

210. *Researches on Acetylenic Compounds. Part LX.\* The Synthesis of Three Natural Polyacetylenic Hydrocarbons.*

By E. R. H. JONES, L. SKATTEBØL, and M. C. WHITING.

The hydrocarbons (III), where  $R = \textit{trans}\text{-Me}\cdot\text{CH}=\text{CH}$ ,  $\textit{cis}\text{-Me}\cdot\text{CH}=\text{CH}$ , and  $\text{Me}\cdot\text{C}\equiv\text{C}\text{-}$ , have been synthesised and shown to be identical with compounds isolated from *Correopsis* species.

FROM plants of the Compositae family a large number of polyacetylenic compounds has been isolated by N. A. and J. S. Sørensen and their co-workers. These include<sup>1</sup> a group of  $\text{C}_{13}$  compounds characterised by the presence of a methyl or acetoxymethyl group at one end of the molecule, and at the other either a vinyl group or an unsubstituted benzene ring. The conclusion is almost inescapable that the benzene ring is formed *in vivo* either by a novel cyclisation of a polyenyne system or from a common intermediate. The acyclic members of this group are easily the most unsaturated compounds yet encountered in Nature (*e.g.*,  $\text{C}_{13}\text{H}_6$ ), and are among the most unstable substances ever isolated. Since they are present in extremely minute quantities, their necessarily tentative identification represents a technical *tour de force*, and requires confirmation by synthesis, for which problems of scale do not arise. Indeed, one of these hydrocarbons, originally formulated<sup>1</sup> as divinyltetra-acetylene (dodeca-1 : 11-dienetetrayne), has been shown by the synthesis of the latter<sup>2</sup> and a consideration of the spectroscopic evidence to be, in all probability, *trans*-trideca-1 : 11-diene-3 : 5 : 7 : 9-tetrayne (III;  $R = \textit{trans}\text{-Me}\cdot\text{CH}=\text{CH}$ ). We now describe synthetical confirmation of this structure, the synthesis of the corresponding *cis*-isomer which has permitted recognition of this compound as being present, together with the *trans*-form, in a garden species of *Correopsis*, and the synthesis of tridec-1-ene-3 : 5 : 7 : 9 : 11-pentayne (III;  $R = \text{Me}\cdot\text{C}\equiv\text{C}$ ), isolated from *Helipterum* species.

For the synthesis of unsymmetrical acetylenic hydrocarbons the oxidative cross-coupling reaction is inherently unsuitable because of the similarity of physical properties between the desired product and its symmetrical analogues, while the approach of Cook, Jones, and Whiting,<sup>3</sup> requiring the removal of hydrogen chloride from terminal groupings in a polyacetylenic dichloride  $\text{R}\cdot\text{CHCl}\cdot[\text{C}\equiv\text{C}]_n\cdot\text{CHClR}'$ , was known to proceed in very low yield for large values of  $n$ . We therefore decided to use the modification employed by Bohlmann<sup>4</sup> for the preparation of the hydrocarbons  $\text{Me}_3\text{C}\cdot[\text{C}\equiv\text{C}]_n\cdot\text{CMe}_3$  ( $n = 5, 6, \text{ and } 7$ ), in which the two  $\text{-CHCl-}$  groups are located in non-terminal positions. This requires the preparation of an unsymmetrical glycol, *e.g.*,  $\text{R}\cdot\text{C}\equiv\text{C}\cdot\text{CH}(\text{OH})\cdot\text{C}\equiv\text{C}\cdot\text{CH}(\text{OH})\cdot\text{C}\equiv\text{C}\cdot\text{R}'$ , which can be prepared efficiently only by a two-stage route from the two appropriate  $\alpha\beta$ -acetylenic aldehydes and acetylene. Since the alkali-metal acetylides (at least, under normal conditions) merely polymerise  $\alpha\beta$ -acetylenic aldehydes, and the latter are likely to interact with the solvent in liquid ammonia experiments, it was first necessary to develop the method recently described for preparing and using ethynylmagnesium bromide.<sup>5</sup>

$\alpha\beta$ -Acetylenic aldehydes have usually been prepared *via* the acetals by Grignard condensations with ethyl orthoformate,<sup>6</sup> but as overall yields are low the use of dimethylformamide<sup>7</sup> was investigated. The aldehydes were obtained directly, without any secondary alcohol being formed; this contrasts with the analogous reaction with ethyl formate, where the initial complex,  $\text{R}\cdot\text{C}\equiv\text{C}\cdot\text{CH}(\text{OEt})\cdot\text{O}\cdot\text{MgBr}$ , can lose an ethoxide ion and

\* Part LIX, preceding paper.

