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## Natural Acetylenes. Part XXVIII.<sup>1</sup> C<sub>17</sub>-Polyacetylenic Alcohols from the Umbellifer Daucus carota L. (carrot): Alkylation of Benzene by Acetylenyl(vinyl)carbinols in the Presence of Toluene-p-sulphonic Acid

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Three acetylenic compounds, the known alcohol (A; X = OH, Y = H) and diol (A; X = Y = OH) and the new monoacetate (A; X = OAc, Y = OH) have been isolated from the roots of the common carrot, Daucus carota L.

$$H_2C=CH\cdot CHX\cdot [C=C]_2 \cdot CHY \cdot CH \stackrel{\leftarrow}{=} CH \cdot [CH_2]_6 Me$$
 (A)

When refluxed with toluene-p-sulphonic acid in benzene, the alcohol and synthetic oct-1-ene-4,6-diyn-3-ol rearranged to the expected primary alcohols (and tosylates) but in addition yielded benzenoid hydrocarbons of the type PhCH<sub>2</sub>·CH=CH·[C=C]<sub>2</sub>R, arising from attack on the solvent.

WE recently<sup>2</sup> refuted an earlier proposal<sup>3</sup> for the structure of 'carotatoxin', a natural toxicant from the Umbellifer Daucus carota L. (carrot), and showed it to

<sup>1</sup> Part XXVII, C. H. Fawcett, D. M. Spencer, R. L. Wain, A. G. Fallis, Sir Ewart R. H. Jones, M. Le Quan, C. B. Page, V. Thaller, D. C. Shubrook, and Miss P. M. Whitham, *J. Chem*, Soc. (C), 1968, 2455. <sup>2</sup> R. K. Bentley and V. Thaller, Chem. Comm., 1967, 439.

be cis-heptadeca-1,9-diene-4,6-diyn-3-ol (I) (i.e. falcarinol <sup>4</sup> or panaxynol <sup>5</sup>). We now describe the complete analysis of the carrot polyacetylenes and an examination

<sup>3</sup> D. G. Crosby and N. Aharonson, *Tetrahedron*, 1967, **23**, 465. <sup>4</sup> F. Bohlmann, U. Niedballa, and K.-M. Rode, *Chem. Ber.*, 1966, **99**, 3552.

<sup>5</sup> M. Takahashi and M. Yoshikura, J. Pharm. Soc. Japan, 1966, **86**, 1053.

of the products obtained when the alcohol (I) was treated with toluene-*p*-sulphonic acid in benzene.

Chromatography of an extract of fresh carrots gave three main polyacetylene fractions. The least polar contained only one polyacetylene which was identified as the alcohol (I).<sup>2</sup>

$$CH_{2}=CH\cdot CH(OH)\cdot [C\equiv C]_{2}\cdot CH_{2}\cdot CH \stackrel{c}{=} CH\cdot [CH_{2}]_{6}Me \quad (I)$$
  
$$CH_{2}=CH\cdot CO\cdot [C\equiv C]_{2}\cdot CH(OH)\cdot CH \stackrel{c}{=} CH\cdot [CH_{2}]_{6}Me \quad (II)$$

$$CH_2 = CH \cdot CO \cdot [C \equiv C]_2 \cdot CO \cdot CH = CH \cdot [CH_2]_6 Me$$
 (III)

$$\label{eq:ch2} \begin{array}{l} {\rm CH_2} = {\rm CH} \cdot {\rm CH} ({\rm OR^1}) \cdot [{\rm C} = {\rm C}]_2 \cdot {\rm CH} ({\rm OR^2}) \cdot {\rm CH} \stackrel{c}{=} {\rm CH} \cdot [{\rm CH_2}]_6 {\rm Mee} \\ ({\rm IV}) \end{array}$$

$$CH_2 = CH \cdot CH(OAc) \cdot [C \equiv C]_2 \cdot CO \cdot CH \stackrel{\sim}{=} CH \cdot [CH_2]_6 Me$$
 (V)

