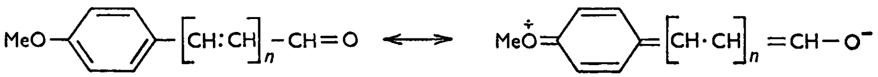
787. *Researches on Polyenes. Part IV.* The* ω-p-*Methoxyphenyl-polyene Aldehydes and their Absorption Spectra.*†

By D. Marshall and M. C. Whiting.

A series of ω-*p*-methoxyphenyl-polyene aldehydes (I; $n = 1$—7) has been prepared by use of a chain-extension method whereby two ethylenic bonds are added without isolation of intermediates. The electronic absorption spectra of the aldehydes are recorded and discussed.

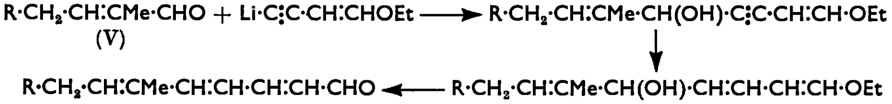
For a projected synthesis of the fungal pigment cortisalin [1] the ω-*p*-methoxyphenyl-polyene aldehydes (I; $n = 2$, 4, and 6) were required as intermediates. Together with homologues with odd values of n these constitute an interesting series for the investigation of relationships between electronic absorption spectra and chain-length in conjugated systems, in that they are intermediate between symmetrical, unpolarised polyenes, such as (II),[2] and highly polarised merocyanines,[3] such as (III). The latter approximate in spectroscopic behaviour to the cyanines, *e.g.*, (IV),[3] and series (II) and (IV) have been employed antithetically in several theoretical discussions.[2,4]



(I)

$Ph{\cdot}[CH{:}CH]_n{\cdot}Ph$ (II) $Me_2N{\cdot}[CH{:}CH]_n{\cdot}CHO$ (III) $Me_2N{\cdot}[CH{:}CH]_n{\cdot}CH{:}\overset{+}{N}Me_2\ X^-$ (IV)

A stepwise chain-extension method was obviously the best solution to the synthetical problem. Inhoffen, Bohlmann, and Rummert's method,[5] in which two double bonds were added to the polyene chain of aldehyde (V) in (effectively) a two-stage process in 50% yield, seemed promising; one of us had investigated this reaction with acetone in 1948, the bromomagnesium derivative, rather than the lithium compound, of ethoxybutenyne being employed successfully. Methoxybutenyne, now commercially available, was condensed with *p*-methoxybenzaldehyde, and after addition of ethanol (with the aim of decomposing the complex; the effect was apparently favourable, although this may not



(R = 2:6:6-trimethyl*cyclo*hexenyl)

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* Part III, *J.*, 1955, 3037.

† Submitted in honour of the seventieth birthday of Sir Ian Heilbron, D.S.O., F.R.S.

[1] Marshall and Whiting, *Chem. and Ind.*, 1954, 1451.

[2] Lewis and Calvin, *Chem. Rev.*, 1939, **25**, 237.

[3] Brooker, Keyes, Sprague, Van Dyke, Van Lare, Van Zandt, and White, *J. Amer. Chem. Soc.*, 1951, **73**, 5326 *et seq.*

[4] Bayliss, *Quart. Rev.*, 1952, **6**, 319, and references there cited.

[5] Inhoffen, Bohlmann, and Rummert, *Annalen*, 1950, **569**, 226.

have been the true reason) lithium aluminium hydride was added.[6] Decomposition of the excess of hydride and addition of mineral acid gave the diene-aldehyde (I; $n = 2$) in a single stage. Under optimal conditions, with tetrahydrofuran as solvent, the yield was 52%. This aldehyde has been described [7] as a yellow oil; as now obtained, it crystallised at once and melted at 80°. From infrared data it was clearly the *trans-trans*-isomer.