<sup>1</sup> J. S. Sørensen and N. A. Sørensen, *Acta Chem. Scand.*, 1954, **8**, 1741; J. S. Sørensen, Holme, Borlaug, and N. A. Sørensen, *ibid.*, p. 1769; J. S. Sørensen and N. A. Sørensen, *ibid.*, p. 1763.

<sup>2</sup> Jones, Thompson, and Whiting, *ibid.*, p. 1944.

<sup>3</sup> Cook, Jones, and Whiting, *J.*, 1952, 2883.

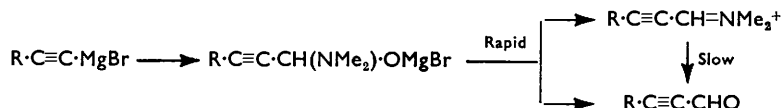
<sup>4</sup> Bohlmann, *Chem. Ber.*, 1953, **86**, 63, 657.

<sup>5</sup> Jones, Skattebøl, and Whiting, *J.*, 1956, 4765.

<sup>6</sup> Viguier, *Ann. Chim. (France)*, 1913, **28**, 447; Lunt and Sondheimer, *J.*, 1950, 3364.

<sup>7</sup> Bouveault, *Bull. Soc. chim. France*, 1904, **31**, 1322; Sicé, *J. Amer. Chem. Soc.*, 1953, **75**, 3697.

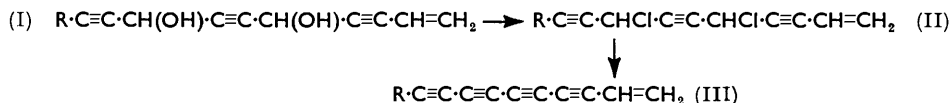
react further. Decomposition of the Grignard complex, however, required an inverse-addition technique, as otherwise dimethylamine, formed locally where basic conditions prevailed, at once added to the acetylenic aldehyde. It was noticed that some of the aldehyde was formed immediately on decomposition of the complex, while the rest became extractable by ether only after the clear acid solution had been kept for some time. Presumably the aldehyde and the dimethyliminium cation were produced simultaneously,



and the latter was only slowly hydrolysed to the former. Similar considerations may well apply in other cases of the Bouveault aldehyde synthesis.<sup>7</sup>

Aldehydes,  $\text{R}\cdot\text{C}\equiv\text{C}\cdot\text{CHO}$ , were readily obtained from hex-1-yne and *cis*- and *trans*-pent-2-en-4-yne<sup>8</sup> by this method in *ca.* 50% yields. From penta-1 : 3-diyne,<sup>9</sup> however, the aldehyde, though obtained in a crude state in fair yield, decomposed explosively on distillation at 70°/15 mm.; only a small amount of (crystalline) product was isolated. Vinylacetylene gave low and very variable yields, apparently because the coarsely divided state of the Grignard complex in this case rendered the reverse-addition technique for decomposition less effective. The corresponding alcohol was conveniently obtained from sodiovinylacetylene, prepared *in situ*,<sup>10</sup> and formaldehyde; it underwent oxidation to the required aldehyde with manganese dioxide in methylene dichloride<sup>11</sup> in fair yield; this procedure is much more satisfactory than the Grignard reaction in this case.