The intermediate polarity fraction showed a diynonene chromophore incompletely separated from a more polar divne component. The former, isolated in traces by repeated t.l.c., must belong to a hydroxyketone of the falcarinolone type (II); it gave a typical mass spectrum and manganese dioxide oxidation yielded a falcarindione (III)-like chromophore.<sup>6</sup> The divne was found to be the hitherto unknown acetylfalcarindiol (IV;  $R^1 = Ac$ ,  $R^2 = H$ ). Its spectra revealed the presence of an acetyl and a hydroxy-group as well as double bonds; the ethylenic protons give rise to complex signals in the  $\tau$  4—5 region: the molecular ion and fragmentation pattern were those expected for a falcarindiol monoacetate. It gave a diacetate (IV;  $R^1 = R^2 = Ac$ ) and was oxidised to the ketoacetate (V). The keto-group of the latter deshielded the protons of both the *cis*-double bond ( $\tau < 4$ ) and the allylic methylene group  $(\tau 7.35)$ ; these shifts are consistent with those observed by Bohlmann<sup>4</sup> for the corresponding protons in the diketone (III) and thus determine the position of the hydroxy-group in the natural material.

The most polar polyacetylene of the carrot was identified as falcarindiol (IV;  $R^1 = R^2 = H$ ), hitherto incompletely described.<sup>4</sup> It gave the diacetate (IV;  $R^1 = R^2 = Ac$ ) and on oxidation followed the reported pattern.

The 1,9-diene-4,6-divne unsaturation is a common feature of the carrot polyacetylenes. They showed in their mass spectra the typical allylic fission,<sup>7</sup> which results in a strong peak at  $(M - [CH_2]_5 Me)$ ; this property can be used conveniently for the characterisation of this type of polyacetylene.

The non-acetylenic compound with  $\lambda_{max}$ . 300 and 263 nm., sometimes present in large amounts, was identified by u.v., i.r., n.m.r., and mass spectra, and by formation of its acetyl derivative, as 3,4-dihydro-8-hydroxy-

- ene-divne absorption. The most polar of these, slightly more polar than the original alcohol, was the expected primary alcohol (VI; R = OH) formed by anionotropic
  - rearrangement. Its structure was deduced from the spectral data and by oxidation with manganese dioxide to an aldehyde. The compound of intermediate polarity, readily hydrolysed to the primary alcohol, proved to be the tosylate (VI; R = OTs) ( $v_{max}$ . <sup>10</sup> 1380, 1185, 1175, and 815 cm.<sup>-1</sup>).

6-methoxy-3-methylisocoumarin.8 It was previously

isolated from carrots kept in cold storage and considered

to be one of the substances responsible for their bitter off-flavour. The co-occurrence of polyacetylenes and

isocoumarins had been observed already; the fungus Marasmius ramealis produces both the polyacetylenic

antibiotic marasin and 8-hydroxy-3-methyl-isocoumarin.9 The reaction of falcarinol (I) with toluene-p-sulphonic acid in benzene which figured in the original investigation  $^{3}$  (cf. ref. 2) gave three products which all exhibited

## $R \cdot CH_2 \cdot CH = CH \cdot [C = C]_2 \cdot CH_2 \cdot CH = CH \cdot [CH_2]_6 Me$ (VI)

The least polar product contained neither hydroxy-nor tosyl groups. The base peak in its mass spectrum was the tropylium ion (m/e 91). This peak usually occurs in the spectra of polyacetylenes which fragment to aromatic radical cations,<sup>11</sup> but is rarely so strong. Other intense peaks were at m/e 304, apparently the molecular ion, and m/e 219, arising from the characteristic fragmentation already referred to. Both the i.r.  $(\nu_{max},\ 743 \ and$ 697 cm.<sup>-1</sup>) and the n.m.r. spectra [ $\tau$  2.77 (5H, s)] suggested the presence of a phenyl group. Participation of the solvent was observed in toluene but not in carbon tetrachloride.

