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110. The Four Isomeric 1,3,5-Undecatrienes. Synthesis and Configurational Assignment

by Ferdinand Näf, René Decorzant, Walter Thommen, Bruno Willhalm
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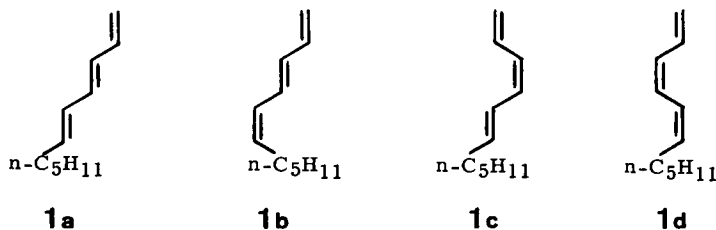
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(17. III. 75)

Summary. The four geometrical isomers of 1,3,5-undecatriene, **1a–d** have been prepared (stereospecifically and non-stereospecifically), using either (1) the *Wittig* reaction, (2) thermal sigmatropic hydrogen shifts, (3) partial reduction of triple bonds by zinc, or (4) organocopper reagents. The thermal behaviour of the four 1,3,5-undecatrienes has been investigated and the products formed have been characterized. The spectra of **1a–d**, and of related compounds, have been discussed in order to corroborate their configurational assignment.

1. Introduction. – Some 1,3,5-undecatrienes isolated from the essential oils of both *Galbanum* [1–3] and the *Hawaiian* seaweed *Dictyopteris* [4] are reported to exhibit interesting olfactive properties.

The configurational assignment of the two 1,3,5-undecatrienes from *Galbanum* oil is, however, controversial (*i.e.* [2] *versus* [3] [4]). Moreover, not all the four undecatrienes **1a–d** have been synthesized hitherto.

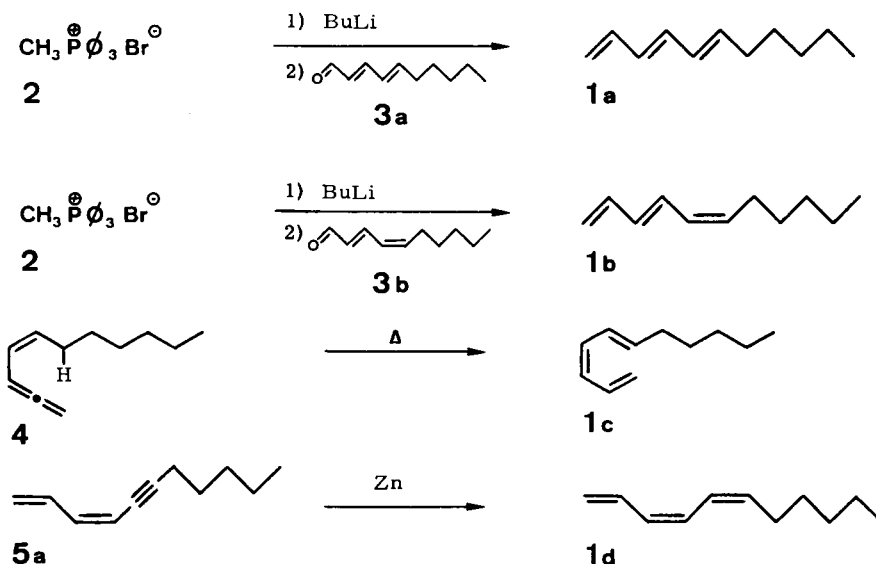


The present publication is therefore concerned with synthesis (stereoselective and non-stereoselective) and spectral analysis of the 1,3,5-undecatrienes **1a–d**. In a further section some thermal reactions are discussed which either yield triene **1c** from the structurally isomeric precursor **4** or transform trienes **1a–d** into structural isomers or dimers. On the basis of these results a rigorous configurational assignment was established for **1a–d**. This assignment is in accord with both [3] (dealing with **1a** and **1b**), and [4] (characterizing **1a–c**), but disproves [2].

Accordingly, the two 1,3,5-undecatrienes found in *Galbanum* essential oil are (*E,Z*)-1,3,5-undecatriene **1b** (strong *Galbanum* type odour, relatively short retention time on GC.¹⁾) and (*E,E*)-1,3,5-undecatriene **1a** (linseed oil, cod-liver oil type odour; longer retention time on GC.)

2. Results and Discussion. – 2.1. *Stereospecific synthesis of the four 1,3,5-undecatrienes 1a–d* (Scheme 1).

Scheme 1

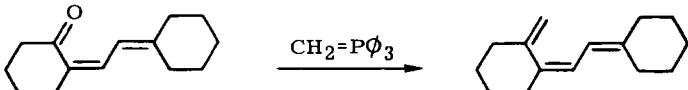


2.1.1. (*E,E*)-1,3,5-undecatriene (**1a**) [5] was specifically prepared by Wittig reaction of (*E,E*)-2,4-decadienal (**3a**) [6] with methylenetriphenylphosphorane. In this we have assumed that no isomerization of the (*E*)-double bonds in aldehyde **3a** has occurred during the reaction. This argument, though obvious, is experimentally supported by the known reaction of (*E*)-cinnamic aldehyde with methylenetriphenylphosphorane to give (*E*)-1-phenyl-1,3-butadiene [7].

2.1.2. (*E,Z*)-1,3,5-undecatriene (**1b**) was prepared by Wittig reaction of (*E,Z*)-2,4-decadienal (**3b**) [6] with methylenetriphenylphosphorane. Again, only one reaction product was formed. This is in agreement with a related case reported by *Harrison & Lythgoe* [8]²⁾.

2.1.3. (*Z,E*)-1,3,5-undecatriene (**1c**) was stereoselectively prepared from the vinylallene **4** by a thermally allowed suprafacial [1,5]-hydrogen shift³⁾.

¹⁾ GC. = gas chromatography; using either an Apiezon capillary column, a packed Carbowax or Silicon oil column. For details see section 2.2.

²⁾  [8]

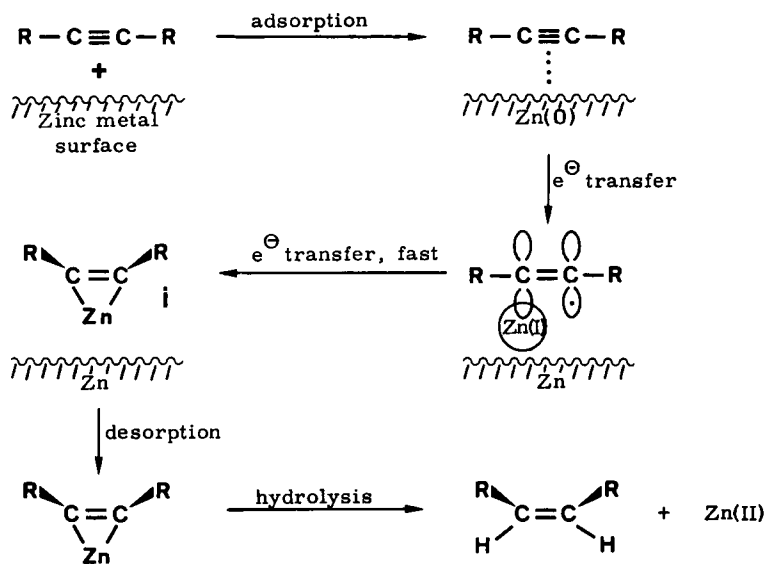
³⁾ For details see section 2.5.

2.1.4. (*Z,Z*)-1,3,5-undecatriene (**1d**). This isomer proved extremely difficult to obtain due to its tendency to undergo a thermal [1,7]-hydrogen shift slightly above room temperature to yield (*Z,Z,E*)-2,4,6-undecatriene (**6**) (see section 2.5.). (*Z*)-Dienyne **5a** appeared to be a suitable precursor which on partial hydrogenation of the triple bond would selectively give the (*Z,Z*)-triene **1d**. However, all classical hydrogenation methods, such as *Lindlar's* catalyst/ H_2 , diimide, and triphenylphosphinerhodium chloride/ H_2 , failed owing to their lack of selectivity.

Morris et al. [9] recently reported that zinc powder in 50% aqueous 1-propanol at reflux stereoselectively reduces triple bonds to (*Z*)-double bonds⁴). Application of this method to (*Z*)-dienyne **5a** gave in 80% yield pure (*Z,Z,E*)-2,4,6-undecatriene (**6**) which must have formed *via* the desired, but thermally unstable, (*Z,Z*)-triene **1d**. In order to be able to run the zinc reduction at room temperature, we tried to activate the zinc by addition of potassium cyanide. And in fact, stirring of (*Z*)-dienyne **5a** in the presence of a large excess of zinc powder, 50% aqueous 1-propanol, and potassium cyanide at $\sim 25^\circ$ for 22 h gave **1d**.

A plausible mechanism to account for the *cis*-selectivity is depicted in Scheme 2.

Scheme 2



Adsorption of the triple bond on the zinc metal surface is followed by two successive one-electron transfers from the 4s orbital of Zn (0) to one π -orbital of the triple bond, yielding the organozinc intermediate **i** with the substituents R in a (*Z*)-configuration. The (*Z*)-geometry of **i** would therefore arise from the fact that zinc is capable of adding both electrons from the same side to the triple bond.

Subsequent desorption of **i** from the metal surface followed by hydrolysis with retention of double bond configuration gives a (*Z*)-olefin.

⁴) We would like to thank Dr. *M. Joyeux, Firmenich SA*, for having brought this method to our attention.

2.2. *Relative retention times of the trienes 1a–c and 6 on GC.* Only the trienes **1a–c** and **6** supported gas chromatography without being transformed. The (*Z,Z*)-isomer **1d** always rearranged to yield triene **6** under all conditions tried.