Like hept-2-ynal,<sup>5</sup> pent-4-en-2-ynal and the two stereoisomers of hex-4-en-2-ynal readily gave ethynylcarbinols on treatment with ethynylmagnesium bromide in tetrahydrofuran. Condensation of the alcohols with the appropriate aldehydes gave the three C<sub>13</sub> glycols (I; R = *cis*- and *trans*-Me·CH=CH and Me·C≡C); the difficulty of handling hexa-2 : 4-diyenal made it preferable to use this in the second stage of the condensation, whereas the hexenynals were employed in the first. Although the glycols (I), after



chromatographic purification, were apparently mixtures of stereoisomers, we preferred to accept loss by crystallising them in order to ensure the maximum purity of the later products, which were bound to be intractable. Treatment with thionyl chloride in ether at 5° gave, in each case, a dichloride (II) which was dehydrochlorinated with potassium ethoxide in ethanol<sup>4</sup> at about -30°, the polyacetylenic hydrocarbons then being isolated chromatographically.

*trans*-Trideca-1 : 11-diene-3 : 5 : 7 : 9-tetrayne (III; R = Me·CH=CH) crystallised readily, and was compared directly with a sample of the hydrocarbon from *Correopsis* roots<sup>1</sup> sent as a solution in hexane from Trondheim. Except that it had proved possible to obtain a slightly purer sample of the latter, the two were readily shown to be identical by comparison of ultraviolet and infrared spectra (cf. Fig. 1).

*cis*-Trideca-1 : 11-diene-3 : 5 : 7 : 9-tetrayne could not be induced to crystallise, but by chromatography it was brought to a state of approximate purity (as analytical data could not be obtained, and even direct weighing of samples for spectroscopic determination was impossible, one cannot be more precise). Its ultraviolet spectrum was almost identical

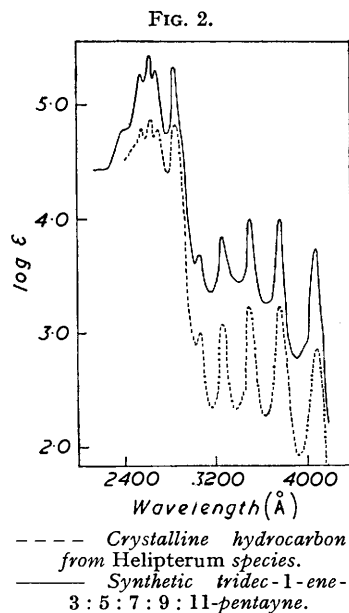
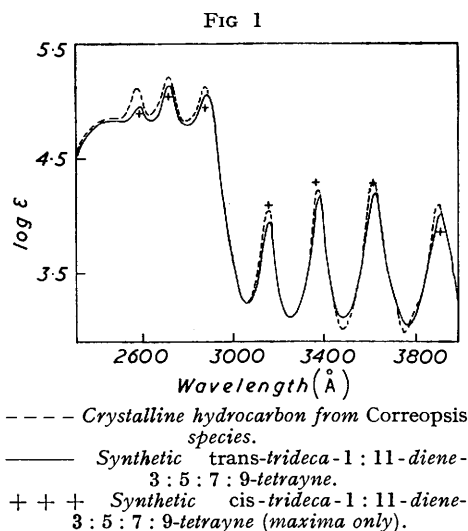
<sup>8</sup> Allan and Whiting, *J.*, 1953, 3314.

<sup>9</sup> Cook, Jones, and Whiting, *J.*, 1952, 2883.

<sup>10</sup> Croxall and Van Hook, *J. Amer. Chem. Soc.*, 1954, **76**, 1700.

<sup>11</sup> Attenburrow, Cameron, Chapman, Evans, Hems, Jansen, and Walker, *J.*, 1952, 1094.

with that of the *trans*-isomer, but its infrared spectrum differed, as expected, especially in the substitution of an intense band at  $713\text{ cm}^{-1}$  (*cis*) for one at  $945\text{ cm}^{-1}$  (*trans*). This spectrum agreed exactly—in several minor as well as in the main bands—with that of a non-crystalline fraction separated chromatographically from the *trans*-isomer in the extracts of *Correopsis* roots<sup>12</sup> (this is the spectrum published by Sørensen and Sørensen<sup>1</sup>). Owing to the use of carbon tetrachloride as solvent, the bands most characteristic stereochemically, in the  $670\text{--}1000\text{ cm}^{-1}$  region, were not, at the time, well observed for the naturally derived compounds. The presence of both isomers of trideca-1:11-diene-3:5:7:9-tetrayne in the extracts of this plant can now be recognised, but the possibility remains that one may be an artefact arising during the isolation.



