253. *Acetylenic Compounds Related to Stilbœstrol. Part III.*[1,2] *Acetylenic Alcohols derived from α-Alkyldeoxyanisoins, and the α-Alkyl-β-ethynylstilbenes.*

By C. W. Shoppee, J. Cymerman Craig, and Ruth E. Lack.

Deoxyanisoin, and its α-methyl and α-ethyl analogues, condense with ethynylmagnesium bromide to give the expected acetylenic alcohols in good yield. The product obtained from α-ethyldeoxyanisoin is the diastereoisomer of that reported as formed on use of sodium acetylide in dioxan.

Dehydration of the acetylenic alcohol (I; R = R′ = H) from deoxyanisoin by either acetic anhydride or phosphorus trichloride in pyridine gave the *trans*-stilbene (II; R = H) in good yield. The α-methyl analogue (I; R = Me, R′ = H) with phosphorus tribromide in chloroform gave by cyclisation the indene (V), accompanied by a Meyer–Schuster rearrangement to the αβ-unsaturated ketone (VII; R = Me). This ketone was also obtained when phosphorus trichloride in pyridine was used, together with the chloroallene (XIII; R = Me), but attempted dehydration by methanolic sulphuric acid yielded the methyl ether (I; R = R′ = Me) and the αβ-unsaturated aldehyde (VIII; R = Me) formed by a Rupe rearrangement.

The α-ethyl analogue (I; R = Et, R′ = H) with phosphorus trichloride in pyridine afforded the αβ-unsaturated ketone (VII; R = Et) (Meyer–Schuster reaction) and the chloro-allene (XIII; R = Et), which was dehydrohalogenated by sodamide in liquid ammonia to the *trans*-stilbene (II; R = Et). The stilbene was also obtained as an amorphous hydrate, believed from spectroscopic evidence to be the *cis*-isomer.

The acetylenic diol (I; R = OH, R′ = H) with phosphorus trichloride in pyridine gave an indene (XX) by cyclisation and rearrangement of an intermediate dichloro-allene, and also the 1,3-diketone (XXI), formed by ketonisation of the dienol resulting from a Meyer–Schuster reaction. The mechanism of the latter rearrangement is discussed.

Although deoxyanisoin condenses normally with hex-1-yne and propyne *via* the Grignard reagent,[1] reaction with sodium or lithium acetylide in liquid ammonia results in molecular fission to give *p*-anisic acid, *p*-anisamide, and 1-*p*-methoxyphenylprop-2-ynol. Similar

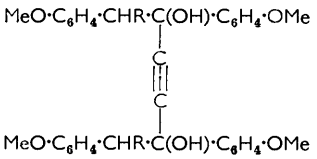
[1] Cymerman Craig, Martin, Moyle, and Wailes, *Austral. J. Chem.*, 1956, **9**, 373, is regarded as Part I of this series.

[2] Cymerman Craig, Moyle, Rowe-Smith, and Wailes, *Austral. J. Chem.*, 1956, **9**, 391, is regarded as Part II of this series.

fission had earlier been found [2] on attempted condensation of benzil or benzoin with the same reagent. The desired acetylenic alcohol (I; R = R′ = H) has, however, been isolated in low yield after prolonged reaction of the ketone with acetylenedimagnesium bromide at 20°. Attempts to increase the yield by carrying out the reaction under reflux gave a product identified by synthesis as 2-methoxy-6-*p*-methoxyphenylnaphthalene.[1]

(I) $MeO\cdot C_6H_4\cdot CHR\cdot C(OR')(C{\equiv}CH)\cdot C_6H_4\cdot OMe$

(II) $MeO\cdot C_6H_4\cdot CR{=}C(C{\equiv}CH)\cdot C_6H_4\cdot OMe$



(III)

Condensation of deoxyanisoin [3] with ethynylmagnesium bromide [4] gave an excellent yield of a product which, after separation from a trace of the dienyne, 1,2,5,6-tetra-*p*-methoxyphenylhexa-1,5-dien-3-yne,[1] was treated with Girard reagent P to remove unchanged ketone. Chromatography of the non-ketonic fraction yielded approximately equal amounts of the acetylenic ether (I; R = H, R′ = Et), formed by etherification of the parent alcohol during the Girard separation, the vinylacetylene (II; R = H) and the alcohol (I; R = R′ = H), identical with the material previously obtained.[1] The vinylacetylene (II; R = H) had the spectral properties of a *trans*-stilbene, and in ethanolic solution was isomerised to the *cis*-compound by ultraviolet light. When heated, it readily dimerised, as shown by a molecular-weight determination (Rast); a normal value for the monomer was obtained by the cryoscopic technique.