The best separations of these trienes were obtained on an Apiezon glass capillary column (0.31 mm $\times$ 50 m) at $\sim 120^\circ$ (He pressure 0.55 atm), the order of increasing retention time being as follows: **1b** $\ll$ **1c** $<$ **1a** $\ll$ **6** (see Fig. 1).

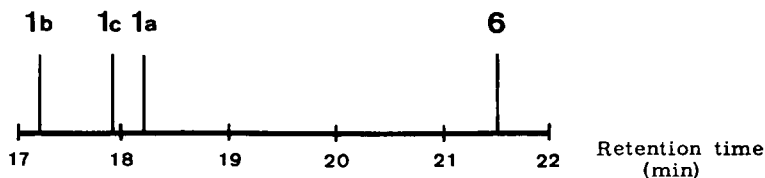


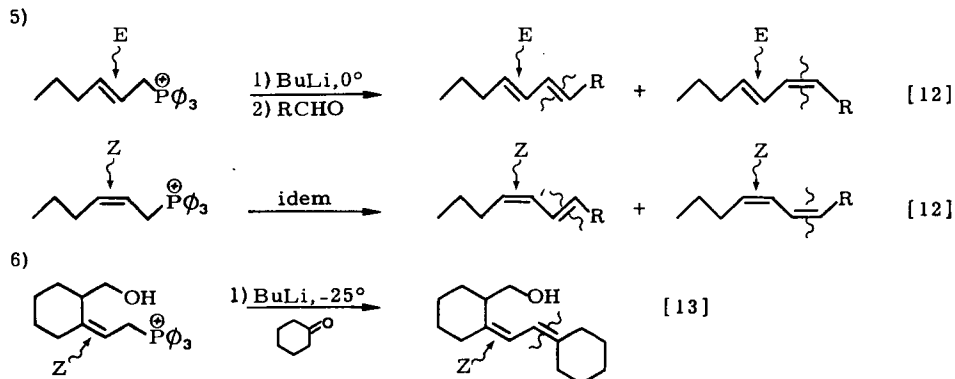
Fig. 1. Gas chromatography of the trienes **1a–c** and **6** using an Apiezon glass capillary column (0.31 mm $\times$ 50 m) at 120° (He pressure 0.55 atm) on a Carlo Erba GI apparatus

Isomers **1c** and **1a** were only separable on this capillary column whereas the other trienes showed also different retention times on packed columns with Sp 1000 (6%), Carbowax (5%) or Silicon oil (5%) as stationary phase (for details see exp. section).

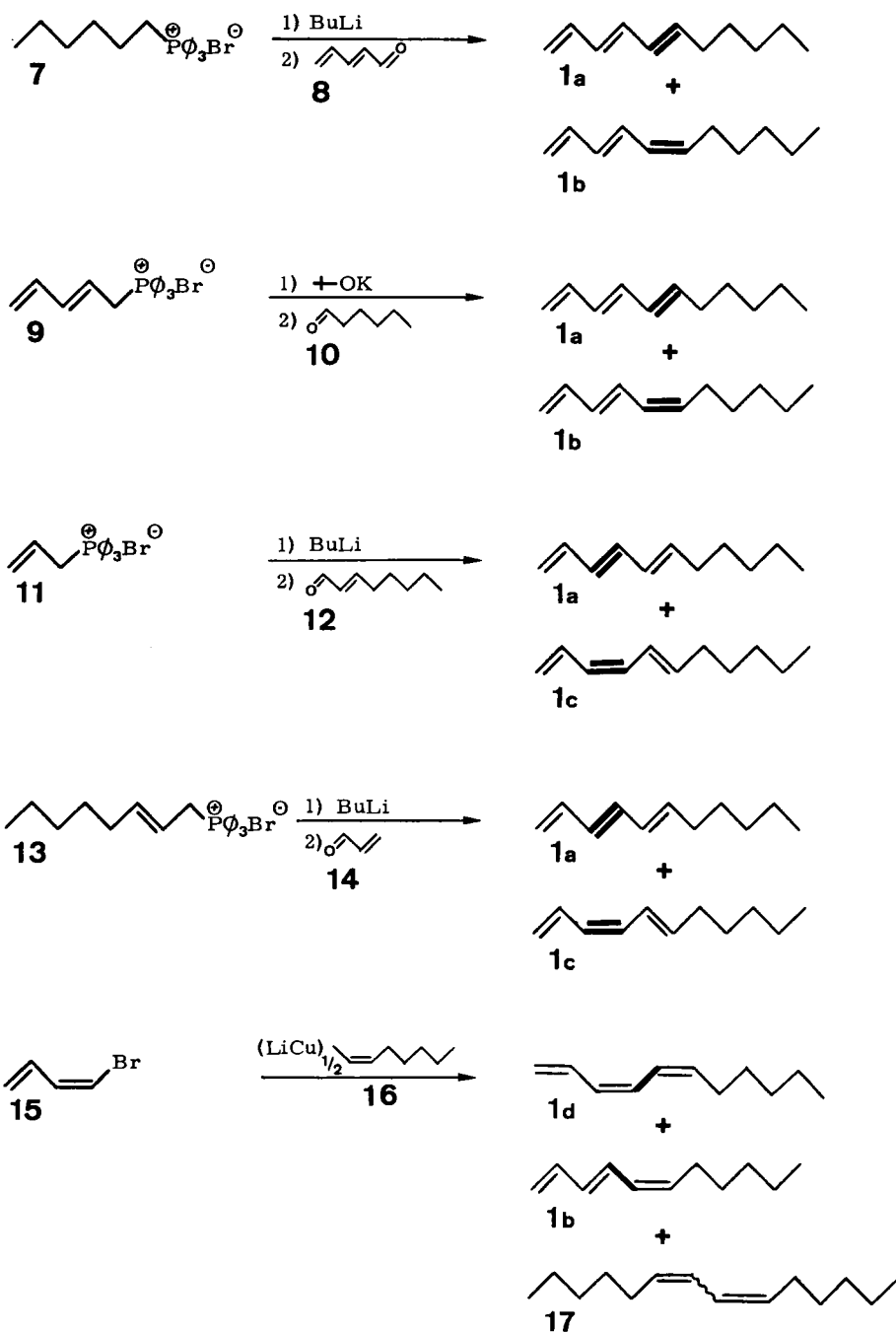
2.3. *Non-selective syntheses giving mixtures of 1,3,5-undecatrienes* (see Scheme 3). Two syntheses, leading to a mixture of **1a** and **1b**, both combine a five-carbon with a six-carbon unit and involve non-stereoselective C(5,6) double bond formation. In the first case (*E*)-2,4-pentadienal (**8**) [10] was allowed to react with hexyldenetriphenylphosphorane [11] (from the corresponding phosphonium salt and butyllithium) to give a mixture of **1a** and **1b** ($\sim 55:45$). The same isomeric mixture was obtained by reaction of (*E*)-pentadienyldenetriphenylphosphorane with hexanal (**10**). In this the geometry of the starting (*E*)-2,4-pentadienyldi-*tert*-butylphosphonium bromide (**9**) (for NMR.-spectrum see Table 3) was preserved during both ylid formation (see NMR.-spectrum of ylid, Table 3) and subsequent reaction with aldehyde **10**.

Preservation of double bond geometry of (*Z*) or (*E*)-allylic phosphonium salts during the Wittig reaction has been demonstrated before *e.g.* by Truscheit & Eiter [12]⁵ and by Harrison & Lythgoe [13]⁶.

Two further, non-stereoselective approaches, leading to the 1,3,5-undecatriene mixture **1a/1c**, both involve combination of a three-carbon unit with an eight-carbon



Scheme 3



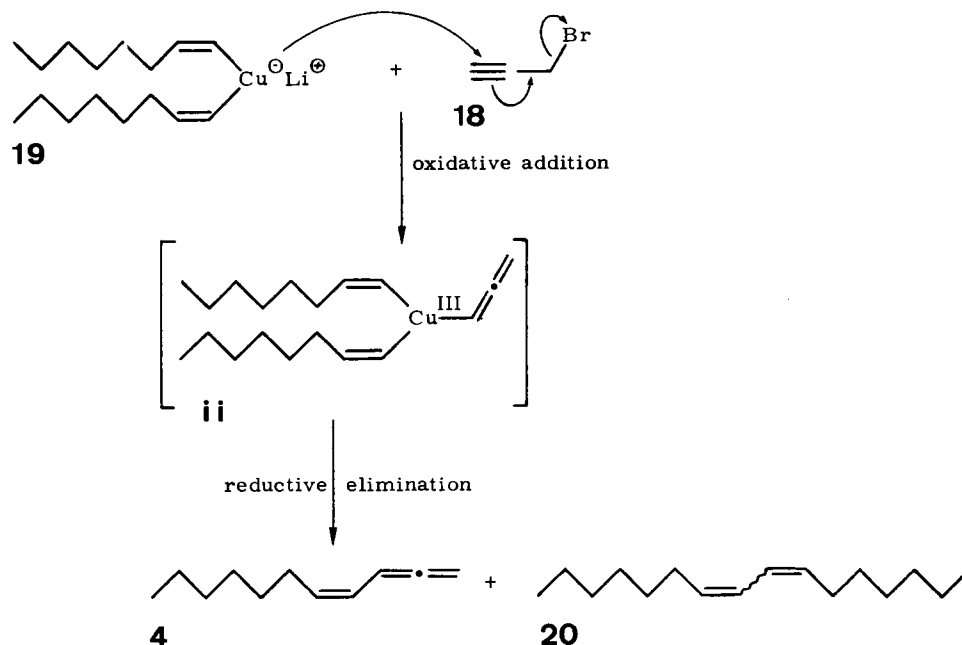
Printed in bold lines: the newly formed bonds.

unit by non-stereoselective C(3,4) double bond formation. (*E*)-2-Octenal **12** [14] and propyridenetriphenylphosphorane [7] yielded the undecatrienes **1a** and **1c** (3:2 ratio; 23% yield), the (*E*)-double bond in the aldehyde being preserved in the products. Likewise, reaction of (*E*)-2-octenylphosphonium bromide (**13**) with *n*-butyllithium followed by addition of acrolein (**14**) gave the same triene mixture **1a/c** (3:2 ratio).