$$\begin{tikzcd}
\mathrm{MeO{\cdot}C_6H_4{\cdot}CHO + BrMg{\cdot}C{\vdots}C{\cdot}CH{:}CH{\cdot}OMe} \arrow[r] & \mathrm{[MeO{\cdot}C_6H_4{\cdot}CH(OMgBr){\cdot}C{\vdots}C{\cdot}CH{:}CH{\cdot}OMe]} \arrow[d] \\
\mathrm{MeO{\cdot}C_6H_4{\cdot}[CH{:}CH]_2{\cdot}CHO + MeOH} \arrow[r] & \mathrm{[MeO{\cdot}C_6H_4{\cdot}CH(OH){\cdot}CH{:}CH{\cdot}CH{:}CH{\cdot}OMe]}
\end{tikzcd}$$

This method is probably general and is the quickest yet described for the conversion, $\mathrm{R{\cdot}CHO} \longrightarrow \mathrm{R{\cdot}[CH{:}CH]_2{\cdot}CHO}$. Applied to benzaldehyde, for example, it gave a 75% yield of 5-phenylpenta-2 : 4-dienal, which at once crystallised, though most earlier workers [8] describe this compound as a liquid. Octa-2 : 4 : 6-trienal was similarly converted into dodeca-2 : 4 : 6 : 8 : 10-pentaenal in 27% yield. In series (I), *p*-methoxycinnamaldehyde gave (I; $n = 3$) in 46% yield, while the dienal itself gave the corresponding tetraenal in 26% yield. Beyond this point the yield fell sharply, despite variations in reaction conditions; for the aldehydes ($n = 5$ and 6), respectively, to 2% and 0·05%, the extreme insolubility of the latter alone making isolation possible. In these cases, however, the intermediate acetylenic alcohols (VI) were readily isolated in good yield and purified.

$$\begin{tikzcd}
\mathrm{MeO{\cdot}C_6H_4{\cdot}[CH{:}CH]_n{\cdot}CHO} \arrow[r] & \mathrm{MeO{\cdot}C_6H_4{\cdot}[CH{:}CH]_n{\cdot}CH(OH){\cdot}C{\vdots}C{\cdot}CH{:}CH{\cdot}OMe} \quad \text{(VI)} \arrow[d] \\
 & \mathrm{MeO{\cdot}C_6H_4{\cdot}[CH{:}CH]_{n+2}{\cdot}CHO}
\end{tikzcd}$$

Hydrogenation with a partially poisoned palladium catalyst,[9] and treatment with aqueous oxalic acid gave the homologous aldehydes (I; $n = 5$ and 6) in 51 and 34% yield, respectively. Rather less satisfactory results were obtained when mineral acids were employed in the final stage, probably because these react with the acetylenic alcohols (VI), a little of which remained.

Condensation of the pentaenal with methoxybutenyne was difficult because of the insolubility of the aldehyde in the reaction mixture, and the product, though having the expected ultraviolet absorption spectrum, was itself very sparingly soluble. After hydrogenation and acid treatment, the heptaenal was obtained in 13% yield from the pentaenal. Clearly further extension of the polyene chain would require modification of the method. The aldehydes (I; $n = 5$ and 6) obtained by the two variants were identical, all showing intense absorption near 1000 cm.$^{-1}$ and very little at 650—850 cm.$^{-1}$; they were thus all-*trans*-compounds,[10] despite the fact that in the preparation of the higher members of the series *cis*-ethylenic linkages must have been present in their immediate precursors. This agrees with earlier work.[11]

The rapid decline in the yield given by the chemical reduction method, as the value of n in the starting material increases from 2 through 3 to 4, requires comment. When the alcohol (VI; $n = 4$) was isolated, and then treated with lithium aluminium hydride in a separate experiment, again only a minute yield of the aldehyde (I; $n = 6$) was formed. Perhaps the most reasonable explanation is that the intermediate complex (VII) can transfer a hydride ion either (*A*) to the adjacent acetylenic carbon atom, or (*B*) to the first carbon atom of the polyene chain. The longer the chain, the more will the carbanion formed by route (*B*) be stabilised relative to that formed by process (*A*). The fact that octa-2 : 4 : 6-trienal gives dodeca-2 : 4 : 6 : 8 : 10-pentaenal in 27% yield, as against the 2% yield when the methyl group is replaced by *p*-methoxyphenyl, is also explained by the potential electron-sink character of the aromatic system.