Thus the benzenoid product was probably the hydrocarbon (VI; R = Ph); it could also be obtained in low yield by similar treatment of the primary alcohol (VI; R = OH). For confirmation we investigated the reaction with the model compound oct-1-ene-4,6-diyn-

$$CH_{2}=CH\cdot CH(OH)\cdot [C=C]_{2}Me \qquad (VII)$$
  
RCH\_{2}\cdot CH=CH\cdot [C=C]\_{2}Me \qquad (VIII)

3-ol (VII), synthesised from acraldehyde and pentadiyne. When this was heated under reflux with toluenep-sulphonic acid in benzene three products were again formed. The least polar was identified as 1-phenyloct-2-ene-4,6-divne (VIII; R = Ph) by comparison with a sample unambiguously synthesised by a Grignard reaction between hexa-2,4-diynal and β-phenylethyl bromide followed by dehydration. N.m.r. spectroscopy indicated the product derived from the alcohol (VII) to consist largely of the trans-isomer, whereas the synthetic phenyloctenediyne was mainly cis. The other products were identified as oct-2-ene-4,6-diyn-1-ol

<sup>&</sup>lt;sup>6</sup> F. Bohlmann, C. Arndt, H. Bornowski, and K.-M. Kleine, Chem. Ber., 1961, 94, 958.

<sup>&</sup>lt;sup>7</sup> Sir Ewart R. H. Jones, S. Safe, and V. Thaller, J. Chem. Soc. (C), 1966, 1220.
<sup>8</sup> E. Sondheimer, J. Amer. Chem. Soc., 1957, 79, 5036.
<sup>9</sup> G. Bendz, Arkiv Kemi, 1959, 14, 511.

P. Rademacher, W. Wiegräbe, and W. Lüttke, *Chem. Ber.*, 1967, 100, 1213; L. J. Bellamy, 'The Infrared Spectra of Complex Molecules,' Methuen, London, 1954, p. 300; R. S. Tipson, *J. Amer. Chem. Soc.*, 1952, 74, 1354.
 R. T. Aplin and S. Safe, *Chem. Comm.*, 1967, 140.

(VIII; R = OH) and its tosylate. This alcohol was synthesised from propyne and pent-2-en-4-yn-1-ol.

## EXPERIMENTAL

U.v. (in ether) and i.r. spectra (in carbon disulphide) were recorded with Unicam SP 800 and Perkin-Elmer 237 spectrophotometers respectively. N.m.r. spectra were obtained with Perkin-Elmer R10 and R14 spectrometers. Mass spectra were determined with an A.E.I. MS 9 spectrometer by use of a direct insertion probe. M.p. (corrected) were determined with a Kofler hot-stage apparatus. Silica gel in column chromatography refers to Whatman SG31. Merck silica gel HF<sub>254</sub> and PF<sub>254+366</sub> were used in t.l.c. (layers 0.3 and 1 mm. thick respectively).

Manganese dioxide was freshly prepared <sup>12</sup> and its activity was tested on cinnamyl alcohol. Light petroleum refers to fraction b.p.  $40-60^{\circ}$ .

Isolation of Polyacetylenes.—Minced carrots (3 kg.) were extracted twice with ether at  $20^{\circ}$ . The extract was dried and concentrated, then diluted with light petroleum and again concentrated under reduced pressure. The fine suspension was run on to a silica gel column ( $25 \times 2.5$  cm.) and chromatographed by gradient elution [light petroleum (1 l.) gradually enriched with ether (2 l.)]. Fractions (50 ml.) were assayed by spectrophotometry (see Table). The polyacetylenes were then purified by preparative t.l.c. on silica gel.