A last, non-stereospecific method led to a mixture of the 1,3,5-undecatrienes **1d** and **1b**. Reaction of lithium di-(*Z*)-1-heptenylcuprate (**16**) [15]⁷⁾ with (*Z*)-1,3-butadienyl bromide (**15**) [17] was hoped to produce **1d** stereospecifically. However, a 7:3 mixture of **1d** and **1b** was isolated in low yield together with the known symmetrical 6,8-tetradecadiene **17** (isomeric mixture) [15].

2.4. Preparation of the precursors. For the preparation of the thermolabile allene **4**, a stereospecific, low-temperature method was needed. The best results were obtained by coupling propargyl bromide (**18**) with lithium di-(*Z*)-1-octenylcuprate (**19**), a reaction which involves an indirect displacement of a propargyl halide by a 1-alkenyl group⁸⁾. Although allene **4** was formed in low yield (~10%) and together with the symmetrical 7,9-hexadecadiene (**20**) (mixture of isomers; ~30%), practically no acetylide was present as a by-product. Simple *Vigreux* distillation at 30–32°/0.05 Torr afforded pure **4**. As in the related C–C coupling reactions involving 1-alkenylcuprates and alkyl halides [15] the (*Z*)-geometry of the 1-alkenyl reagent was preserved in product **4**.

Scheme 4



⁷⁾ For an excellent review on C–C bond formation using organocopper reagents see [16].

⁸⁾ This reaction is closely related to the known transformations of propargyl acetates [18], propargyl chlorides [19] or propargyl epoxides [20] with lithium dialkylcuprates to yield alkyl substituted allenes.

The mechanism of such C–C coupling reactions involving organocuprates has not been fully investigated and might be more complex than is generally believed. Nevertheless, by analogy with earlier proposals (see *e.g.* [16], [18b] and [21]) we assume that in our case the copper (III) intermediate **ii** plays a decisive role as depicted in *Scheme 3*. Collapse of this formal copper (III) species would easily account for both product and by-product formation.

A 2:3 mixture of (*Z*)-1,3,5-undecadienyne (**5a**) and (*E*)-1,3,5-undecadienyne (**5b**) was obtained from 4-bromo-1,5-undecenyne (**21**) [2] by 1,5-diazabicyclo[5.4.0]-undec-5-ene (DBU) in DMSO at 50°.

(*E*)-2,4-Pentadienylphosphonium bromide (**9**) was readily obtained from (*E*)-2,4-pentadienyl bromide (**22**) [22] and triphenylphosphine (98%). Likewise, (*E*)-2-octenyltriphenylphosphonium bromide (**13**) was prepared from (*E*)-2-octenyl bromide (**23**) [23] and triphenylphosphine.

2.5. *Thermal behaviour of the trienes 1c, 1d, 1a, 1b and 4* (*Scheme 5 and 1*). **1c**, upon heating, undergoes an electrocyclic reaction to give 5-pentyl-1,3-cyclohexadiene (**24**), the activation parameters being comparable to those of closely related examples (see *Table 1*).

Scheme 5

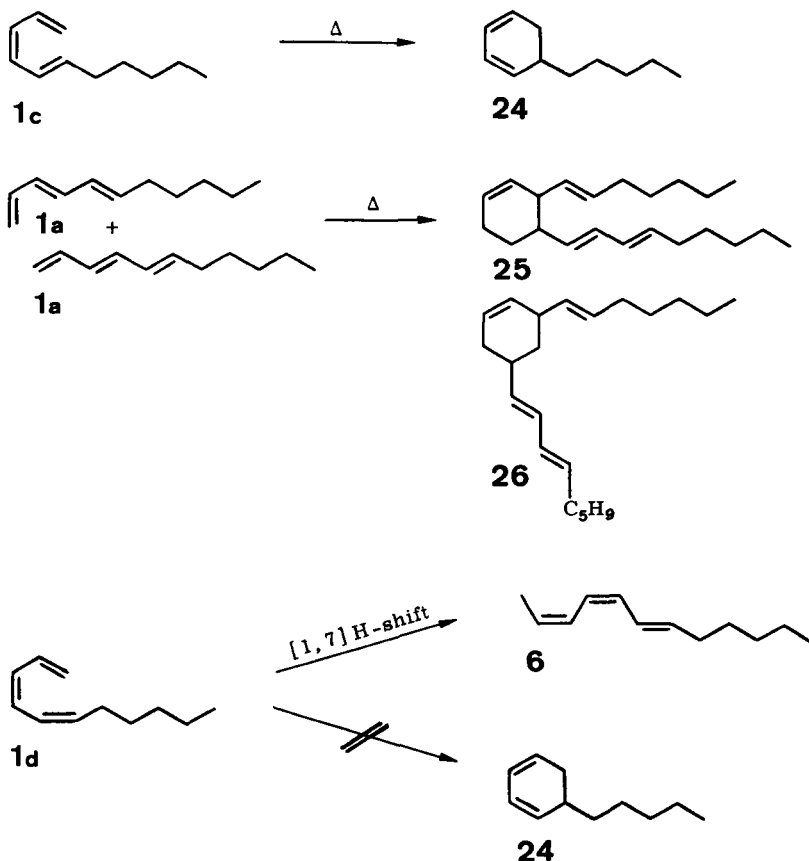
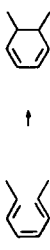
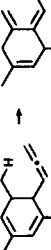
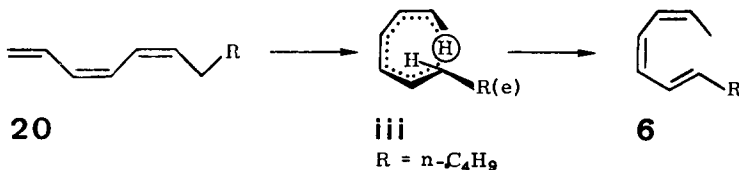


Table 1. First order rate constants and activation parameters for some thermal cyclization of conjugated trienes to give cyclohexadienes, and for some thermally allowed [1,5] H-shifts

Reaction	Temperature [°C]	$K \times 10^3$ [min ⁻¹]	log A	Ea [kcal/mol]	$\Delta G^\ddagger$ [kcal/mol]	$\Delta H^\ddagger$ [kcal/mol]	$\Delta S^\ddagger$ [eu]	Ref.
1c → 24	148.7	12.670	12.831	28.40 ± 0.08	30.18 ± 0.14 (at 25°C)	27.80 ± 0.08 (at 25°C)	-7.9 ± 0.2 (at 25°C)	
	139.9	6.640						
	130.9	2.969						
	121.7	1.304						
	111.7	0.498						
4 → 1c	81.0	9.918	10.456	20.19 ± 0.31	25.21 ± 0.57 (at 25°C)	19.59 ± 0.31 (at 25°C)	-18.8 ± 0.1 (at 25°C)	
	76.1	6.699						
	70.1	3.936						
	65.35	2.647						
	59.35	1.536						
			11.9 ± 0.7	29.9 ± 0.5			-7.3 (at 500°K)	[24]
			10.5 ± 0.1	31.8 ± 0.2			-13.8 (at 500°K)	[25]
			12.0	31.0			-5.0	{ [26a] [27a]
				24.6			-7	[26b] [28]
						28.6 (at 132°C)		
						28.8 (at 170°C)	-14.0 (at 170°C)	[29]

Interestingly, the all-(*Z*)-triene **1d** does not cyclize to give **24** but prefers the thermally allowed antarafacial sigmatropic [1,7]-hydrogen shift to give **6** in a highly stereoselective manner. This is due to the extremely low activation energy of this hydrogen shift. The corresponding thermal [1,7]-hydrogen shifts in the D vitamins (see *e.g.* [27b] and [30])⁹⁾ are known to have activation energies of ~ 20 kcal/mol [27b] and we guess that our shift might have a similar or an even lower activation energy.

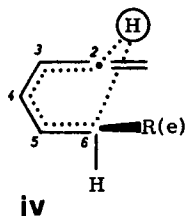
The stereochemistry of the product **6** is accounted for by assuming a helix-type transition state **iii** [30] with substituent R in an equatorial *exo* position.



Such a transition state has maximum orbital overlap in conjunction with minimum conformational strain as can be seen from *Dreiding* models.

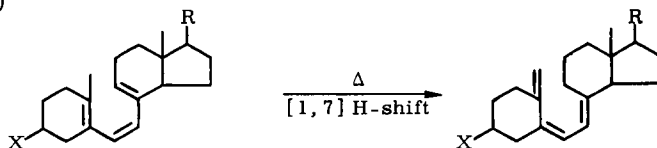
The thermal behaviour of the trienes **1a** and **1b** has not been thoroughly investigated in the present work. On heating either **1a** or **1b**, or a mixture of **1a** and **1b** at 150° for 10 h a [4+2]-cycloaddition took place, in accordance with *Naves* [3]. However, in all cases GC. analysis of the dimers obtained revealed a rather complex mixture of various stereo or/and structural isomers. The 'cleanest' reaction product resulted from the dimerization of the all-(*E*)-isomer **1a**, and the main compound **25** ($\sim 85\%$ of the mixture) could readily be purified by GC. Spectral data (see section 2.6.) of **25** prove the 'logical *Diels-Alder* structure' shown on *Scheme 5*.