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[6] Cf. Chanley and Sobotka, *J. Amer. Chem. Soc.*, 1949, **71**, 4140; Bates, Jones, and Whiting, *J.*, 1954, 1854.

[7] Vorländer and Gieseler, *J. prakt. Chem.*, 1929, **121**, 237.

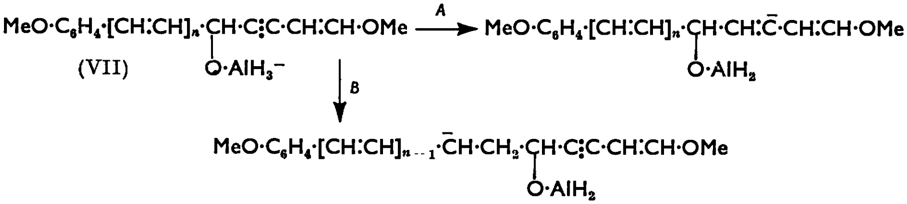
[8] Kethur, Klein, and Wietbrock, *Ber.*, 1936, **69**, 2078; cf. Kuhn and Wintersteiner, *Helv. Chim. Acta*, 1929, **12**, 493.

[9] Lindlar, *Helv. Chim. Acta*, 1952, **35**, 446.

[10] Allan, Meakins, and Whiting, *J.*, 1955, 1874.

[11] Braude and Coles, *J.*, 1951, 2085.

The *p*-methoxyphenyl-polyene aldehydes are all highly crystalline, relatively insoluble, and stable to oxygen, in the solid state at least, at moderate temperatures. Reduction of the aldehyde (I; $n = 2$) to the primary alcohol gave a compound which rapidly suffered



$$\mathrm{MeO{\cdot}C_6H_4{\cdot}[CH{:}CH]_n{\cdot}\underset{O{\cdot}AlH_3^-}{\underset{|}{CH}}{\cdot}C{\vdots}C{\cdot}CH{:}CH{\cdot}OMe} \xrightarrow{A} \mathrm{MeO{\cdot}C_6H_4{\cdot}[CH{:}CH]_n{\cdot}\underset{O{\cdot}AlH_2}{\underset{|}{CH}}{\cdot}CH{:}\bar{C}{\cdot}CH{:}CH{\cdot}OMe}$$

(VII)

$$\Big\downarrow B$$

$$\mathrm{MeO{\cdot}C_6H_4{\cdot}[CH{:}CH]_{n-1}{\cdot}\bar{C}H{\cdot}CH_2{\cdot}\underset{O{\cdot}AlH_2}{\underset{|}{CH}}{\cdot}C{\vdots}C{\cdot}CH{:}CH{\cdot}OMe}$$

atmospheric oxidation. Even the methyl esters corresponding to series (I) were somewhat less stable; clearly the mesomeric effect illustrated plays a considerable part in this stabilisation, although crystal lattice forces are doubtless important too. The solubilities of the aldehydes (I; $n = 5$, 6, and 7) in chloroform at 25° were determined spectroscopically, values of 3·5, 0·4, and 0·05 g./l. being obtained, solubility thus decreasing by a factor of 8 for each additional $\cdot CH{:}CH\cdot$ group in the chain. Extrapolation suggests that absorption spectra could still be determined for (I; $n = 8$ and 9), but hardly for the decaenal, and not at all for higher homologues.

The ultraviolet absorption spectra of the aldehydes (I) are tabulated below and illustrated in Fig. 1, chloroform being used as solvent. Unlike the simple polyenes, the mono- or di-phenylpolyenes, or even compounds containing the *p*-methoxyphenyl-polyene system, *e.g.*, the alcohols (VI), the *p*-methoxyphenyl-polyene aldehydes show broad, rounded absorption maxima without discernible vibrational fine-structure. In this they resemble merocyanines and cyanines[3,4] (*e.g.*, III and IV). However, as Fig. 2 indicates, $\lambda_{max.}$ is approximately proportional to $n^{\frac{1}{2}}$; in this, series (I) has affinities with the simple polyenes, rather than with the cyanines or merocyanines.[2] Although the flatness of the maxima makes precise location impossible, it appears that series (I) deviates slightly from the Lewis–Calvin relationship for polyenes[2] at large values of n, as the simple polyenes probably do also.* The coefficient k, in the equation $\lambda^2 = kn$, is about 1·9, as compared with values of 2·0 and 2·3 for diphenyl-[16] and dimethyl-polyenes,[12] respectively.