Fractions	$\lambda_{max.}$ (nm.)	Chromophore
9-12	256, 242, 230	Diyne
14	291, 275, 260	Diyn-onene
15, 16	291, 275, 260	Diyn-onene
	260, 244, 232	Diyne
17	258, 244, 232	Diyne
	300, 263	Isocoumarin
18, 19	300, 263	Isocoumarin
20 - 23	258, 244, 232	Diyne

Fractions 9—12 gave cis-heptadeca-1,9-diene-4,6-diyn-3-ol (I) <sup>4,5</sup> (80 mg.),  $\lambda_{max.}$  256 ( $\varepsilon$  200), 242 (400), and 230 (400) nm.; i.r. and n.m.r. data identical with lit. values; m/e 244 ( $M^+$ , 4%) and 159 (100). The alcohol (15 mg.) and manganese dioxide (100 mg.) in methylene chloride (25 ml.) were shaken for 3 hr. to give cis-heptadeca-1,9-diene-4,6-diyn-3-one (8 mg.); u.v. and i.r. data identical with lit.<sup>6</sup> values;  $\tau$  (CCl<sub>4</sub>) 9·10 (t, J 6 Hz,  $CH_3$ ·CH<sub>2</sub>), 8·70br (Me[CH<sub>2</sub>]<sub>5</sub>·CH<sub>2</sub>), 7·92 (m, CH<sub>2</sub>·CH<sub>2</sub>·CH:CH), 6·95 (d, J5 Hz, CiC·CH·CH<sub>2</sub>·CH:CH), ca. 4·5 (m, CH:CH), and ca. 3·7 (m, CH<sub>2</sub>:CH·CO); m/e 242 ( $M^+$ , 8%) and 157 (100).

Fractions 14-17 gave cis-3-acetoxyheptadeca-1,9-diene-4,6-diyn-8-ol (IV;  $R^1 = Ac$ ,  $R^2 = H$ ) (15 mg.),  $\lambda_{max.}$  259 ( $\epsilon$  200), 245 (400), and 233 (400) nm.;  $\nu_{max}$  3600, 3430, 1015 (OH), 1745, 1215 (acetate), 975, 940 (CH:CH<sub>2</sub>), and 660 (cis-CH:CH) cm.<sup>-1</sup>;  $\tau$  (CCl<sub>4</sub>) 9.10 (t, J 6 Hz, CH<sub>3</sub>·CH<sub>2</sub>), ca. 8.7br (Me[CH<sub>2</sub>]<sub>5</sub>·CH<sub>2</sub>), 7.92 (s, CH<sub>3</sub>·CO), ca. 7.9 (m, CH<sub>2</sub>·CH<sub>2</sub>·CH:CH), and 4-5 (m, CH<sub>2</sub>:CH, CH:CH, CH·OH, CH·OAc); m/e 302 (25%), 217 (14), 175 (40), 157 (100). The alcohol (5 mg.) in acetic anhydride (0.5 ml.) containing a trace of pyridine at 20° for 3 hr. gave, after chromatography, the diacetate (IV;  $R^1 = R^2 = Ac$ ),  $\lambda_{max}$ , 259 (rel. E 0.5), 245 (1.0), and 232 (1.0) nm.;  $v_{max}$  1745, 1215 (acetate), 975, 940 (CH<sub>2</sub>:CH), and 663 (cis-CH:CH) cm.<sup>-1</sup>; m/e 344 (7%), 302 (10), 260 (100), and 259 (96). The alcohol (IV;  $R^1 = Ac$ ,  $R^2 = H$ ) (8 mg.) and manganese dioxide (60 mg.) in methylene chloride (20 ml.) were shaken for 4 hr. The solution was filtered, concentrated, and chromatographed to give cis-3-acetoxyheptadeca-1,9-diene-4,6-diyn-8-one (V) (5 mg.),  $\lambda_{max}$  291 (rel. E 0.9), 274 (1.0), and 260 (0.6) nm.;  $\nu_{max}$  1750, 1210 (acetate), and 1650 (ketone) cm.<sup>-1</sup>;  $\tau$  (CCl<sub>4</sub>) 9.10 (t, J 6 Hz, CH<sub>3</sub>·CH<sub>2</sub>), ca. 8.7br (Me[CH<sub>2</sub>]<sub>5</sub>·CH<sub>2</sub>), 7.89 (s, CH<sub>3</sub>·CO), 7.35 (m, CO·CH:CH-CH<sub>2</sub>), 4.0—4.8 (m, CH<sub>2</sub>·CH·CH·OAc), and 3.6—4.0 (m, CH:CH·CO). The minor component isolated from fractions 14—17 had  $\lambda_{max}$  290 (rel. E 0.9), 274 (1.0), and 259 (0.6) nm. [lit.<sup>6</sup> for falcarinolone (II), 290, 273.5, and 259 nm.]; m/e 258 (M<sup>+</sup>, 30%) and 173 (100); after an ethereal solution was shaken with manganese dioxide for 3 hr. it had  $\lambda_{max}$  304 (rel. E 0.5), 286 (0.75), 270 (0.9), and 255 (1.0) nm. [lit.<sup>6</sup> for falcarindione (III), 303 ( $\varepsilon$  6100), 285 (8900), 268 (10,400), 253 (12,500), and 242 (14,200) nm.].