When the reaction was carried out for a shorter period and the mixture was worked up by means of methanol, without treatment with Girard's reagent, chromatography afforded the corresponding methyl ether (I; R = H, R′ = Me), unchanged deoxyanisoin, and the alcohol (I; R = R′ = H). Some of the diol (III; R = H) was also obtained. The ethers (I; R = H, R′ = Et and Me respectively) were identical with samples prepared from the parent alcohol with ethanol and methanol, respectively, by acid-catalysis.

When α-methyldeoxyanisoin was prepared by the method of Dodds, Golberg, Lawson, and Robinson,[5] the product had m. p. 43°; these authors reported a value of 53—57° for their material. The two crystalline modifications (we are indebted to Dr. R. I. Cox for the sample, m. p. 53°) showed essentially identical infrared spectra. Reaction of this ketone with ethynylmagnesium bromide gave a small amount of the diol (III; R = Me) and an excellent yield of the alcohol (I; R = Me, R′ = H).

α-Ethyldeoxyanisoin had the m. p. reported by Wilds and Biggerstaff,[6] and condensed readily with ethynylmagnesium bromide to yield a trace of the diol (III; R = Et) and, as the main product, the amorphous alcohol (I; R = Et, R′ = H), which gave correct analytical figures and eventually crystallised as a hydrate, m. p. 43°, shown from its infrared spectrum to be intramolecularly hydrogen-bonded. When this preparation was repeated under heat-wave conditions of unusually low humidity (<15%) and high temperature (39—42°), this alcohol was obtained as a solid, m. p. 105°, showing ultraviolet absorption identical with that of the hydrate.

Hofstetter and Wilder Smith [7] reported the preparation of the alcohol (I; R = Et, R′ = H) as a solid, m. p. 95°, by interaction of the ketone with sodium acetylide in dioxan. The ultraviolet absorption spectrum of their compound (for which we are indebted to Dr. E. Hofstetter) was substantially identical with that of our material, m. p. 105°, but a mixed m. p. showed a depression to 80—83°.

These isomers were shown to be the two possible diastereoisomeric racemates by

[3] Carter, Cymerman Craig, Lack, and Moyle, *J.*, 1959, 476.
[4] Jones, Skatteböl, and Whiting, *J.*, 1956, 4765.
[5] Dodds, Golberg, Lawson, and Robinson, *Proc. Roy. Soc.*, 1939, *B*, **127**, 140.
[6] Wilds and Biggerstaff, *J. Amer. Chem. Soc.*, 1945, **67**, 789.
[7] Hofstetter and Wilder Smith, *Helv. Chim. Acta*, 1953, **36**, 1706.

catalytic hydrogenation: for the hydrate of m. p. 43° afforded 3,4-di-*p*-methoxyphenylhexan-3-ol, m. p. 83°, while Hofstetter and Wilder Smith's [7] compound of m. p. 95° gave the isomeric saturated alcohol, m. p. 115°. Both forms of this hexanol have been obtained by Wilds and Biggerstaff [6] from α-ethyldeoxyanisoin with ethylmagnesium bromide. It is interesting that the reaction of this ketone with ethynylmagnesium bromide should lead entirely to the diastereoisomer of m. p. 105°, while reaction with sodium acetylide in dioxan [7] gave rise to an oil from which only the material of m. p. 95° could be obtained crystalline. That this oil consisted of a mixture of the two possible racemates was shown by its catalytic hydrogenation [7] to a mixture of the stereoisomeric di-*p*-methoxyphenylhexanols, identical with that obtained by Dodds, Golberg, Lawson, and Robinson.[5] The reason for this is undoubtedly to be sought in the steric inhibition to attack of the bulky ethynylmagnesium bromide–tetrahydrofuran complex on the ketone group of α-ethyldeoxyanisoin, itself strongly enveloped by the hindering α-ethyl group, and thus spatially equivalent to a phenyl t-butyl ketone, known to be sterically retarded towards normal Grignard addition.

Anisoin readily reacted with an excess of ethynylmagnesium bromide, to give the diol (I; R = OH, R′ = H), together with some of the tetrol (III; R = OH).

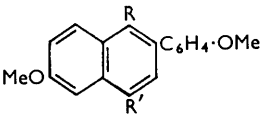
The ultraviolet absorption spectra of the alcohols of types (I) and (III) exhibited, as expected, $\lambda_{max.}$ 230 mμ (ε *ca.* 20,000) and 275 mμ (ε *ca.* 3000), characteristic of the 4-methoxybenzyl alcohol chromophore, as in 1,2-di-*p*-methoxyphenylethanol.[2]