TABLE. *Light-absorption maxima in chloroform.*

n	$\lambda_{max.}$ (Å)	$10^3\varepsilon$	$\lambda_{max.}$ (Å)	$10^3\varepsilon$	$\lambda_{max.}$ (Å)	$10^3\varepsilon$	$\lambda_{max.}$ (Å)	$10^3\varepsilon$
				Aldehydes (I)				
1	3220	30·5						
2	3520	42·0	2490	10·8				
3	3820	52·0	2720	8·0				
4	4030	61·5	2920	10·6				
5	4250	68·7	3120	9·8	2580	10·3		
6	4400	78·0	3310	9·3	2830	10·4	2590	11·1
7	4570	90·2	3510	9·9	3040	11·6	2750	12·3
				Alcohols (VI)				
3 †	3410 *	46	3290	57	3170 *	47		
4	3710 *	53	3570	68·5	3420 *	54		
5	4020	87	3810	104	3640	71·5		

* Inflexion. † In ethanol.

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* The data published for the higher dimethylpolyenes ($n > 7$) in Part III,[12] however, overstate this deviation; Bohlmann and Mannhardt[13] have recently prepared the pure all-*trans*-isomers of $CH_3{\cdot}[CH{=}CH]_n{\cdot}CH_3$, where $n = 8$, 9, and 10, and observed absorption at appreciably longer wavelengths. Our spectra, and that for $CH_3{\cdot}[CH{=}CH]_9{\cdot}CH_3$ published by Bohlmann,[14] must be attributed to mixtures of *cis*-isomers, the all-*trans*-forms having been eliminated by their insolubility. Similar considerations probably apply to the spectra recorded by R. Kuhn[15] for the hydrocarbons $Ph{\cdot}[CH{=}CH]_n{\cdot}Ph$, where $n = 11$ and 15.

[12] Nayler and Whiting, *J.*, 1955, 3037.

[13] Bohlmann and Mannhardt, *Chem. Ber.*, 1956, **89**, 1307.

[14] Bohlmann, *Chem. Ber.*, 1952, **85**, 386.

[15] R. Kuhn, *Angew. Chem.*, 1937, **50**, 703.

[16] Hausser, R. Kuhn, and Smakula, *Z. phys. Chem.*, 1935, **29**, 384.

Oscillator strength values for the aldehydes (I) were calculated, by using the equation[17]

$$f = 4{\cdot}31 \times 10^{-9}\int \varepsilon d\bar{\nu}$$

with integration between the extrapolated point of zero absorption on the long wavelength side, and the longest-wavelength minimum of the plot of ε against $\bar{\nu}$. [This is a somewhat arbitrary procedure, but it should be consistent within series (I); in the case of (I; $n = 7$) inclusion of the region between 40,000 and 28,300 cm.$^{-1}$ would increase the value of f by about 0·5.] Fig. 3 illustrates the results; it is clear that a linear relation between n and f exists. The only previous attempt to show such a relation, the work of Hausser, Kuhn, and Smakula[16] on the diphenylpolyenes, was much less successful because of the experimental scatter of the points. A linear relationship for f values is required by Braude's " chromophore areas " theory,[18] which in its simplest form further requires that the

Fig. 1.