Fractions 20—23 gave cis-heptadeca-1,9-diene-4,6-diyne-3,8-diol (IV;  $R^1 = R^2 = H$ )<sup>4</sup> (17 mg.),  $\lambda_{max}$  258 ( $\varepsilon$  200), 244 (400), and 232 (400) nm.;  $\nu_{max}$  3600, 3420, 1015 (OH), 984, 933 (CH:CH<sub>2</sub>), and 663 (cis-CH:CH) cm.<sup>-1</sup>;  $\tau$ (CCl<sub>4</sub>) 9·10 (t, J 6 Hz,  $CH_3$ ·CH<sub>2</sub>), ca. 8·7br (Me[CH<sub>2</sub>]<sub>5</sub>·CH<sub>2</sub>), 7·89 (m, CH<sub>2</sub>·CH<sub>2</sub>·CH:CH), 4·3—5·2 (m, CH<sub>2</sub>:CH, CH:CH). CH·OH twice), 4·1 (ddd, J 17, 9, and 5 Hz, CH<sub>2</sub>:CH·CH). Acetylation (as before) gave the diacetate (IV;  $R^1 = R^2 = Ac$ ). The diol (5 mg.) and manganese dioxide (40 mg.) in methylene chloride (15 ml.) were shaken for 2 hr. The solution was filtered, concentrated, and chromatographed to give the very unstable diketone (III),  $\lambda_{max}$  see before. A more polar fraction had  $\lambda_{max}$  291 (rel. E 0·8), 276 (1·0), and 260 (0·95) nm. [see falcarinolone (II) data]; when shaken with further manganese dioxide it gave more of the diketone.

Reaction of cis-Heptadeca-1,9-diene-4,6-diyn-3-ol with Toluene-p-sulphonic Acid.—(a) In benzene. A solution of the alcohol (40 mg.) and toluene-p-sulphonic acid (300 mg.) in benzene (100 ml.) was heated under reflux for 10 min. The usual isolation procedure followed by chromatography on a silica gel plate in hexane-acetone (5:2) gave bands of  $R_{\rm F}$  0.4, 0.5, and 0.8.