Tridec-1-ene-3:5:7:9:11-pentayne (III;  $R = \text{Me}\cdot\text{C}\equiv\text{C}$ ) crystallised readily but was extraordinarily unstable to light. The ultraviolet absorption spectrum (Fig. 2) is considerably more intense than that recorded for the natural hydrocarbon by Sørensen, Holme, Borlaug, and Sørensen.<sup>1</sup> It is also more intense than that of a specimen isolated in Oxford from a hexane solution of a concentrate supplied by Professor Sørensen. Despite the discrepancies in intensity, the very characteristic fine structure (especially the triple peak at  $2400\text{--}2500\text{ Å}$ , an exceptional feature) leaves no doubt that the two substances responsible for this spectrum were identical. Similarly, the infrared spectrum of the best specimen of the natural hydrocarbon showed strong bands in the aliphatic C-H and the carbonyl stretching regions; but the characteristic and unusual triple C=C stretching frequency at  $2105$ ,  $2180$ , and  $2215\text{ cm}^{-1}$ , and the C-H out-of-plane deformation modes of the vinyl group were common to the two spectra, and also to that already published.<sup>1</sup>

Ultraviolet absorption spectra for the intermediates employed are in the annexed Table. Infrared spectra were as expected. To the generalisations of Allan, Meakins, and Whiting<sup>13</sup> on compounds of these types we would add that conjugation with an acetylenic linkage moves the C=O stretching band in aldehydes to about  $1660\text{--}1665\text{ cm}^{-1}$ , and that in the C-H out-of-plane deformation, the usual bands at  $910$  and  $990\text{ cm}^{-1}$  for vinyl groups are displaced to about  $920\text{ cm}^{-1}$  (rather variable) and  $970\text{ cm}^{-1}$ .

<sup>12</sup> J. S. Sørensen and N. A. Sørensen, personal communications.

<sup>13</sup> Allan, Meakins, and Whiting, *J.*, 1955, 1874.

## Ultraviolet absorption maxima of intermediates.

Vinylacetylenic aldehydes,  $R\cdot C\equiv C\cdot CHO$ , and their derivatives.

R =	CH=CH <sub>2</sub>		Me·CH=CH( <i>t</i> )		Me·CH=CH( <i>c</i> )		Me·C≡C	
	λ (Å)	10 <sup>-3</sup> ε	λ (Å)	10 <sup>-3</sup> ε	λ (Å)	10 <sup>-3</sup> ε	λ (Å)	10 <sup>-3</sup> ε
Aldehyde (hexane) .....	2520	10·9	2540	10·5	2560	8·3		
	2640	10·4	2620	13·6	2640	10·7		
Semicarbazone (alcohol) ...	2830	23	2740	11·9	2765	9·7		
			2900	22·6	2905	26·2	2890	21·9
Ethylnylcarbinol (alcohol)...	2235	9·5					3045	22·8
	2330	7·5	2285	14·2	2270	12·6		

Glycols (I) in alcohol.

	2250	27·0	2245	23·5	2240	12·7
	2310 *	25·0	2325 *	20·8	2340	10·5

\* Inflexion.

## EXPERIMENTAL

General precautions necessary for dealing with polyacetylenic compounds were described in Part XXXIX.<sup>9</sup> The highly unsaturated hydrocarbons (III) were far too unstable for carbon and hydrogen determinations, and were therefore characterised by ultraviolet and infrared absorption spectra.