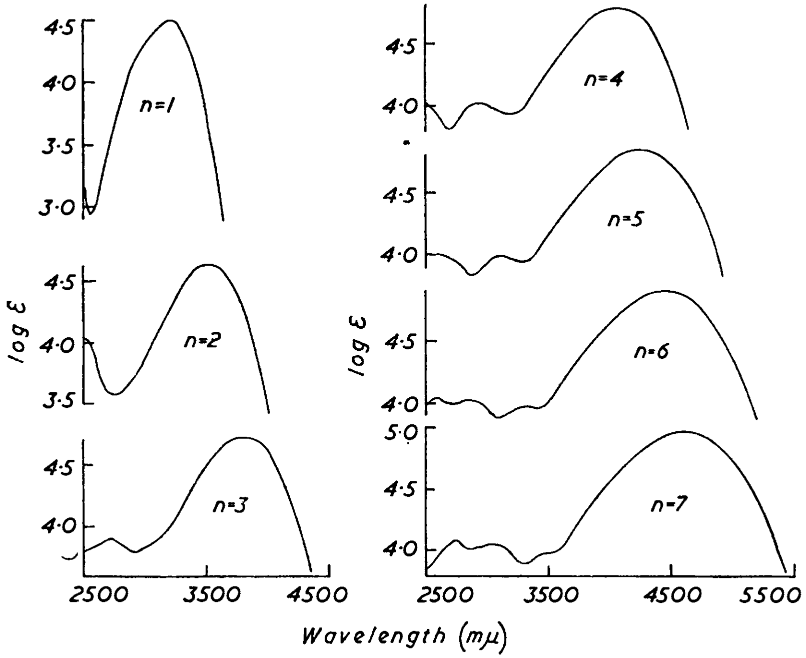


Fig. 2.

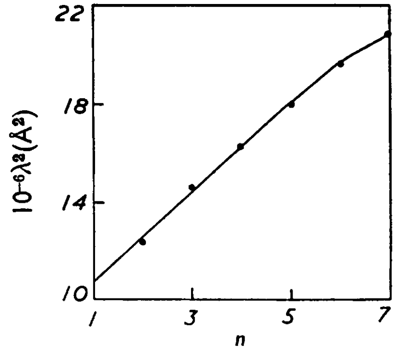
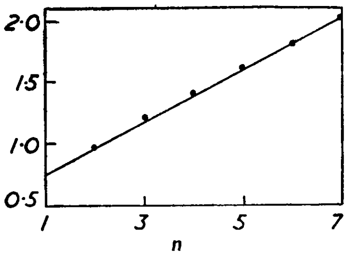


Fig. 3.



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[17] Maccoll, *Quart. Rev.*, 1947, **1**, 16.
[18] Braude, *J.*, 1950, 379.

increment per ·CH:CH· grouping should not vary between one series and another. In Part III,[12] however, the dimethylpolyenes were shown to have oscillator strengths which increased from the triene to the hexaene according to a roughly linear law, but with an increment per ·CH:CH· grouping of approximately 0·5, as against about 0·21 (increased to *ca.* 0·27 when absorption down to 40,000 cm.$^{-1}$ is included) in the present series (I). The early value [16] for the diphenylpolyenes is of the order of 0·22. Evaluation of these results must clearly await more information.

EXPERIMENTAL

Melting points denoted m. p.(K) were determined on the Kofler block; those denoted m. p.(cap.) in an evacuated capilliary tube. Infrared and ultraviolet absorption spectra were determined with Perkin–Elmer model 21 and Unicam SP500 spectrophotometers, respectively.

6-*Ethoxy*-2-*methylhex*-5-*en*-3-*yn*-2-*ol*.—A solution of ethylmagnesium bromide was prepared in ether (80 c.c.) from magnesium (2·7 g.). 1-Ethoxybut-1-en-3-yne [20] (10 g.) was added slowly, and the mixture was stirred until the evolution of ethane ceased (1 hr.), then cooled to 0° while acetone (5·8 g.) in ether (5 c.c.) was added slowly. After 1·5 hr., cold, saturated ammonium chloride solution was added. After being washed with sodium hydrogen carbonate solution, the ether was dried and evaporated. Distillation gave the *alcohol* (9·2 g.), b. p. 80°/0·5 mm., n_D^{19} 1·4926—1·4948 (Found: C, 70·15; H, 9·2. $C_9H_{14}O_2$ requires C, 70·1; H, 9·15%). Light absorption in ethanol: maximum, 2390 Å; $\varepsilon = 16,000$.