The most polar zone gave heptadeca-2,9-diene-4,6-diyn-1-ol (VI; R = OH) (7 mg.),  $\lambda_{max}$  282 (rel. E 0.8), 266 (1.0), 252 (0.7), and 239 (0.3) nm.;  $\nu_{max}$  3620, 3450 (OH), 950 (trans-CH:CH), and 662 (cis-CH:CH) cm.<sup>-1</sup>;  $\tau$  (CDCl<sub>3</sub>) 9·11 (t, J 6 Hz, CH<sub>3</sub>·CH<sub>2</sub>), 8·7br (Me[CH<sub>2</sub>]<sub>5</sub>·CH<sub>2</sub>), 7·96br (d, J 6 Hz, CH<sub>2</sub>·CH<sub>2</sub>·CH:CH), 6·94 (d, J 6 Hz, C:C·CH<sub>2</sub>-CH:CH), 5·80br (CH:CH·CH<sub>2</sub>OH: addition of trifluoroacetic acid gave a quartet, J 5 and 1 Hz), 4·54 (m, CH<sub>2</sub>·CH:CH-CH<sub>2</sub>), 4·24br (d, J 16 Hz, C:C·CH:CH), and 3·62 (dt, J 16 and 5 Hz C:C·CH:CH·CH<sub>2</sub>); m/e 244 (24%) and 159 (100). An ethereal solution of this alcohol shaken with manganese dioxide for 3 hr. gave heptadeca-2,9-diene-4,6-diynal,  $\lambda_{max}$  311 (rel. E 1·0), 292 (0·95), 275 (0·6), and 266 (0·35) nm.;  $\nu_{max}$  2710 and 1687 (CHO) cm.<sup>-1</sup>; m/e 242 (5%), 157 (100), and 128 (77).

T.l.c. of the eluate from the intermediate polarity zone showed two components, one of these moving at the same rate as the secondary alcohol (I). The ethereal solution was shaken with manganese dioxide for 5 hr., then chromatographed to give *cis*-heptadeca-1,9-diene-4,6-diyn-3-one (V) (3 mg.), identical with the sample obtained before, and *heptadeca-2,9-diene-4,6-diyn-1-yl tosylate* (VI; R = *p*-TsO) (11 mg.),  $\lambda_{max}$  (ether) 283 (rel. E 0.8), 267 (1.0), 253 (0.7), and 240 (0.4) nm.;  $\nu_{max}$  2260 (CiC), 1380, 1185, 1175 (SO<sub>2</sub>), 960 (*trans*-CH:CH), 815 (*para*-substituted

<sup>12</sup> J. Attenburrow, A. F. B. Cameron, J. H. Chapman, R. M. Evans, B. A. Hems, A. B. A. Jansen, and T. Walker, *J. Chem. Soc.*, 1952, 1094.

benzene ring), and 675 (*cis*-CH:CH) cm.<sup>-1</sup> An ethereal solution of the tosylate shaken vigorously with hydrochloric acid (0.05N) for several hr. gave the alcohol (VI; R = OH) (see before).

The least polar zone gave 1-phenylheptadeca-2,9-diene-4,6-diyne (VI; R = Ph) (13 mg.), estimated to consist of 80% trans,cis- and 20% cis,cis-isomers,  $\lambda_{max}$ . 284 (rel. E 0·8), 268 (1·0), 254 (0·65) and 240 (0·45) nm.;  $\nu_{max}$ . 2225 (CiC), 955 (trans-CH:CH), 743, and 697 (Ph) cm.<sup>-1</sup>;  $\tau$ (CDCl<sub>3</sub>) 9·11 (t, J 6 Hz, CH<sub>3</sub>·CH<sub>2</sub>), 8·7br (Me[CH<sub>2</sub>]<sub>5</sub>·CH<sub>2</sub>), 7·96br (d, J 6 Hz, CH<sub>2</sub>·CH<sub>2</sub>·CH:CH), 6·97 (d, J 6 Hz, CiC-CH<sub>2</sub>·CH:CH), 6·56 (80% trans), and 6·34 (20% cis) (each d, J 7 Hz, PhCH<sub>2</sub>·CH:CH), ca. 4·55 (m, CH<sub>2</sub>·CH·CH·CH<sub>2</sub>), ca. 4·50 (d, J 16 Hz, CiC·CH:CH), 3·57 (dt, J 16 and 7 Hz, CiC·CH:CH·CH<sub>2</sub>), and 2·79 (s, C<sub>6</sub>H<sub>5</sub>); m/e 304 (48%), 219 (75), and 91 (100).