Allene **4** undergoes a thermally allowed suprafacial sigmatropic [1,5]-hydrogen shift, the transition state **iv** accounting for the geometry of the product formed. In the preferred transition state the carbons C(2,3,4,5,6) are more or less coplanar, C(6)



and C(2) being bridged by the migrating hydrogen and the large substituent R at C(6) oriented equatorially [27c]. A closely related stereochemical preference has been reported for the thermal rearrangement of (*Z*)-1,3-hexadiene to give (*Z,E*)-2,4-hexadiene [31]. The activation parameters measured for **4** $\rightarrow$ **1c** (see *Table 1*) require dis-

9)



cussion. Our $E_a = 20.19$ kcal/mol is – to the best of our knowledge – the lowest activation energy ever measured for a [1,5]-hydrogen shift. This extremely low value¹⁰, as compared to the activation energies of other [1,5]-hydrogen shifts (see *e.g.* [27c]), must originate from either additional stabilization of the transition state or destabilization of the ground state molecule by the C(1)-C(2) double bond. The large negative entropy of activation is in good accord with the idea of a concerted reaction *via* the highly ordered transition state **iv**.

2.6. Discussion of the spectra. The four isomeric 1,3,5-undecatrienes display similar but not identical *UV.-spectra*, differing clearly from each other in their extinction values whereas the isomers **1d** and **1b** as well as **1c** and **1a** have identical absorption maxima (see *Table 2*). In the light of the empirical correlation between extinction and

Table 2. *UV. spectra of trienes 1a–d in either hexane or 95% ethanol*

Compound	Configuration	$\lambda_{\max}$ (ϵ) [nm]
1a	3 E, 5 E	255 (37'300), 264 (50'800), 274 (40'600)
1b	3 E, 5 Z	257.5 (31'800), 266 (41'900), 276 (33'200)
1c	3 Z, 5 E	254.5 (29'200), 263 (35'900), 273.5 (26'800)
1d	3 Z, 5 Z	258 (28'900), 266 (35'500), 275.5 (27'200)

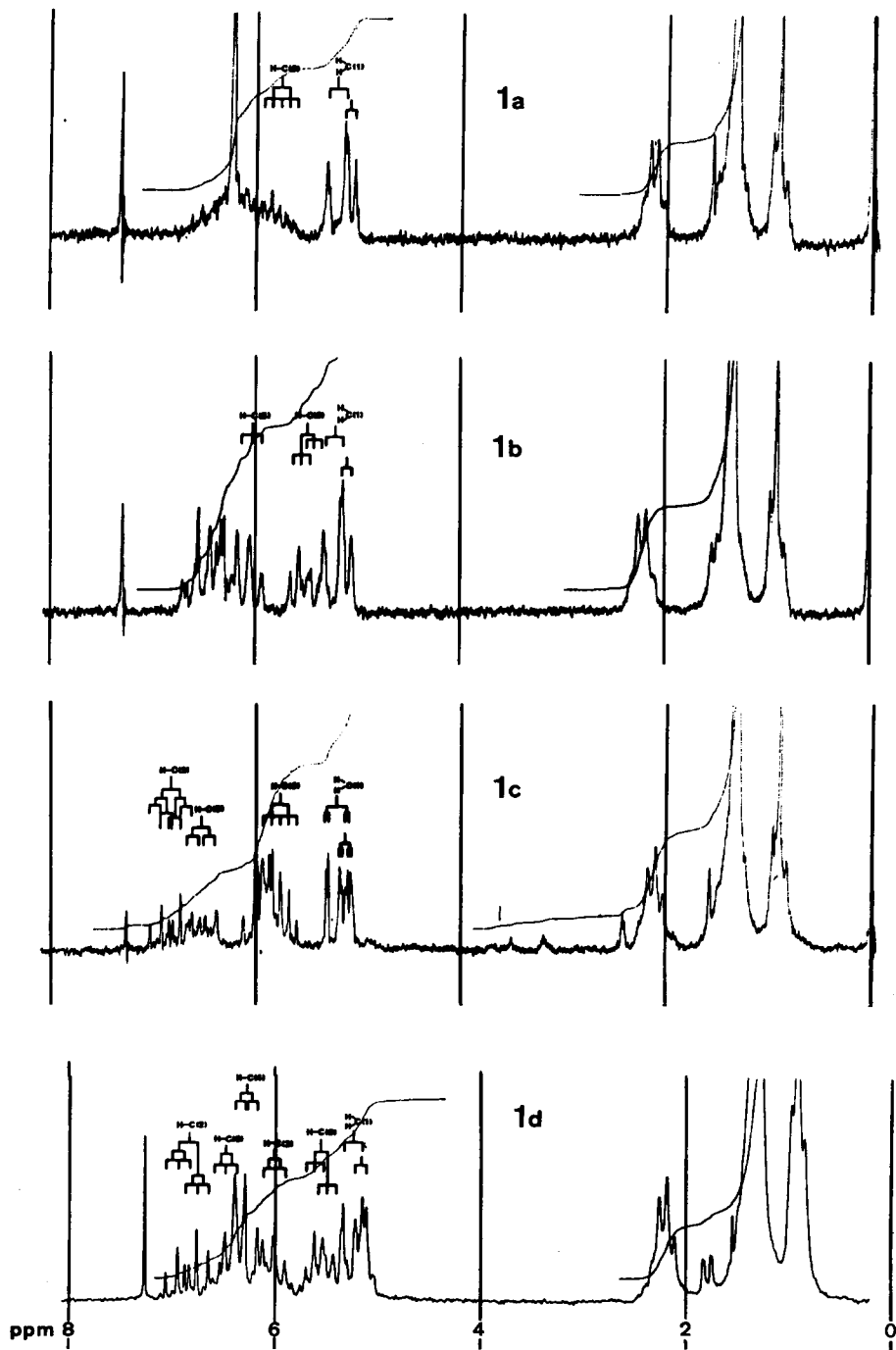
conformation of conjugated polyenes [32] the all-(*E*)-isomer **1a** should have the highest and the all-(*Z*)-isomer **1d** the lowest absorption. This is in accord with our measured values. On the other hand, the reported bathochromic shift of the absorption maxima of polyenes by a (*Z*)- in contrast to a (*E*)-double bond [32] is not fully in accord with our measurements: interestingly, only the (*Z*)-C(5)-C(6), and not the (*Z*)-C(3)-C(4) double bond, induced a bathochromic shift of $\sim 2\text{--}3$ nm!

The *mass spectra* of the trienes **1a–c** exhibit very similar fragmentation patterns with slight differences only in the peak intensities. No mass spectrum of the (*Z,Z*)-triene **1d** was obtained, as it is not stable at the inlet temperature of the mass spectrometer.

The *IR. and NMR.-spectra* however, show peaks or peak areas *typical of each isomer*. Since a detailed examination of the IR.-spectra in the present case is very complex and might not be conclusive enough for configurational assignment¹¹, our main effort was focused on ¹H-NMR. (see *Table 3*, and *Fig. 2*).

¹⁰) Somewhat higher values for similar [1,5]-hydrogen shifts to a sp-hybridized carbon have been reported by Skattebøl [28] and Schmid *et al.* [29], see *Table 1*.

¹¹) *Cf.* [2].