3-p-*Methoxyphenylprop*-2-*en*-1-*ol*.—Methyl *p*-methoxycinnamate (4·0 g.) and lithium aluminium hydride (0·6 g.) were heated under reflux in ether for 1 hr. Addition of water and then aqueous tartaric acid, and isolation of the neutral fraction gave the alcohol (3·4 g.), m. p.(K) 76—79° (Karrer [19] gives m. p. 79—80°).

p-*Methoxycinnamaldehyde*.—The above alcohol (1·0 g.) and active manganese dioxide (8·2 g.) were shaken in tetrachloroethylene (100 c.c.) for 2 hr. Filtration, evaporation of the solvent, and crystallisation from light petroleum gave the aldehyde (0·9 g.) as plates, m. p.(K) 59—60° (Vorländer and Gieseler [7] give m. p. 58°).

5-p-*Methoxyphenylpenta*-2 : 4-*dienal*.—1-Methoxybut-1-en-3-yne (14·6 g.) in tetrahydrofuran (20 c.c.) was added dropwise to a stirred solution of ethylmagnesium bromide, prepared from magnesium (3·2 g.) in tetrahydrofuran (90 c.c.), the mixture being maintained at *ca.* 40°. After the mixture had been stirred for a further hour at 20°, a solution of *p*-methoxybenzaldehyde (18·1 g.) in tetrahydrofuran (20 c.c.) was added dropwise, with external ice cooling, during 20 min. After being stirred for a further 2 hr. at 20° the mixture was again cooled to 0° and treated with ethanol (5 c.c.), then after 20 min. with lithium aluminium hydride (4·0 g.), added during 45 min. in small portions. The mixture was stirred at 20° for 3 hr., once more cooled in ice, and treated successively with ethyl acetate (6 c.c.; added gradually), water (30 c.c.), sulphuric acid (4N; 150 c.c.), and ether (200 c.c.). Isolation of the neutral fraction and crystallisation from light petroleum gave the *aldehyde* (13·1 g., 52%), as cream needles, m. p.(K) 76—78°, raised to 79—80° on recrystallisation (Found: C, 76·5; H, 6·65. $C_{12}H_{12}O_2$ requires C, 76·55; H, 6·45%). (Vorländer and Gieseler [7] describe this substance as a yellow oil.)

Analogous reactions were carried out in ether (*A*) and ether–benzene (*B*), and other reactants varied as indicated below:

Solv.	$LiAlH_4$ (mol.)	Alcohol	Yield (%)	Solv.	$LiAlH_4$ (mol.)	Alcohol	Yield (%)
A	1·0	None	25	*A*	1·0	Ethanol (1 mol.)	27
A	1·5	None	18	*A*	1·0	β-Naphthol (1 mol.)	20
B	1·0	None	17	*A*	1·0 *	Ethanol (1 mol.)	15
B	0·5	None	3				

* Refluxed for 1 hr.

5-*Phenylpenta*-2 : 4-*dienal*.—The method described above being used, benzaldehyde (26·5 g.) in tetrahydrofuran (40 c.c.) was added to a solution of the Grignard reagent prepared from magnesium (7·5 g.) and methoxybutenyne (27·3 g.) in tetrahydrofuran (175 c.c.). After 1·5 hr. at 20°, ethanol (11·5 c.c.) and lithium aluminium hydride (9·5 g.) were added at 0°, and the mixture was stirred for 18 hr. at 20°. Distillation of the neutral fraction gave a liquid (32 g.),

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[19] Karrer, *Helv. Chim. Acta*, 1928, **11**, 1209.
[20] Johnson, *J.*, 1946, 1009.

b. p. 102—104°, which solidified. Crystallisation gave the *aldehyde* (30 g.) as thick needles, m. p. (K) 42—43°. (Kethur, Klein, and Wietbrock [8] give m. p. 38—39°.)

