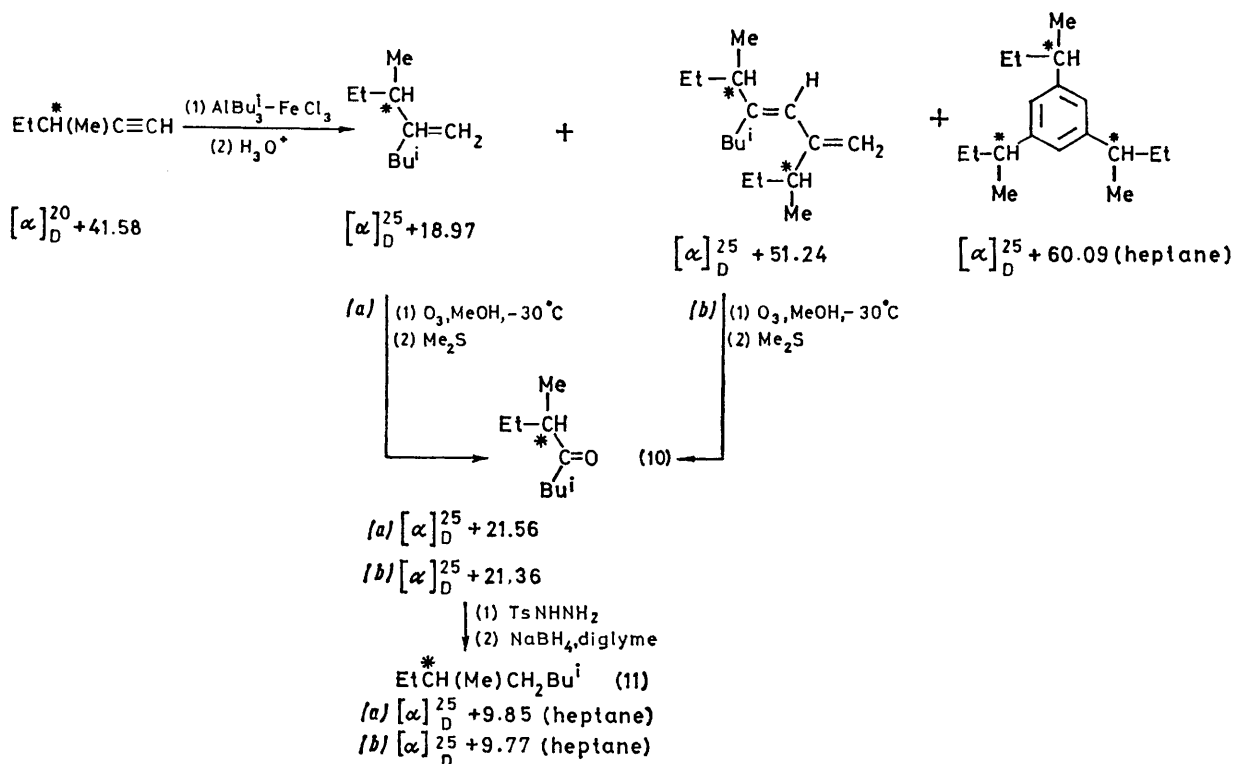
verify if the carbon atom adjacent to the triple bond of compound (1) is directly involved in the reaction, we have investigated the stereochemistry of the reaction carried out with (*S*)-3-methylpent-1-yne (1b).

In the experimental conditions adopted [25 °C, (1) : Al = 0.5 : 1, (1) : Fe = 60 : 1 (Table 3, entry 20)], (*S*)-(1b), $[\alpha]_D^{20} + 41.58^\circ$, optical purity 89%,⁶ afforded after 30 min a complex mixture of products, from which by preparative g.l.c., (*S*)-(3b), $[\alpha]_D^{25} + 18.97^\circ$, (3*S*,7*S*)-(6b), $[\alpha]_D^{25} + 51.24^\circ$, and 1,3,5-tris-[(*S*)-1-methylpropyl]benzene (8b), $[\alpha]_D^{25} + 60.1^\circ$ (heptane), optical purity 87%,⁷ 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 (3*S*,7*S*)-(6b) were converted, by ozonolysis, into (*S*)-2,5-dimethylheptan-4-one (10),⁸ having respectively $[\alpha]_D^{25} + 21.56$ and $+ 21.36^\circ$. The optical purity of the two samples of (10) was evaluated by reduction of their tosylhydrazones, with NaBH₄ in diglyme,⁹ into (*S*)-2,5-dimethylheptane (11), $[\alpha]_D^{25} + 9.85^\circ$, optical purity 92%,¹⁰ and