(b) In toluene. The procedure (a) gave heptadeca-2,9diene-4,6-diyn-1-ol, its tosylate, and 1-tolylheptadeca-2,9-diene-4,6-diyne (VI;  $R = MeC_6H_4$ ), m/e 318 (90%), 233 (100), 105 (94), and 91 (90).

(c) In carbon tetrachloride. The procedure (a) gave only the primary alcohol and its tosylate.

Reaction of Heptadeca-2,9-diene-4,6-diyn-1-ol (VI; R = OH) with Toluene-p-sulphonic Acid in Benzene.—The procedure just described gave a small conversion (10—15%) into hepta-2,9-diene-4,6-diyn-1-yl tosylate (VI; R = p-TsO) and 1-phenylheptadeca-2,9-diene-4,6-diyne (VI; R = Ph), identified by comparison with the previous products.

Oct-1-ene-4,6-divn-3-ol (VII).—Pentadiyne 13 (1.92 g., 0.03 mole) in ether (15 ml.) was added dropwise to an ethereal solution of ethylmagnesium bromide (0.035 mole)[from ethyl bromide (3.8 g.) and magnesium (0.84 g.)] and heated under reflux for 2 hr. under nitrogen. Acraldehyde  $(2\cdot 3 \text{ g}_{\cdot,0}, 0\cdot 05 \text{ mole})$  in ether  $(10 \text{ ml}_{\cdot,0})$  was then slowly added, and the mixture was kept at  $20^{\circ}$  overnight. Isolation with ether and chromatography gave oct-1-ene-4,6diyn-3-ol (1.38 g., 38%) as an oil which did not crystallise, and partially decomposed on distillation at 0.1 mm.;  $\lambda_{\rm max}$  255 (z 300), 241 (400), and 228 (400) nm.;  $\nu_{\rm max}$  (film) 3540, 3350, 1070 (OH), 2220 (C:C), 1632, 985, and 935 (CH:CH<sub>2</sub>) cm.<sup>-1</sup>;  $\tau$  (CCl<sub>4</sub>) 8.05 (d, J 1 Hz, CH<sub>3</sub>·C:C), 5.18 (m, CH·OH),  $4\cdot 4$ — $4\cdot 9$  (m, CH:CH<sub>2</sub>), and ca.  $4\cdot 1$  (ddd, J 17, 9, and 5 Hz, CH·CH:CH<sub>2</sub>); m/e 120 (8%) and 91 (100)

Reaction of Oct-1-ene-4,6-diyn-3-ol with Toluenep-sulphonic Acid in Benzene.—By the procedure described for heptadeca-1,9-diene-4,6-diyn-3-ol, oct-1-ene-4,6-diyn3-ol (50 mg.) and toluene-*p*-sulphonic acid (500 mg.) in benzene (100 ml.) gave *cis/trans-oct-2-ene-4*,6-*diyn-1-ol* (VIII; R = OH) (8 mg.), identified by comparison with authentic *trans*-isomer (see later), oct-2-ene-4,6-diyn-1-yl tosylate (VIII; R = *p*-TsO) (8 mg.), which when shaken with dilute hydrochloric acid gave the parent alcohol, and 1-*phenyloct-2-ene-4*,6-*diyne* (VIII; R = Ph) (12 mg.), which was estimated to be a mixture of 70% *trans-* and 30% *cis-*isomers,  $\lambda_{max}$  284 ( $\varepsilon$  15,000), 268 (17,500), 254 (11,500), and 240 (7 $\partial$ 00) nm;  $\nu_{max}$  2325, 2130, 2035 (CiC), 953 (*trans*-CH:CH), 780, 740, and 955 (Ph) cm.<sup>-1</sup>;  $\tau$  (CCl<sub>4</sub>) 8·02 (s, CH<sub>3</sub>·CiC), 6·56 (d, *J* 7 Hz, CH<sub>2</sub>·CH:CH-*trans*), 6·35 (d, *J* 8 Hz, CH<sub>2</sub>·CH:CH-*cis*), *ca.* 4·5br (d, *J* 16 Hz, CiC·CH:CH-*trans*), *ca.* 4·5br (d, *J* 10 Hz, CiC·CH:CH-*cis*), *ca.* 3·8 (m, CH<sub>2</sub>·CH:CH-*cis*), 3·63 (dt, *J* 16 and 7 Hz, CH<sub>2</sub>·CH:CH-*trans*), and 2·83 (s, Ph); *m/e* 180 (39%) and 165 (100).