*Hept-2-ynal*.—A solution of hex-1-yne (20·5 g.) in dry ether (50 c.c.) was added dropwise to one of ethylmagnesium bromide in ether (150 c.c.), prepared from magnesium (6 g.) and an excess of ethyl bromide. The mixture was heated under reflux for 1 hr., transferred to a dropping-funnel, and added, during 1 hr., to a stirred solution of dimethylformamide (55 g.) in dry ether (100 c.c.) with external cooling (ice-salt). After being stirred for a further hour at 20° the resultant fine suspension was poured gradually into vigorously stirred 5% sulphuric acid (1 l.). After 18 hr., extraction with ether, evaporation of the solvent through a short Fenske column, and distillation gave the aldehyde (14·1 g., 51%), b. p. 54—55°/16 mm.,  $n_D^{20}$  1·4516 (Goebel and Wenzke<sup>14</sup> give b. p. 61·8—62·5°/18 mm.,  $n_D^{25}$  1·4499).

*trans-Hex-4-en-2-ynal*.—*trans*-Pent-2-en-4-yne (15 g.) similarly gave this aldehyde (10·8 g., 50%), b. p. 50—51°/14 mm.,  $n_D^{17}$  1·5246 (Found: C, 76·6; H, 6·55.  $C_8H_8O$  requires C, 76·6; H, 6·4%), which solidified at -25°. The *semicarbazone* formed plates, m. p. 150—156°, from aqueous methanol (Found: C, 55·4; H, 6·2.  $C_7H_8ON_3$  requires C, 55·65; H, 6·2%).

*cis-Hex-4-en-2-ynal*.—*cis*-Pent-2-en-4-yne (15 g.) similarly gave this aldehyde (11·0 g., 51%), b. p. 40—41°/14 mm.,  $n_D^{20}$  1·5133 (Found: C, 76·55; H, 6·55%). Its *semicarbazone* formed plates, m. p. 173—175°, from aqueous methanol (Found: C, 55·35; H, 6·1%).

*Pent-4-en-2-yn-1-ol*.—1:4-Dichlorobut-2-ene (125 g.) was added slowly to a stirred suspension of sodamide, prepared from sodium (64 g.) in liquid ammonia (1·5 l.) in a vacuum-flask. Dry paraformaldehyde (30 g.) was added, and the mixture was stirred for 40 hr., then transferred to a stainless-steel bucket, where most of the ammonia was allowed to evaporate. Extraction with ether, evaporation of the latter through a 10 cm. Fenske column, and distillation gave pent-4-en-2-yn-1-ol (23 g., 28%), b. p. 55—58°/17 mm.,  $n_D^{22}$  1·4961 (Gverdtstiteli<sup>15</sup> gives b. p. 55—58°/10 mm.,  $n_D^{20}$  1·4988).

*Pent-4-en-2-ynal*.—(a) An excess of vinylacetylene<sup>16</sup> was passed in a stream of nitrogen into a solution of ethylmagnesium bromide, prepared in ether (350 c.c.) from magnesium (12 g.) with ice-cooling. After being heated under reflux the solution was added with stirring to a solution of dimethylformamide (95 g.) in ether (150 c.c.) during 2 hr.; the complex separated in a coarsely aggregated, rather variable form. Decomposition with 5% sulphuric acid, as above, and isolation of the product gave the crude aldehyde (7·6 g., 19%, or less), b. p. 65—66°/100 mm.,  $n_D^{17}$  1·4962.

(b) Pent-4-en-2-yn-1-ol (20 g.) in methylene dichloride (750 c.c.) was shaken with active manganese dioxide (200 g.). Filtration, evaporation of the solvent through a 10 cm. Fenske column, and distillation of the residue gave the aldehyde (5·9 g., 30%), b. p. 65°/100 mm.,  $n_D^{19}$

<sup>14</sup> Goebel and Wenzke, *J. Amer. Chem. Soc.*, 1937, **59**, 2301.<sup>15</sup> Gverdtstiteli, *Doklady Akad. Nauk S.S.S.R.*, 1948, **60**, 57.<sup>16</sup> Eglinton and Whiting, *J.*, 1950, 3650.

1-5015, probably purer than the specimen described above. Prepared by either route this compound formed a *semicarbazone*, m. p. 135—151° (decomp.) (Found: C, 52.25; H, 5.15.  $C_6H_7ON_3$  requires C, 52.5; H, 5.1%). The aldehyde itself showed the expected ultraviolet and infrared absorption spectra (see above), but proved very unstable.