+9.77°, optical purity 91%,¹⁰ respectively (Scheme 2). The data obtained confirm, within the accuracy limits, the complete stereospecificity of the process, also indicating that the carbon atom α 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 AlBu₃ⁱ with the iron salt. On the basis of previous results,^{11,12} 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.¹³ It has been shown previously that reaction of an iron complex with organometallic compounds leads to alkyl-iron species,^{11,12,14} which are catalytically active in the oligomerization of unsaturated substrates.¹⁵ Since no reaction is observed when iron trichloride is treated at -20 °C with a pentane solution



SCHEME 2

EXPERIMENTAL

Triethylaluminium, tri-isobutylaluminium (Fluka A.G. Co.), and tris-(2-methylbutyl)aluminium¹⁸ 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)⁶ and the other alk-1-yne (1) employed were synthesized from the corresponding α -olefins by published methods;^{6,19} [1-²H₁]hex-1-yne was obtained from hex-1-yne by a published procedure.²⁰ 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 LiAlH₄ before using. 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. were carried out on a Perkin-Elmer F 21 chromatograph (300 × 0.80 cm columns). Optical rotations were measured with a Perkin-Elmer 142 automatic polarimeter; unless otherwise specified, rotations refer to pure liquid. ¹H N.m.r. spectra were obtained with a JEOL JNM-PS-100 spectrometer on CCl₄ solutions; chemical shifts are expressed on the δ scale downfield from SiMe₄. 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 FeCl₃. 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⁻¹). 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.³ 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-methyleneoctane² (3a) ($\geq 97\%$ pure; 5 g, 23%) and a C₁₆ 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-4-ene^{2,3} (5a) and (Z,E)-2-methyl-5-butylundeca-4,6-diene (7a). The mixture was separated by preparative g.l.c. (8% Carbowax 20 M + 2% KOH; 125 °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 LiAlH₄ according to the procedure described elsewhere.²¹ 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⁻¹) of the ether layer showed the presence of 2-methyloctan-4-ol²² together with minor amounts of an α,β -unsaturated alcohol of molecular formula C₁₅H₃₀O, *m/e* 226 (M⁺), 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), $[\alpha]_D^{20} +41.58^\circ$,⁸ 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_D^{25} 1.421 1; d_4^{25} 0.743 2; $[\alpha]_D^{25} +18.97^\circ$; and a fraction (2.8 g) containing (E)-(3S,7S)-3,7-dimethyl-6-(2-methylpropyl)-4-methylenon-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_D^{25} 1.456 0; d_4^{25} 0.801 6; $[\alpha]_D^{25} +51.24^\circ$. 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), $[\alpha]_D^{25} +60.1^\circ$ (*c* 2.23 in n-heptane).⁷

(S)-2,5-Dimethylheptan-4-one (10).⁸—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)-2-methylbutyryl chloride (24 g, 0.20 mol) {b.p. 72 °C at 160 mmHg; α_D^{25} (*l* = 1) +18.02°; from (S)-2-methylbutanoic acid, $[\alpha]_D^{25} +19.47^\circ$ }²³ 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_D^{25} 1.413 3; d_4^{25} 0.811 6; $[\alpha]_D^{25} +22.46^\circ$.