trans-Oct-2-ene-4,6-diyn-1-ol.—1-Bromopropyne (600 mg., 0.005 mole) in methanol (5 ml.) was added dropwise to a stirred mixture of trans-pent-2-en-4-yn-1-ol (410 mg., 0.005 mole), aqueous ethylamine (6 ml., 40%), cuprous chloride (30 mg.), hydroxylamine hydrochloride (1.0 g.), and methanol (2 ml.) under nitrogen. After 30 min. stirring the product was isolated with ether and chromatographed to give trans-oct-2-ene-4,6-diyn-1-ol (480 mg.), m.p. 64—65° (from ether-light petroleum) (lit.<sup>14</sup> gives only  $\lambda_{max}$  in MeOH) (Found: C, 80.25; H, 6.75. C<sub>8</sub>H<sub>8</sub>O requires C, 80.0; H, 6.65%),  $\lambda_{max}$ . 281 ( $\varepsilon$  14,800), 265 (17,800), 252 (12,900), 239 (5900), and 230 (2000) nm.;  $\nu_{max}$ . 3600 (OH), 2238, 2030 (CiC), and 950 (trans-CH:CH) cm.<sup>-1</sup>;  $\tau$  (CDCl<sub>3</sub>) 8.05 (s, CH<sub>3</sub>·CiC), 5.88 (d, J 5 Hz, CH<sub>2</sub>-CH:CH), 4.30 (d, J 16 Hz, CiC·CH:CH), and 3.70 (dt, J 16 and 5 Hz, CH:CH<sub>2</sub>).

1-Phenyloct-2-ene-4,6-diyne (VII; R = Ph).—Hexa-2,4diynal <sup>15</sup> (92 mg., 0.001 mole) in ether (15 ml.) was added dropwise to an ethereal solution of  $\beta$ -phenylethylmagnesium bromide [0.005 mole; from  $\beta$ -phenylethyl bromide (980 mg.) and magnesium (120 mg.)] under nitrogen. After 30 min. stirring the product was isolated and chromatographed to give 1-phenylocta-4,6-diyn-3-ol,  $\lambda_{max}$ . (ether) 256 (rel. E 0.56), 242 (1.00), and 230 (0.83) nm.

The alcohol was dissolved in carbon tetrachloride (50 ml.) and heated under reflux with toluene-*p*-sulphonic acid (300 mg.) for 30 min. to give, after chromatography, 1-*phenyloct-2-ene-4*,6-*diyne* (VIII; R = Ph) (60 mg.), which did not crystallise (Found: C, 92.95; H, 7.05.  $C_{14}H_{12}$  requires C, 93.3; H, 6.65%). Estimation by n.m.r. indicated 75% *cis-* and 25% *trans-*isomers.

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<sup>&</sup>lt;sup>13</sup> J. B. Armitage, E. R. H. Jones, and M. C. Whiting, *J. Chem. Soc.*, 1952, 1993.

<sup>&</sup>lt;sup>14</sup> F. Bohlmann and P. Herbst, Chem. Ber., 1958, 91, 1631.

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