*Hexa-2 : 4-diyнал*.—A solution of ethylmagnesium bromide, prepared in ether from magnesium (4.8 g.), was treated with penta-1 : 3-diyne (12 g.) and added to dimethylformamide (40 g.), and the product was isolated as described above. On distillation 2.6 g. of a liquid, b. p. 67—70°, were obtained; then, with the bath-temperature at about 80°, the remainder of the product exploded violently. No attempt was made to analyse the aldehyde, which crystallised at  $-15^\circ$ , but a *semicarbazone* (decomp. at 173°) was obtained (Found: C, 56.4; H, 4.85.  $C_7H_7ON_3$  requires C, 56.35; H, 4.75%).

*Nona-1 : 4-diyн-3-ol*.—A suspension of ethynylmagnesium bromide<sup>5</sup> was prepared from magnesium (4.8 g.) in tetrahydrofuran (200 c.c.) and cooled to 0°. A solution of hept-2-ynal (15 g.) in tetrahydrofuran (20 c.c.) was added with stirring during 1 hr., with ice-cooling, and the mixture was then stirred for 18 hr. at 20°. Decomposition with saturated ammonium chloride solution and isolation with ether gave the *alcohol* (15.8 g., 85%), b. p. 69°/0.5 mm.,  $n_D^{19}$  1.4730 (Found: C, 79.6; H, 8.95.  $C_9H_{12}O$  requires C, 79.4; H, 8.9%).

*trans-Oct-6-ene-1 : 4-diyн-3-ol*.—*trans*-Hex-4-en-2-ynal (16.2 g.) and ethynylmagnesium bromide, prepared from magnesium (6 g.), similarly gave this *alcohol* (17.7 g., 86%), b. p. 53—54°/0.05 mm.,  $n_D^{21}$  1.5188 (Found: C, 79.5; H, 6.65.  $C_8H_8O$  requires C, 80.0; H, 6.65%).

*cis-Oct-6-ene-1 : 4-diyн-3-ol*.—Similarly prepared from *cis*-hex-4-en-2-ynal (9.9 g.) and magnesium (3.6 g.), this *alcohol* (10.7 g., 85%) had b. p. 44—45°/0.05 mm.,  $n_D^{18}$  1.5162 (Found: C, 80.2; H, 6.85%).

*Hept-6-ene-1 : 4-diyн-3-ol*.—Pent-4-en-2-ynal (5.8 g.) was condensed with ethynylmagnesium bromide, prepared from magnesium (3.0 g.) as above. The *alcohol* (5.4 g., 70%) had b. p. 41—42°/1 mm.,  $n_D^{15}$  1.5138 (Found: C, 79.45; H, 5.7.  $C_7H_8O$  requires C, 79.25; H, 5.7%). The lower yield obtained in this case may reflect lower purity of the starting material; on the other hand, this alcohol, unlike its analogues, polymerised extensively when stored at  $-15^\circ$  for a few weeks.

*trans-Trideca-1 : 11-diene-3 : 6 : 9-triyne-5 : 8-diol* (I; R = Me·CH=CH).—A solution of *trans*-octa-1 : 4-diyн-3-ol (6 g.) in tetrahydrofuran (25 c.c.) was added during 1 hr. to an ice-cooled solution of ethylmagnesium bromide, prepared from magnesium (2.7 g.) in tetrahydrofuran (50 c.c.). After an additional hour, the temperature was lowered to *ca.*  $-15^\circ$  while a solution of pent-4-en-2-ynal (3.3 g.) in tetrahydrofuran (5 c.c.) was added during 30 min. The mixture was stirred at 0° for 7 hr. Decomposition with ammonium chloride solution and isolation with ether gave a partly crystalline product which was chromatographed on deactivated alumina. The ether eluate was crystallised from benzene, giving the *glycol* (3.1 g., 38%) as needles, m. p. 123—124° (Found: C, 77.7; H, 6.1.  $C_{13}H_{12}O_2$  requires C, 78.0; H, 6.05%). A polymorphic form, m. p. 76—78°, was obtained from light petroleum.