In order to determine its optical purity, according to a

TABLE 4

Spectral data for products of iron trichloride-catalysed reactions

	¹ H N.m.r. (δ)	$\nu_{\max.}/\text{cm}^{-1}$	Mass spectrum (<i>m/e</i>) ^a
(3a) ^b	0.85—1.80 (14 H, m, aliphatic), 1.92 (14 H, m, allylic) 4.61 (1 H, d, <i>J</i> 2.3 Hz, =CH ₂), 4.65 (1 H, d, <i>J</i> 2.3 Hz, =CH ₂)	3 075, 3 068, 1 645, 1 383, 1 168, 920, 890, 822, 735	140 (10%, <i>M</i> ⁺), 83 (19%), 70 (23%), 69 (12%), 57 (20%), 56 (100%)
(5a) ^b	0.85—1.78 (21 H, m, aliphatic), 2.02 (6 H, m, allylic) 4.62 (1 H, m, <i>J</i> 2.6 and 0.5 Hz, =CH ₂), 4.92 (1 H, m, <i>J</i> 2.6 and 1.5 Hz, =CH ₂) 5.19 (1 H, t of t, <i>J</i> 7.0 and 1.2 Hz, -CH=)	3 080, 1 630, 1 380, 1 365, 1 168, 895, 728	222 (57%, <i>M</i> ⁺), 179 (41%), 165 (100%), 124 (39%), 123 (73%), 109 (85%), 95 (66%), 81 (68%), 67 (41%)
(6a)	0.81—1.80 (21 H, m, aliphatic), 2.04 (6 H, m, allylic) 4.66 (1 H, m, <i>J</i> 2.4 Hz, =CH ₂), 4.81 (1 H, m, <i>J</i> 2.4 and 1.2 Hz, =CH ₂) 5.57 (1 H, s, -CH=)	3 078, 1 628, 1 380, 1 365, 1 167, 893, 740, 730	222 (7%, <i>M</i> ⁺), 165 (100%), 123 (36%), 109 (46%), 95 (40%), 81 (52%), 67 (42%)
(7a) ^c	0.86—1.83 (21 H, m, aliphatic), 2.07 (6 H, m, allylic) 5.17 (1 H, t, <i>J</i> 7.4 Hz, -CH=), 5.57 (1 H, d of t, <i>J</i> 15.5 and 6.8 Hz, -CH=) 6.20 (1 H, d, <i>J</i> 15.5 Hz -CH=)	3 025, 1 380, 1 365, 1 168, 963, 860, 730	222 (25%, <i>M</i> ⁺), 179 (47%), 124 (70%), 123 (44%), 109 (44%), 95 (49%), 81 (76%), 79 (38%), 67 (100%)
(3b)	0.81—1.72 (15 H, m, aliphatic), 1.77—2.12 (3 H, m, allylic) 4.67 (1 H, m, =CH ₂), 4.73 (1 H, m, =CH ₂)	3 080, 3075, 3 065, 1 640, 1 380, 1 365, 1 165, 920, 890, 825, 760	140 (13%, <i>M</i> ⁺), 83 (37%), 70 (48%), 69 (100%), 57 (17%), 56 (28%)
(6b)	0.80—1.75 (23 H, m, aliphatic), 2.07 (4 H, m, allylic) 4.73 (1 H, m, <i>J</i> 2.4 and 1.5 Hz, =CH ₂), 4.89 (1 H, d, <i>J</i> 2.4 Hz, =CH ₂) 5.64 (1 H, s, -CH=)	3 080, 1 628, 1 380, 1 365, 1 168, 1 020, 920, 898, 775	222 (6%, <i>M</i> ⁺), 165 (100%), 137 (32%), 123 (42%), 109 (90%), 95 (38%), 81 (32%), 57 (34%)
(3c)		3 080, 1 640, 1 380, 1 365, 1 165, 920, 890	154 (7%, <i>M</i> ⁺), 112 (35%), 83 (30%), 70 (82%), 69 (100%)
(3d)		3 080, 1 640, 1 635, 1 393, 1 385, 1 372, 1 365, 1 260, 1 230, 1 223, 1 168, 898	168 (2%, <i>M</i> ⁺), 112 (30%), 83 (14%), 70 (33%), 69 (18%), 57 (100%)