Fig. 2. $90\text{ MHz } ^1\text{H-NMR}$ spectra (in CDCl_3) of 1a-d

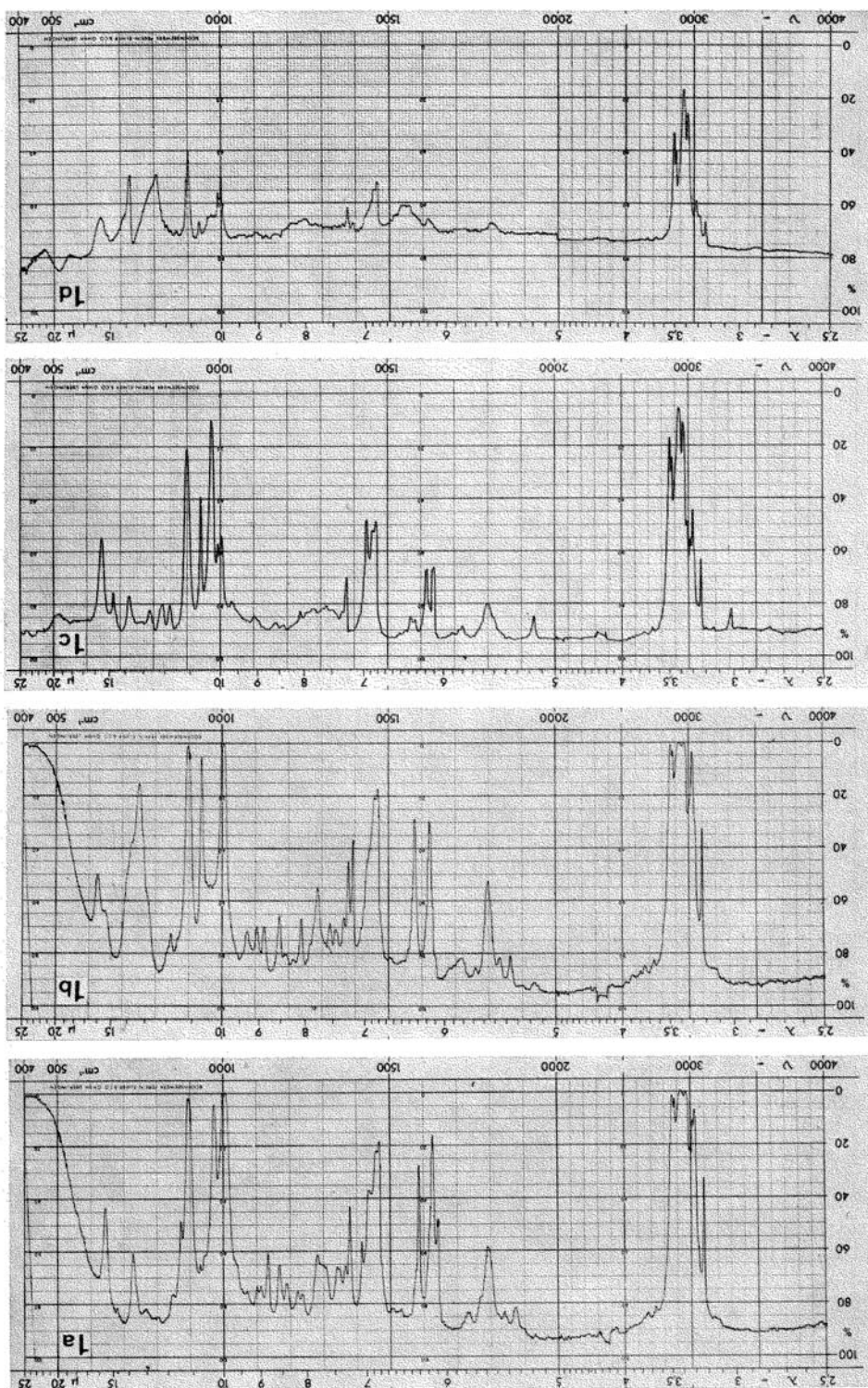
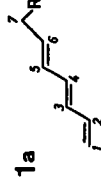
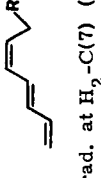
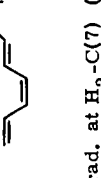
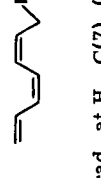
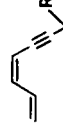
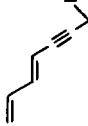
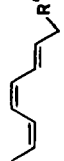


Fig. 3. IR. spectra of **1a-d** (**1a-c** neat, **1d** in CCl_4)

Table 3. 90 MHz $^1\text{H-NMR}$ spectra (in CDCl_3) of compounds 1a-d, 4, 5a-b, and 6. Chemical shift values δ (ppm), multiplicity, and coupling constants J (Hz) of the protons at C(1) to C(7)

Compound	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)
1a  Irrad. at $\text{H}_2\text{-C}(7)$ (~ 2.13)	5.08; d; $J = 9$ / 5.20; d; $J = 15$					5.74; d x t; $J = 14$; $J' = 7$ 5.74; d; $J = 14$	2.13; m 
1b  Irrad. at $\text{H}_2\text{-C}(7)$ (~ 2.22)	5.11; d x d; $J = 10$; $J' = 1.5$ / 5.24; d x d; $J = 15$; $J' = 1.5$				6.03; d x d x t; $J = 11$; $J' = 10$; $J'' = \sim 1.5$ 6.03; d x d; $J = 11$; $J' = 10$	5.51; d x t; $J = 11$; $J' = 7.5$ 5.51; d; $J = 11$	2.22; m 
1c  Irrad. at $\text{H}_2\text{-C}(7)$ (~ 2.13)	5.12; d x d; $J = 10$; $J' = 2$ / 5.22; d x d; $J = 17$; $J' = 2$	6.83; d x d x d; $J = 17$; $J' = 10$; $J'' = 10$			6.52; d x d x t; $J = 15$; $J' = 10$; $J'' = \sim 1.5$ 6.52; d x d; $J = 15$; $J' = 10$	5.76; d x t; $J = 15$; $J' = 7$ 5.76; d; $J = 15$	~ 2.13 ; m 
1d  Irrad. at $\text{H}_2\text{-C}(7)$ (~ 2.22)	5.17; d x d; $J = 10$; $J' = 2$ / 5.24; d x d; $J = 17$; $J' = 2$	6.85; d x d x d; $J = 17$; $J' = 10$; $J'' = 10$	6.0; d x d x f s; $J = 11$; $J' = 10$	6.27; d x d; $J = 11$; $J' = 10$	6.47; d x d x t; $J = 10$; $J' = 10$; $J'' = \sim 1$ 6.47; d x d; $J = 10$; $J' = 10$	5.53; d x t; $J = 10$; $J' = 7$ 5.53; d; $J = 10$	~ 2.22 ; m 

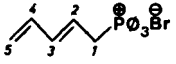
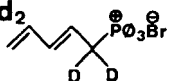
4  Irrad. at $H_2-C(7)$ (~2.16)	4.91; d x fs; J = 6.5 4.91; d x d; J = 6.5; J' = 2		6.1; d x t; J = 10; J' = 6.5	5.82; d x d x fs; J = 10; J' = 10 5.82; d x d; J = 10; J' = 10	5.41; d x t x fs; J = 10; J' = 8 5.41; d x fs; J = 10	2.16; m ~~~~~	
5a  Irrad. at $H_2-C(7)$ (~2.4)	5.25; d x d; J = 10; J' = -1.5/ 5.34; d x d; J = 17; J' = -1.5	6.9; d x d x d; J = 17; J' = 10; J'' = 10	6.3; d x d; J = 10; J' = 10	5.49; d x fs; J = 10 5.49; d x d; J = 10; J' = ~2		~2.4; m ~~~~~	
5b  Irrad. at $H_2-C(7)$ (~2.3)	5.12; d x d; J = 9; J' = ~2/ 5.27; d; J = 15			5.64; d x t; J = 15; J' = 2 5.64; d; J = 15		~2.3; m ~~~~~	
6  Irrad. at $H_2-C(8)$ (2.15) Irrad. at $H-C(1)$ (1.78)	1.78; d x fs; J = 7 ~~~~~	5.59; d x q; J = 10; J' = 7 5.59; d; J = 10	6.39; d x d; J = 10; J' = 10	6.18; d x d; J = 10; J' = 10	6.08; d x d; J = 10; J' = 10	6.52; d x d x t; J = 15; J' = 10; J'' = 1.5 6.52; d x d; J = 15; J' = 10	5.74; d x t; J = 15; J' = 7 5.74; d; J = 15

R = n-C₄H₉; R' = n-C₃H₇

+) See also [4d]

The large number of polyenes and enynes prepared during this work much facilitated the interpretation of each individual spectrum. Protons in typical surroundings showed characteristic splitting patterns, having identical coupling constants and nearly the same chemical shift values through the whole series. On these grounds and with the aid of double irradiation technique, the olefinic protons at C(5), and C(6) in **1a-d** could be observed directly, and the configuration of the C(5)–C(6) double bond was assigned by way of coupling constants. However, the protons at the central C(3)–C(4) double bond were observable only in the (*Z,Z*)-isomer **1d**: the C(3) proton ($d \times d \times fs$; $J = 10$ Hz; $J' = 10$ Hz) at 6.0 ppm (long range coupled with the terminal methylenes), and the C(4) proton ($d \times d$; $J = 11$ Hz; $J' = 10$ Hz) at 6.27 ppm (deshielded by the C(7)-methylidene protons). The missing information, concerning configurational assignment of the central C(3)–C(4) double bond, was easily obtained through the

Table 4. 90 MHz ^1H -NMR. spectra of the phosphonium salts **9**, **9-1-d₂** and **13** (all in CDCl_3) and of the ylid **9'** (in DMSO-d_6). Chemical shift values δ (ppm), multiplicity, and coupling constants J (Hz) of the protons at C(1) to C(n)

Compound	C(1)	C(2)	C(3)	C(5)
9  Irrad. at ^{31}P	4.58; $d \times d$; $J = 16$; $J' = 7$ 4.58; d ; $J = 7$	5.58; 12-line system 5.58; $d \times t$; $J = 15$; $J' = 7$		5.07; d with fine splitting; $J = 8$ / 5.1; d with fine splitting; $J = 17$
9-1-d₂  Irrad. at ^{31}P		5.56; $d \times d$; $J = 15$; $J' = 6$ 5.56; d ; $J = 15$		
9'  Irrad. at H-C(2) and H-C(4) (~6.1) Irrad. at ^{31}P	2.8; $d \times d$; $J = 21$; $J' = 12$ 2.8; d ; $J = 21$ 2.8; d ; $J = 12$		5.42; $d \times d$; $J = 14$; $J' = 11$ 5.42; $d \times d$; $J = 14$; $J' = 11$ 5.42; $d \times d$; $J = 14$; $J' = 11$	4.03; $d \times d$; $J = 10$; $J' = 2$ / 4.29; $d \times d$; $J = 17$; $J' = 2$ 4.03; d ; $J = 2$ / 4.29; d ; $J = 2$ 4.03; $d \times d$; $J = 10$; $J' = 2$ / 4.29; $d \times d$; $J = 17$; $J' = 2$
13  Irrad. at ^{31}P	4.63; $d \times d$; $J = 15$; $J' = 7$ 4.63; d ; $J = 7$	5.33; $dx dx t$; $J = 15$; $J' = 6$; $J'' = 7$ 5.33; $d \times t$; $J = 15$; $J' = 7$	5.96; $dx dx t$; $J = 15$; $J' = 6$; $J'' = 7$ 5.96; $d \times t$; $J = 15$; $J' = 7$	

R = $n\text{-C}_5\text{H}_{11}$

aforementioned reactions, *i.e.* stereoselective syntheses of **1a–d** from configurationally well defined products, or stereospecific transformations of **1d** and **1c** into well defined products.