Dodeca-2 : 4 : 6 : 8 : 10-*pentaenal* [with P. NAYLER].—A solution of the Grignard reagent from magnesium (6·6 g.), ethyl bromide, and methoxybutenyne (20 g.) was prepared in tetrahydrofuran (170 c.c.). A solution of octa-2 : 4 : 6-trienal (30 g.) in tetrahydrofuran (150 c.c.) was added slowly, without cooling; after 1·5 hr. at 20°, alcohol (13·5 c.c.) and solid lithium aluminium hydride (9·3 g.) were added successively, with stirring. After 1 hr. water was added, followed by saturated aqueous tartaric acid, and the neutral fraction was isolated with ether. Evaporation of solvent and treatment of the residue with cold ether left 8·6 g. of crude aldehyde undissolved, yielding the aldehyde (8 g.), m. p. (K) 160—163°, on crystallisation from methanol; this had $\lambda_{max.}$ 3850 Å in chloroform (Schmitt and Obermeit [21] give m. p. 165°). A further 5 g. (m. p. 161—164°) was obtained by treatment of the ether-soluble fraction with 80% methanol.

7-p-*Methoxyphenylhepta*-2 : 4 : 6-*trienal*.—By the same general method, *p*-methoxycinnamaldehyde (12·6 g.) in tetrahydrofuran (30 c.c.) was treated with the Grignard reagent from magnesium (2·55 g.) and methoxybutenyne (10·8 g.) in tetrahydrofuran, then with lithium aluminium hydride overnight at 20°. Decomposition of the complex and addition of ether precipitated part of the product (4·5 g.), and crystallisation of the neutral fraction yielded a further 3·1 of the *aldehyde*, which separated from benzene–light petroleum as lemon-yellow needles, m. p.(K) 134·5—135·5° (Found : C, 78·4; H, 6·7. $C_{14}H_{14}O_2$ requires C, 78·5; H, 6·6%).

9-p-*Methoxyphenylnona*-2 : 4 : 6 : 8-*tetraenal*.—5-*p*-Methoxyphenylpenta-2 : 4-dienal (22·8 g.) in tetrahydrofuran (50 c.c.) was similarly condensed with the Grignard reagent from magnesium (3·84 g.) and methoxybutenyne (16·4 g.). Addition of ethanol and lithium aluminium hydride, decomposition, and addition of ether precipitated the product almost completely; after crystallisation from benzene the *tetraenal* formed golden-yellow needles, m. p.(K) 178—179° (Found : C, 79·75; H, 6·8. $C_{16}H_{16}O_2$ requires C, 79·95; H, 6·7%).

1-*Methoxy*-11-p-*methoxyundeca*-1 : 6 : 8 : 10-*tetraen*-3-*yn*-5-*ol* (V; $n = 3$).—By the above procedure 7-*p*-methoxyphenylhepta-2 : 4 : 6-trienal (4·25 g.) in tetrahydrofuran (60 c.c.) was condensed with the Grignard reagent from magnesium (1 g.) and methoxybutenyne (4·6 g.) in tetrahydrofuran (40 c.c.). Addition of concentrated aqueous ammonium nitrate solution (75 c.c.) and ether (75 c.c.) with agitation and ice-cooling gave an organic extract which was washed with potassium hydrogen carbonate solution, dried, and evaporated at 20° under reduced pressure. Crystallisation of the residue from benzene–light petroleum gave the desired *alcohol* (4·37 g., 74%), as a cream powder, m. p. (K) 112—120° (decomp.) (Found: C, 76·75; H, 6·8. $C_{19}H_{20}O_3$ requires C, 77·0; H, 6·8%).

11-p-*Methoxyphenylundeca*-2 : 4 : 6 : 8 : 10-*pentaen*-1-*al*.—(*a*) The foregoing alcohol (4·37 g.) in ethyl acetate (350 c.c.) was shaken in hydrogen in the presence of a partially poisoned palladium catalyst [9] (210 mg.) and quinoline (135 mg.) until 0·94 mol. of hydrogen had been absorbed. Uptake then ceased. After filtration, tetrahydrofuran (30 c.c.) and saturated aqueous oxalic acid (20 c.c.) were added; the mixture slowly deposited crystals. After being set aside overnight at 20° the *aldehyde* (2·7 g., 51% overall) formed pale orange leaflets or laths, m. p.(cap.) 202—203° (Found : C, 80·9; H, 6·95. $C_{18}H_{18}O_2$ requires C, 81·15; H, 6·8%).