(3e)	0.80—1.67 (16 H, m, aliphatic), 1.85 (4 H, m, allylic) 4.68 (2 H, s, =CH ₂)	3 080, 3 070, 1 640, 1 378, 1 365, 1 165, 920, 890, 820, 770	154 (8%, <i>M</i> ⁺), 83 (19%), 70 (28%), 69 (16%), 57 (64%), 56 (100%)
(6e)	0.83—1.73 (25 H, m, aliphatic), 2.04 (6 H, m, allylic) 4.79 (1 H, m, =CH ₂), 4.85 (1 H, m, =CH ₂), 5.60 (1 H, s, -CH=)	3 080, 1 628, 1 378, 1 368, 1 165, 920, 895, 770	250 (8%, <i>M</i> ⁺), 179 (100%), 137 (26%), 123 (67%), 109 (70%), 95 (56%), 81 (49%), 57 (61%)
(3f)	0.82—1.77 (18 H, m, aliphatic), 1.88 (4 H, m, allylic) 4.64 (1 H, m, =CH ₂), 4.69 (1 H, m, =CH ₂)	3 072, 3 063, 1 640, 1 378, 1 365, 1 165, 920, 888, 823, 770	168 (18%, <i>M</i> ⁺), 83 (31%), 70 (76%), 69 (29%), 57 (45%), 56 (100%)
(6f)	0.84—1.80 (29 H, m, aliphatic), 2.04 (6 H, m, allylic) 4.68 (1 H, m, =CH ₂), 4.85 (1 H, m, =CH ₂) 5.63 (1 H, s, -CH=)	3 080, 1 628, 1 378, 1 367, 1 168, 920, 893, 772	278 (1%, <i>M</i> ⁺), 193 (71%), 138 (61%), 123 (100%), 109 (49%), 96 (57%), 95 (98%), 81 (50%), 69 (32%), 57 (33%)
(3g)	0.82—1.77 (18 H, m, aliphatic), 1.90 (4 H, m, allylic) 4.64 (1 H, m, =CH ₂), 4.69 (1 H, m, =CH ₂)	3 065, 3 070, 1 645, 1 383, 1 368, 1 167, 920, 890, 823, 725	168 (24%, <i>M</i> ⁺), 83 (53%), 70 (47%), 69 (37%), 57 (36%), 56 (100%)
(6g)	0.84—1.76 (29 H, m, aliphatic), 2.04 (6 H, m, allylic) 4.70 (1 H, m, =CH ₂), 4.86 (1 H, m, =CH ₂), 5.62 (1 H, s, -CH=)	3 080, 1 628, 1 380, 1 368, 1 168, 920, 895, 725	278 (7%, <i>M</i> ⁺), 193 (100%), 123 (18%), 109 (18%), 95 (20%), 81 (21%)
(6h)	0.83—1.53 (17 H, m, aliphatic), 2.06 (6 H, m, allylic) 4.67 (1 H, m, <i>J</i> 2.5 Hz, =CH ₂), 4.81 (1 H, m, <i>J</i> 2.5 Hz, =CH ₂) 5.47 (1 H, s, -CH=)	3 080, 1 630, 1 380, 893, 743, 730	194 (31%, <i>M</i> ⁺), 165 (38%), 137 (85%), 123 (91%), 110 (65%), 109 (69%), 95 (91%), 81 (81%), 67 (55%), 41 (100%)

^a Only parent and important fragmentation peaks are reported. ^b See ref. 2. ^c See ref. 4.

literature method,⁹ 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), $[\alpha]_D^{25} + 9.65^\circ$ (ref. 10) showed $[\alpha]_D^{25} + 10.15^\circ$ (*c* 8.77 in *n*-heptane).

Ozonolysis of (S)-(3b).—The olefin (2.1 g, 15 mmol), $[\alpha]_D^{25} + 18.97^\circ$, 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), $[\alpha]_D^{25} + 51.24^\circ$, gave (10) (0.52 g, 50%), $[\alpha]_D^{25} + 21.36^\circ$, by the ozonolysis procedure.

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