The two dienyne **5a/b** exhibited relatively simple NMR.-spectra, all protons were observable (see *Table 3*) and the configurational assignment proved straightforward.

Also the allene **4** showed a simple NMR.-spectrum with the assignments given in *Table 3*.

The NMR.-spectrum of triene **6**, the thermal rearrangement product of **1d**, proved more complex. Only the protons at C(2), C(5), and C(6) were clearly recognizable, namely by successive irradiation at H–C(1) (the H–C(2) signal was reduced to a doublet; $J = 10$ Hz), and at H–C(8) (the H–C(7) signal was reduced to a doublet; $J = 14$ Hz; and the H–C(6) signal lost its fine structure, *i.e.* the H–C(8)/H–C(6) coupling). The three remaining olefinic protons, H–C(3), H–C(4), and H–C(5), each one a doublet of a doublet with two equal coupling constants (~ 10 Hz), were located *tentatively* as shown on *Table 3*.

The objective of the NMR.-analysis of phosphonium salts **9**, **9-1-d₂**, and **13**, and ylid **9'** (see *Table 4*) was the configurational assignment of the C(2)–C(3) double bond in the compounds **9** and **13**, all being precursors of the triene syntheses demonstrated in *Scheme 3*. Determination of the H–C(2)/H–C(3) coupling constants, which are $J = 15$ Hz in all cases, established the (*E*)-configuration of **9**, **9-1-d₂**, **13** and **9'**.

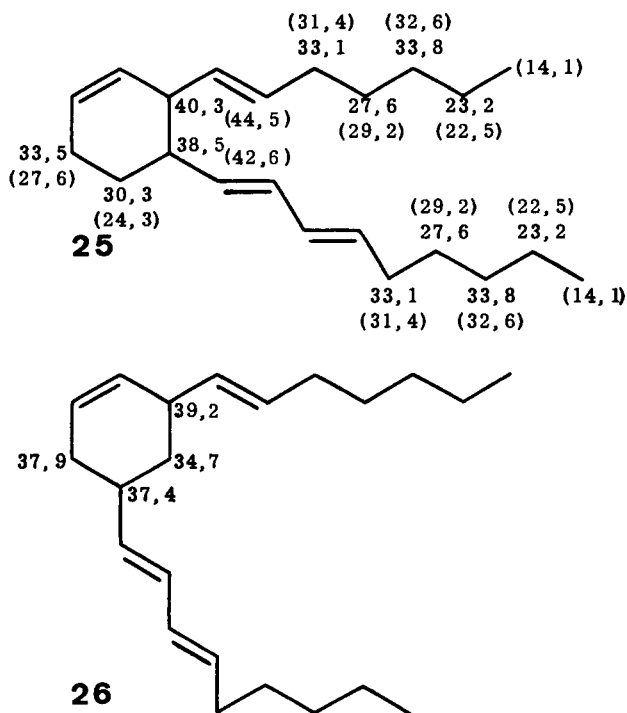


Fig. 4. Calculated ^{13}C chemical shift values for **25** and **26**. In brackets: experimental values favoring **25**

In all cases the signals of the protons at C(2) were analyzed, making use of spin-spin decoupling (irradiation of ^{31}P or ^1H) as outlined in Table 4.

Dimer **25** (see also [3]). – The 90 MHz ^1H -NMR. shows 8 olefinic protons (5.2–6.25 ppm), one doubly allylic methine proton as multiplet (at ~ 2.5 ppm), 7 allylic protons (1.8–2.2 ppm), 14 methylenes and 2 terminal methyl groups (~ 0.88 ppm). Terminal vinylic protons are absent. In the infra red the acyclic (*E,E*)-diene is seen at 982 cm^{-1} , and the cyclohexene double bond absorbs at 680 cm^{-1} . No (*Z*)-double bond is recognized (expected at $\sim 750\text{ cm}^{-1}$). The UV. shows a conjugated acyclic diene chromophor ($\lambda_{\text{max}} = 234\text{ nm}$; $\epsilon = 28900$). These data are in good agreement with structure **25**. Further support of structure **25** was obtained through ^{13}C -NMR.-spectroscopy. The experimentally observed chemical shift values compare better with the values calculated¹²⁾ for **25** than with those calculated for **26** (see Fig. 4).

Our thanks are due to Professor Paul Müller and Jean-Claude Perlberger, University of Geneva, for having calculated the activation parameters of the thermal rearrangements, and to Manfred Pawlak und Fred Wuffli for valuable gas chromatographic assistance.

After completion of the present manuscript a publication by Jaenike & Seferiadis [36] appeared dealing with the preparation of the four isomeric 1,3,5-octatrienes. Synthetic (*E,Z*)-1,3,5-octatriene has been shown to be identical with Fucoserratene, the female sex attractant isolated from the ova of the seaweed *Fucus serratus* L.

Experimental Part¹³⁾

(with the collaboration of Peter Degen and Therese Manz)

1) (*E,E*)-1,3,5-Undecatriene (**1a**) from (*E,E*)-2,4-decadienal (**3a**) [6] and methylenetriphenylphosphorane. Triphenylmethylphosphonium bromide (**2**) (1.07 g; 3 mmol), suspended in dry ether (10 ml), was treated with a 1,3*N* solution of butyllithium in hexane (2.3 ml; 3 mmol) at $15\text{--}20^\circ$. After the yellow reaction mixture obtained had been stirred for $3\frac{1}{2}$ h at room temperature all-(*E*)-decadienal **3a** [6] (304 mg; 2 mmol; 97% isomerically pure) in dry ether (10 ml) was added at room temperature. The solution was decolorised and a precipitate was formed. The reaction mixture was stirred overnight, then decomposed with water, and twice extracted with pentane. The pentane extract was washed (brine), dried (MgSO_4) and concentrated to give 0.37 g of crude product. Bulb distillation at $100\text{--}105^\circ/10\text{ mm}$ gave 232 mg (77%) of **1a** (96%)¹⁴⁾ isomerically pure by GC.).

Spectral data of **1a** (further purified by GC.): 90 MHz ^1H -NMR.: see Fig. 2 and Table 3. – IR.: see Fig. 2. – UV.: see Table 1. – MS.: 150 (M^+ , 25), 93 (25), 91 (24), 80 (60), 79 (100), 77 (39), 67 (10), 53 (3), 41 (19), 27 (10).

¹²⁾ Method of Grant & Paul [33].

¹³⁾ ^1H -NMR. spectra: Hitachi Perkin Elmer R-20 B in CCl_4 with TMS ($\delta = 0$ ppm) as internal standard; Bruker HX 90/15" in CDCl_3 with TMS ($\delta = 0,00$ ppm) as internal standard; abbreviations *s* = singlet, *d* = doublet, *t* = triplet, *q* = quartet, *m* = multiplet, *fs* = long range fine splitting, *J* = spin-spin coupling constant (Hz). ^{13}C -NMR. spectra were recorded on a Bruker HX 90/15" instrument, operating at 22.63 MHz in the FT mode. CDCl_3 was used as solvent with TMS ($\delta = 0$ ppm) as internal standard. IR. spectra: Perkin Elmer 125, max. in cm^{-1} . Mass spectra: Atlas CH_6 , inlet temp. $\sim 150^\circ$; electron energy $\sim 70\text{ eV}$; intensities of molecular ions (M^+) and fragment ions (highest peak(s) of each group) are given as *m/e* in % of the most abundant peak (base peak = 100%). UV. spectra: Unicam SP 700 A. Gas chromatography (GC.) on packed columns: Carlo Erba Fractovap GT or Perkin Elmer F 30. Gas chromatography on capillary columns: Carlo Erba Fractovap GI.

¹⁴⁾ 6% SP 1000 on Chromosorb G 80–100 mesh, 5 mm $\times$ 5 m, 150° , 40 ml He/min.

2) (E,Z)-1,3,5-Undecatriene (**1b**) from (E,Z)-2,4-decadienal (**3b**; 97% isomerically pure) [6a, b] and methylidenetriphenylphosphorane. Using the reaction conditions described in experiment 1) and after bulb distillation at 100–105°/10 mm, 243 mg (81%) of **1b** was obtained. Isomeric purity ~ 92%¹⁴).

Spectral data of **1b** (further purified by GC.): 90 MHz ¹H-NMR.: see Fig. 2 and Table 3. – IR.: see Fig. 7. – UV.: see Table 1. – MS.: 150 (M⁺, 41), 93 (42), 91 (44), 80 (93), 79 (100), 77 (59), 67 (22), 53 (7), 41 (33), 27 (18).

3) (Z,E)-1,3,5-Undecatriene (**1c**) from vinylallene **4**. Vinylallene **4** on a sealed tube, heated at ~ 85° for 5 h, was completely transformed into **1c**. Similarly, vinylallene **4** on passing through a gas chromatograph (Carlo Erba GT, injection at ~ 200°, column 5 mm × 2,5 m at 130°, detector at 200°) was transformed into **1c**.

Spectral data of **1c** (purified by GC.): 90 MHz ¹H-NMR.: see Fig. 2 and Table 3. – IR. see Fig. 3. – UV.: see Table 1. – MS.: 150 (M⁺, 19), 93 (16), 91 (19), 80 (42), 79 (100), 77 (31), 66 (10), 55 (3), 53 (3), 41 (19), 27 (12).

4) (Z,Z)-1,3,5-Undecatriene (**1d**). A mixture of dienyne **5a** (52 mg; 0.35 mmol), 1-propanol/water 1:1 (15 ml), zinc powder (5 g) and potassium cyanide (260 mg; 4 mmol) was stirred at ~ 20–25° for 22 h under protection of argon in the dark. The reaction product was filtered through celite, and the filtrate was extracted twice with pentane. The organic extract was washed (water), dried (MgSO₄), concentrated and chromatographed on silica gel 0.05–0.2 mm (1 g). Elution with pentane gave 39 mg of **1d**, ~ 95% pure by NMR.