(*b*) If reduction was effected *in situ* with lithium aluminium hydride, the trienal (1·86 g.) gave the pentaenal (50 mg., 2%), m. p.(cap.) 202—203°, when ether was added to the tetrahydrofuran solution.

Since completion of this work, Wizinger and Kölliker have reported [22] the preparation of this aldehyde by condensation of *p*-methoxybenzaldehyde and crotonaldehyde. Their product was isolated by crystallisation only, and must inevitably have contained hexadecaheptaenal, etc., and the aldehydes (I; $n = 7, 9, \ldots$) in minor quantities; they report it as scarlet crystals, m. p. 198·5—200°, $\lambda_{max.}$ 4220 Å (in alcohol). Our specimen had $\lambda_{max.}$ 4165 Å in this solvent.

1-*Methoxy*-13-p-*methoxyphenyltrideca*-1 : 6 : 8 : 10 : 12-*pentaen*-3-*yn*-5-*ol* (V; $n = 4$).—Addition of a solution of 9-*p*-methoxyphenylnona-2 : 4 : 6 : 8-tetraenal (7·5 g.) in warm tetrahydrofuran (400 c.c.) to one of the Grignard reagent from magnesium (2·25 g.) and methoxybutenyne (10·2 g.) in tetrahydrofuran (115 c.c.), and isolation of the product as above gave the *alcohol* (6·05 g., 60%) as a cream powder, m. p.(K) 138—142° (decomp.) (Found: C, 78·05; H, 6·85. $C_{21}H_{22}O_3$ requires C, 78·25; H, 6·9%).

13-p-*Methoxyphenylpentadeca*-2 : 4 : 6 : 8 : 10 : 12-*hexaenal*.—The above alcohol (6·05 g.) in

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[21] Schmitt and Obermeit, *Annalen*, 1941, **547**, 285.

[22] Wizinger and Kölliker, *Helv. Chim. Acta*, 1955, **38**, 372.

ethyl acetate (520 c.c.) was shaken in hydrogen in the presence of lead-poisoned palladium [9] (280 mg.) and quinoline (180 mg.) until 1·1 mol. had been absorbed. Filtration and addition of tetrahydrofuran (80 c.c.) and saturated aqueous oxalic acid resulted in the slow separation of the *aldehyde* (3·13 g., 34% overall), which formed scarlet prisms, m. p. 230—231° (decomp.), after crystallisation from xylene.

1-*Methoxy*-15-p-*methoxyphenylpentadeca*-1 : 6 : 8 : 10 : 12 : 14-*hexaen*-3-*yn*-5-*ol* (V; $n = 5$).—A suspension of 11-*p*-methoxyphenylundeca-2 : 4 : 6 : 8 : 10-pentaenal (500 mg.) in tetrahydrofuran (40 c.c.) was added to a solution of the Grignard reagent prepared from magnesium (140 mg.) and 1-methoxybutenyne (620 mg.) in tetrahydrofuran. A homogeneous solution resulted, and after 2 hr. the complex was decomposed and the neutral fraction isolated. Crystallisation from acetone–light petroleum gave a pale yellow *alcohol* (450 mg., 70%), m. p.(cap.) 148° (decomp.) (Found : C, 79·4; H, 7·0. $C_{23}H_{24}O_3$ requires C, 79·3; H, 6·95%).

15-p-*Methoxyphenylpentadeca*-2 : 4 : 6 : 8 : 10 : 12 : 14-*heptaenal*.—The above alcohol (200 mg.) in ethyl acetate (70 c.c.) was shaken in hydrogen in the presence of the palladium–lead catalyst (10 mg.) and quinoline (6 mg.); absorption apparently ceased after the uptake of 0·25 mol. Hydrolysis to the aldehyde as described above and crystallisation from pyridine gave the *aldehyde* (30 mg., 13% overall) as purple-red microscopic prisms, m. p.(cap.) 240—241° (decomp.) (Found : C, 82·25; H, 7·2. $C_{22}H_{22}O_2$ requires C, 83·0; H, 6·95%).

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