*cis-Trideca-1 : 11-diene-3 : 6 : 9-triyne-5 : 8-diol* (I; R = Me·CH=CH) was similarly prepared by condensing *cis*-octa-1 : 4-diyн-3-ol (3.0 g.) with pent-4-en-2-ynal (1.8 g.). Chromatography on deactivated alumina gave an ether eluate which was, with considerable difficulty, induced to crystallise under benzene-light petroleum (1.2 g., 27%, m. p. 80—85°). After recrystallisation the *diol* formed needles, m. p. 88° (Found: C, 78.0; H, 6.05%).

*Tridec-1-ene-3 : 6 : 9 : 11-tetrayne-5 : 8-diol* (I; R = Me·C≡C) was similarly prepared by condensing hept-6-ene-1 : 4-diyн-3-ol (2.7 g.) with crude hexa-2 : 4-diyнал (2.3 g., as above). After chromatography, trituration with benzene gave a solid (850 mg.), which on crystallisation from benzene-light petroleum yielded the *glycol*, m. p. 111—114° (slight decomp.) (Found: C, 77.5; H, 5.25.  $C_{13}H_{10}O_2$  requires C, 78.8; H, 5.25%).

*trans-Trideca-1 : 11-diene-3 : 5 : 7 : 9-tetrayne* (III; R = Me·CH=CH).—A solution of *trans*-trideca-1 : 11-diene-3 : 6 : 9-triyne-5 : 8-diol (1.2 g.) in dry ether (3 c.c.) was treated with thionyl chloride (1.5 c.c.) at 5° for 2 hr. Addition of water and more ether gave an upper phase which was dried and evaporated at room temperature, leaving a dark liquid which, without purification, was dissolved in dry ether (10 c.c.). This solution was added dropwise to a stirred solution of potassium ethoxide, prepared from potassium (1.5 g.) in ethanol (25 c.c.) and cooled to  $-30^\circ$ . The mixture was stirred for 30 min., the bath-temperature being allowed to rise to 0°. Addition of water and isolation with ether gave a semi-solid product which was chromatographed on activated alumina; the light petroleum eluates were evaporated to *ca.* 5 c.c. and set aside

at  $-30^{\circ}$ , a solid separating which, crystallised several times from pentane, gave the hydrocarbon (*ca.* 25 mg.) as pale yellow needles, which decomposed (without melting) above  $40^{\circ}$  and rapidly became brown in diffused daylight, even at  $-5^{\circ}$ . Catalytic hydrogenation resulted in an uptake of 10.1 mols.

*cis-Trideca-1 : 11-diene-3 : 5 : 7 : 9-tetrayne* (III;  $R = Me \cdot CH=CH$ ).—The corresponding *cis*-glycol (880 mg.) and thionyl chloride (1 c.c.) gave a crude dichloro-compound, which was treated with potassium ethoxide (from 1.5 g. of potassium) as described above. The hydrocarbon (*ca.* 20 mg.) was a liquid, even after repeated chromatography, but its ultraviolet and infrared spectra agreed with the postulated structure.

*Tridec-1-ene-3 : 5 : 7 : 9 : 11-pentayne* (III;  $R = Me \cdot C \equiv C$ ).—The tetra-acetylenic glycol (800 mg.) and thionyl chloride (1 c.c.) in ether (2 c.c.) gave a crude dichloride, which was added to a solution of potassium ethoxide, prepared from potassium (1 g.) in ethanol (15 c.c.), at  $-40^{\circ}$  for 15 min. Isolation and then chromatography gave a yellow zone, and when this was eluted with light petroleum a solid was readily obtained. Several recrystallisations from pentane gave the hydrocarbon (*ca.* 100 mg.) as yellow needles, extraordinarily sensitive to light; the ultraviolet absorption spectrum illustrated characterises this substance and proves its identity with the natural product.

THE DYSON PERRINS LABORATORY,  
OXFORD UNIVERSITY,

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