As **1d** is thermally extremely unstable and undergoes a [1,7]-hydrogen shift to give **6** (see experiment 15) the temperature during the formation and purification of **1d** should not exceed 25°.

The reproducibility of this experiment proved poor, *i.e.* on some runs there was still same starting material left.

Spectral data of **1d**: 90 MHz ¹H-NMR.: see Fig. 2 and Table 3. – IR.: see Fig. 3. – UV.: see Table 1.

5) Mixture of **1a** and **1b** from (E)-2,4-pentadienal (**8**) [10] and hexylidenetriphenylphosphorane. *n*-Hexyltriphenylphosphonium bromide (**7**) [11] (2.35 g; 5.5 mmol), suspended in dry ether (19 ml), was treated with a 1.63*N* solution of butyllithium in hexane (3.36 ml; 5.5 mmol) at 25–28°. After the red reaction mixture had been stirred 1 h at room temperature pentadiene (**8**) (0.45 g; 5.5 mmol) in abs. ether (~ 7 ml) was added dropwise with stirring at ~ 10°. The reaction mixture was stirred 30 min at 20° and 30 min at reflux temperature, then cooled to room temperature and filtrated through celite. The filtrate was washed (water), dried (MgSO₄), concentrated and distilled in a bulb distillation apparatus at ~ 60°/0.01 Torr: 370 mg (45%) of an isomeric mixture, **1a/1b** ~ 1:1¹⁴).

6) Mixture of **1a** and **1b** from (E)-pentadienylidenetriphenylphosphorane and *n*-hexanal (**10**). (E)-Pentadienyltriphenylphosphonium bromide (**9**) (20.45 g; 50 mmol) was added portionwise to a stirred suspension of finely powdered potassium *t*-butoxide (6.74 g; 60 mmol) in dry dimethylformamide (DMF) (100 ml) at ~ 25°. The deeply red suspension was stirred an additional 3 h at 35–40° and then cooled to 15°. Freshly distilled *n*-hexanal (5 g; 50 mmol) in dry DMF was added at 14–20° with stirring and external cooling (ice). After this mixture had been heated to 35–42° for 1 h it was cooled to 20°, diluted with pentane (100 ml) and filtrated through celite. The filtrate was shaken with hexane and the layers were separated. After this procedure had been repeated three times, the hexane extracts, containing the trienes, were united, washed (aqueous sat. NH₄Cl solution), dried (MgSO₄), concentrated, stabilized by addition of ~ 100 mg 3-*t*-butyl-4-hydroxyanisole (BHA), and distilled at ~ 85°/10 mm: ~ 6.3 g (84%) of **1a** and **1b** (ratio ~ 1:1¹⁴). The same 1:1 mixture of **1a** and **1b** (~ 80%) was obtained if sodium methylsulfinylmethide in DMSO (*cf.* [34]) was used for this Wittig reaction.

7) Undecatrienes **1a** and **1c** from (E)-2-octenal (**12**) [14] and propenylidenetriphenylphosphorane [7]. 2-Propenyltriphenylphosphonium bromide (**11**) [7] (1.91 g; 5 mmol) suspended in dry ether (10 ml) was treated with 1.3*N* *n*-butyllithium (3.9 ml; 5 mmol) at 15–20°. After stirring had been continued for 3 h at room temperature *trans*-2-octenal (**12**) [14] (0.5 g; 4 mmol) in dry ether (10 ml) was added at 15–20°. Stirring was continued for 4 h at room temperature after which water (10 ml) was added. Extraction with pentane (twice), washing (brine), drying (MgSO₄), concentration and

bulb distillation at 110–115°/10 Torr gave 203 mg (34%) of a mixture of **1c** and **1a** (ratio 2:3 by NMR. and GC. analysis¹⁵).

8) *Mixture of undecatrienes 1a and 1c from (E)-2-octenylidenetriphenylphosphorane and acrolein (14).* (E)-2-Octenyltriphenylphosphonium bromide (**13**) (2.26 g; 5 mmol) suspended in dry ether (10 ml) was treated with 1.3N *n*-butyllithium (3.9 ml; 5 mmol) at 15–20°. After stirring had been continued for 3 h at room temperature freshly distilled acrolein (0.22 g; 4 mmol) in dry ether (10 ml) was added at 15–20°. Stirring was continued for 4 h at room temperature. After water (10 ml) had been added the mixture was extracted with pentane. The pentane extract was washed (brine), dried (MgSO₄), concentrated and bulb distilled at 110–115°/10 Torr to give ~138 mg (23%) of **1c** and **1a** (ratio 2:3 by NMR. and GC. analysis¹⁵).

9) *Mixture of 1d and 1b from (Z)-1,3-butadienyl bromide (15) [17] and lithium di-(Z)-1-heptenylcuprate (16) [15]; triene 6 by thermal rearrangement of 1d.* To a solution of lithium di-(Z)-1-heptenylcuprate (**16**) (44 mmol) in abs. ether (40 ml), prepared as described in [15], was added dropwise at –40° (Z)-1,3-butadienyl bromide (**15**) [17] (1.45 g; 11 mmol) in abs. ether (10 ml). Stirring was continued 5 h at –40 to –20°, 5 h at –10° and 5 h at room temperature. The reaction mixture was poured into an iced ammonium chloride solution, filtered through celite, extracted with ether, washed (successively with aqueous Na₂S₂O₃ and water), dried (MgSO₄) and concentrated. The crude product (~7 g) was chromatographed on silica gel 0.2–0.05 mm (100 g) with hexane as solvent. An oil (~4 g) was obtained which, after passage through a gas chromatograph (injector at 140°, detector at 140°, column: 5% Carbowax at 140°) showed three peaks. The three peaks were collected and analyzed by NMR.: peak 1 (~6% of the oil) being **1b**, peak 2 (~8% of the oil) being (Z,Z,E)-2,4,6-undecatriene (**6**), and peak 3 (~84% of the oil) being the known 6,8-tetradecadiene (**17**) (mixture of isomers) [15].

A second chromatography of the oil (~2 g) on silica gel < 0.08 mm (100 g) with hexane as solvent eluted the 6,8-tetradecadiene [15] in the first (~1 g) and in the second fraction (~270 mg). The third fraction (~20 mg) consisted according to gas chromatographic analysis of peaks 1 and 2 (ratio ~1:1) described above. However, NMR. analysis of this non-thermolyzed mixture showed the presence of **1a** and of **1d**; triene **6** being therefore formed from **1d** thermally in the gas chromatograph.

10) *Allene 4 from propargyl bromide (18) and lithium di-(Z)-1-octenylcuprate (19).* An ethereal solution of (Z)-1-octenyllithium, prepared at –10° from (Z)-1-octenyl bromide [6a] (9.5 g; 50 mmol) in abs. ether (40 ml) and granulated lithium containing 1.5% Na¹⁶ (1.4 g; 200 mmol), was added dropwise to a stirred suspension of dry, powdered Cu(I) (4.76 g; 25 mmol) in abs. ether (100 ml) at –10 to –20°. During this the colour changed from yellow to red and finally to dark brown. The resulting brown solution was allowed to stir for 30 min at –10°, and was then treated with propargyl bromide (**18**) (2.38 g; 20 mmol) in abs. ether (10 ml) at –30°. Stirring was continued for 2 h at –30° and then for 18 h at 25°. The reaction mixture was poured into an iced aqueous NH₄Cl solution and extracted with pentane. The pentane extract was washed (brine), dried (MgSO₄) and concentrated (temperature ≤ 25°) to give 4.2 g of crude product. Chromatography on silica gel 0.05–0.2 mm (50 g) with hexane gave 2.35 g of an oil which was distilled through a Vigreux column. Fraction one, b.p. 30–32°/0.05 Torr, contained 290 mg (10% yield) of pure allene **4**. Fraction two, b.p. 72–80°/0.05 Torr, contained 1.6 g (30% yield) of 7,9-hexadecadiene (**20**) (mixture of isomers).

Spectral data of 4: 90 MHz ¹H-NMR.: see Table 3. – IR. (neat): 3020, 1936, 1684, 842, 760 cm^{–1}.

Spectral data of 20: 60 MHz ¹H-NMR.: 0.9 (3 H, *t'*); 2.15 (4 H, *m*); 5.4 (2 H, *m*); 6.17 (2 H, *d* with fine splitting, *J* ~ 8 Hz). – MS.: 222 (*M*⁺, 20), 151 (2), 138 (8), 124 (8), 110 (32), 95 (40), 81 (56), 67 (100), 54 (35), 41 (48), 29 (25).

11) (Z)-1,3,5-Undecadienyne (**5a**) [2] and (E)-1,3,5-undecadienyne (**5b**) [2] from 4-bromo-1,5-undecenyne (**21**) [2]. 4-Bromo-1,5-undecenyne (**21**) (2.29 g; 10 mmol) in abs. dimethyl sulfoxide (DMSO) (6 ml) were added to a stirred solution of 1,5-diazabicyclo[5.4.0]undec-5-ene (DBU) (1.67 g; 11 mmol) in abs. DMSO (9 ml) at 50°. A slightly exothermic reaction took place. After the reaction mixture had been stirred an additional 30 min at 50–60° it was poured onto iced water,

¹⁵) Apiezon glass capillary column 0.31 mm × 50 m (*H. & G. Jaeggi*, Labor f. Gaschromatographie, CH-9043 Trogen); 120°, He pressure 0.55 atm.

¹⁶) Metallgesellschaft Frankfurt a.M., Germany.

extracted with pentane, washed (water), dried (MgSO_4), concentrated, and distilled at 87–89°/10 mm. 1.01 g (68%) of an isomeric mixture was obtained containing **5a** (40%)¹⁷ and **5b** (60%). The pure compounds were isolated by GC.

Spectral data of 5a: 90 MHz ^1H -NMR.: see Table 3. – IR. (neat): 3090, 3035, 2220, 2200, 1615, 995, 905, 780 cm^{-1} . – MS.: 148 (M^+ , 11), 133 (1), 119 (11), 105 (78), 91 (100), 79 (33), 65 (32), 51 (12), 41 (31), 27 (18).

Spectral data of 5b: 90 MHz ^1H -NMR.: see Table 3. – IR. (neat): 3090, 3035, 2210, 1622, 995, 940, 900 cm^{-1} . – MS.: 148 (M^+ , 34), 133 (5), 119 (12), 105 (41), 91 (100), 79 (32), 65 (31), 51 (13), 41 (29), 27 (16).

12a) (E)-2,4-Pentadienyltriphenylphosphonium bromide (**9**) from (E)-2,4-pentadienyl bromide (**22**) [22]. Bromide **22** (91.5 g; 0.62 mol) in toluene was mixed with a solution of triphenylphosphine (184 g; 0.703 mol) in toluene (240 ml). After ~ 5 min a solid started to crystallize, and the mixture was allowed to stand for 60 h at room temperature. The crystalline reaction product was filtered off, washed with toluene and dried *in vacuo* 8 h at 80°/12 Torr and 4 h at 80°/0.1 Torr: 250 g (98%) of crystals, m.p. 206–207°. For the 90 MHz ^1H -NMR. see Table 4.

b) (E)-2,4-Pentadienylphosphonium-1- d_2 bromide (**9-1- d_2**) from **9**¹⁸. A sample of **9** (100 mg) was dissolved in CDCl_3 (0.5 ml) in an NMR. tube and shaken with D_2O (0.05 ml) in the presence of a catalytic amount of K_2CO_3 (~0.5 mg) for ~5–10 min. NMR.-analysis showed the presence of pure dideuterated compound **9-1- d_2** . For the 90 MHz ^1H -NMR. see Table 4.

c) (E)-2,4-Pentadienylidenetriphenylphosphorane (**9'**) in $\text{DMSO}-d_6$ for NMR. measurements. Sodium hydride dispersion (50%) (192 mg; 4 mmol) was washed twice with anhydrous ether and then allowed to react with dimethylsulfoxide- d_6 (3.5 ml) at ~80° for 1 h. This reagent was cooled to room temperature and treated with phosphonium bromide **4** (1.64 g; 4 mmol). After stirring for $1\frac{1}{2}$ h at 23° the resulting deep red reaction mixture was centrifuged and then the red solution was analyzed by NMR. (see Table 4).

13) (E)-2-Octenyltriphenylphosphonium bromide (**13**). A solution of triphenylphosphine (19.6 g; 0.075 mol) in dry benzene (50 ml) was treated with *trans*-2-octenyl bromide (**23**) [23] (14.3 g; 0.075 mol) and then allowed to stand at room temperature overnight. The precipitate formed was filtered, washed with a little benzene and dried over P_2O_5 *in vacuo*: 24.8 g (73%) of **13**, m.p. 157–158°.

14) Kinetic measurements. – a) 5-Pentyl-1,3-cyclohexadiene (**24**) from (Z,E)-1,3,5-undecatriene (**1c**) by thermal cyclization. Six samples of **1c** (~15 mg) were sealed in glass tubes (20 × 2 mm) and placed in a vigorously stirred oil bath controlled to $\pm 0.1^\circ$. The temperature was continuously monitored with a Mettler TM 15 digital thermometer and recorded on a chart as a function of time. The sample tubes were withdrawn at regular intervals and quenched in liquid nitrogen. The samples were then analyzed by gas chromatography with a Carlo Erba Fractovap GT (column: 2.5 m × 5 mm, 20% Carbowax on Chromosorb W 60/80; temp. 40 ml He/min) which was connected to a Hewlett-Packard integrator 337 B for calculation of the peak areas. In order to be able to neglect the influence of the glass wall on the reaction an additional sample containing glass powder was heated at the highest temperature (148.7°) during 150 min. The reaction followed first order rate, and the data (calculated on a computer) are shown in Table 1.

b) Thermal rearrangement of **4** to give **1c**. Six samples, consisting of a mixture of allene **4** (15 mg) and methyl benzoate (internal standard, 10 mg), were sealed in glass tubes (20 × 2 mm) and placed in a vigorously stirred oil bath controlled to $\pm 0.1^\circ$. The temperature was continuously monitored with a Mettler TM 15 digital thermometer and recorded on a chart as a function of time. The sample tubes were withdrawn at regular intervals and quenched in an ice-water bath. The samples were then transferred into an NMR. tube and diluted with CDCl_3 to a total volume of ~0.1 ml. The NMR. spectra of the reaction mixture obtained (**1c**, **4** and methylbenzoate) were recorded on a Bruker HX 90 apparatus and integrated five times. The reaction followed first order rate, and the data (calculated on a computer) are shown in Table 1.

Spectral data of 24: 90 MHz ^1H -NMR.: 0.9 (3 H, '*t*'); 1.85–2.5 (3 H, *m*); 5.5–6.0 (4 H, *m* with sharp peak at 5.85). – UV. (hexane): λ_{max} = 260 nm (ϵ = 32500). – MS.: 150 (M^+ , 15), 91 (7), 79 (100), 41 (8), 27 (7).

¹⁷) Analyzed by GC.: 20% Carbowax on Chromosorb W AW 50–80 mesh, 150°, 40 ml He/min.

¹⁸) For leading references on deuterium labelling see [35].

15) (Z, Z, E)-2,4,6-Undecatriene (**6**) from dienyne **5a** via the not-isolated triene **1d**. A mixture of dienyne **5a** (100 mg; 0.68 mmol), 1-propanol/water 1:1 (25 ml), and zinc powder (10 g) was heated at reflux for 6 h. The cold reaction mixture was filtered through celite and extracted with pentane. The pentane extract was washed (water), dried (MgSO_4), concentrated and bulb distilled at 110–120°/Torr to give ~80 mg (80%) of pure **6**.

Spectral data of 6: 90 MHz ^1H -NMR.: see Table 3. – IR. (neat): 3035, 1635, 980, 960, 938, 710 cm^{-1} . – UV. (95% ethanol): λ_{max} = 259 (ϵ = 29600), 269 (ϵ = 36400), 278 (ϵ = 28200) nm. – MS.: 150 (M^+ , 44), 132 (3), 121 (7), 107 (39), 93 (73), 91 (46), 79 (100), 67 (16), 55 (16), 41 (33), 29 (23).

16) *Thermal behaviour of 1a*. Triene **1a** (2.1 g; 14 mmol) was heated in a sealed tube at 150° for 10 h. Distillation of the reaction product at 125–127°/0.01 Torr gave 1.62 g of product containing one major peak (~85%) by GC.¹⁹ The analytical sample was specially purified by GC. Under the same conditions a mixture of **1a** and **1b** (ratio ~1:1) led to a complex mixture of isomeric products with the molecular weight 300.

Spectral data of 25: 90 MHz ^1H -NMR.: 0.88 (6 H, 't'); ~1.35 (14 H, m); 1.80–2.2 (7 H, m); 2.5 (1 H, m); 5.2–6.25 (8 H, olefinic m's) ppm. – IR. (neat): 3020, 1645, 982, 680 cm^{-1} . – UV. (95% EtOH): λ_{max} = 234 nm (ϵ = 28900). – MS.: 300 (M^+ , 6), 271 (<1), 257 (<1), 243 (<1), 229 (1), 215 (<1), 203 (<1), 189 (1), 176 (4), 164 (<1), 150 (100), 131 (6), 117 (8), 105 (9), 93 (32), 91 (34), 80 (84), 79 (92), 67 (24), 55 (19), 43 (28), 41 (41), 29 (25).

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¹⁹) 4% SOMB on Chromosorb G AW DMCS 80–100 mesh, programme: 100–260° 3°/min, 60 ml He/min.

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111. Biosynthesis of Juvenile Hormone in the *Cecropia* Moth. Labelling Pattern from 1-[¹⁴C]-Propionate through Degradation to Single Carbon Atom Derivatives*

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(13. II. 75)

Summary. In the adult male *cecropia* moth, 1-[¹⁴C]-propionate is incorporated specifically into juvenile hormone I (1). By chemical degradation it was found that only C(7) and C(11) are labelled, each carbon atom bearing 50% of the radioactivity originally present in *JH-I*. It is concluded that propionate serves as a precursor of homomevalonate, which in turn is a precursor for *JH-I*. Application of 2-[¹⁴C]-propionate and 3-[¹⁴C]-propionate leads to extensive randomization of the label. Apparently propionate is metabolized such that C(2) and C(3) can be reused as smaller fragments—probably acetate—while C(1) is either highly diluted or removed from the propionate in a metabolically inactive form.

The insect juvenile hormones I and II (*JH-I*, 1; *JH-II*, 2) are the only known terpenoid compounds where methyl groups biosynthetically derived from C(3') of mevalonate are formally replaced by ethyl groups. They were discovered in adult males of the saturniid moth *Hyalophora cecropia* [1] [2] and were also isolated from the related species *Hyalophora gloveri* [3] and *Samia cynthia* [4]. Juvenile hormone is produced by *corpora allata*, a pair of glands associated with the insect brain. It was

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