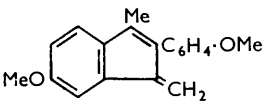
The alcohol (I; R = R′ = H) was unaffected by treatment with potassium hydrogen sulphate in toluene at 130°, whilst the use of the same reagent at 210° for 30 seconds gave only an insoluble polymer. Acetic anhydride at 100° for 2 hr. was ineffective, but at 130° after 0·75 hr. the vinylacetylene (II; R = H) was obtained in 50% yield. By doubling the reaction time this yield was raised to 65%, but 20% of polymer and 20% of unchanged alcohol were also obtained; increase of the reaction period to 3 hr. reduced the yield of stilbene to 33% and increased that of polymer to 40%, no alcohol being recovered. The ease of polymerisation of the product indicated the need for a low-temperature dehydration method, and use of phosphorus trichloride in pyridine at 20° readily gave an excellent yield of the stilbene (II; R = H), which showed light absorption ($\lambda_{max.}$ 219 and 329 mμ) identical with that of the related *trans*-stilbenes previously reported.[1] On irradiation it was transformed into the *cis*-isomer ($\lambda_{max.}$ 221 and 308 mμ) with reduced intensity of the longer-wavelength band; similar *trans* ⟶ *cis* changes have been previously noted for stilbene derivatives.[2,8,9]

The alcohol (I; R = Me, R′ = H) was unchanged by acetic anhydride at 140° for 2 hr., but treatment with phosphorus tribromide in chloroform at 0° produced two substances. The first product, m. p. 85°, had the composition and molecular weight of the stilbene (II; R = Me) but was yellow and had an infrared spectrum devoid of absorption in both of the regions associated with the C≡CH and C=C groupings. Earlier work [1] on the alcohol (I; R = R′ = H) gave an unexpected cyclisation product, 2-methoxy-6-*p*-methoxyphenylnaphthalene (IV; R = R′ = H), but analogous formulation of the compound, m. p. 85°, as (IV; R = Me, R′ = H) was excluded by the absence of the three ultraviolet absorption peaks characteristic of a 2-phenylnaphthalene.[1] The compound showed intense absorption at 905 cm.$^{-1}$ characteristic of the vinylidene group, and this, together with its colour, indicated cyclisation in the alternative way to give 6-methoxy-2-*p*-methoxyphenyl-3-methyl-1-methyleneindene (V); on recrystallisation and heating to 70°, the material was transformed into a high-melting colourless substance of unchanged composition, no longer absorbing in the vinylidene region. A similar cyclisation has been reported by Hofstetter and Wilder Smith,[10] who found that the related vinyl alcohol (VI) with dehydrating agents gave 3-ethyl-6-methoxy-2-*p*-methoxyphenyl-1-methylindene.

[8] Haddow, Harris, Kon, and Roe, *Phil. Trans.*, 1948—1949, *A*, **241**, 147.
[9] Lewis, Magel, and Lipkin, *J. Amer. Chem. Soc.*, 1940, **62**, 2973.
[10] Hofstetter and Wilder Smith, *Helv. Chim. Acta*, 1953, **36**, 1949.

The second product was the αβ-unsaturated ketone (VII; R = Me), identified by its infrared absorption at 1650 cm.$^{-1}$ and its 2,4-dinitrophenylhydrazone, and derived from the alcohol (I; R = Me, R′ = H) by a Meyer–Schuster rearrangement.[11]

(IV) 



(V)

$MeO{\cdot}C_6H_4{\cdot}CHEt{\cdot}C(OH)(CH{=}CH_2){\cdot}C_6H_4{\cdot}OMe$ (VI)

$MeO{\cdot}C_6H_4{\cdot}CR{=}C(COMe){\cdot}C_6H_4{\cdot}OMe$ (VII)

On treatment with methanolic sulphuric acid at 70°, the alcohol (I; R = Me, R′ = H), gave the methyl ether (I; R = R′ = Me), exhibiting light absorption identical with the ether (I; R = H, R′ = Me) and with the alcohols (I; R′ = H). A second product, isomeric with the ketone (VII; R = Me), was the αβ-unsaturated aldehyde (VIII; R = Me), formed from the alcohol (I; R = Me, R′ = H) by the Rupe rearrangement;[12] its analogue (VIII; R = Et) was obtained by Hofstetter and Wilder Smith[10] from the alcohol (I; R = Et, R′ = H). The mechanism of this rearrangement has been postulated[13] to be anionotropic change of the system (IX; X = OH) *via* the allenic carbonium ion (X) to the allenic enol (XI; X = OH), which tautomerises to give the αβ-unsaturated aldehyde (XII).

(VIII) $MeO{\cdot}C_6H_4{\cdot}CHR{\cdot}C(=CH{\cdot}CHO){\cdot}C_6H_4{\cdot}OMe$

(IX) $X{\cdot}CRR'{\cdot}C{\equiv}CH$ $\quad CRR'{=}C{=}CH^+$ (X)

(XI) $CRR'{=}C{=}CHX$ $\quad CRR'{=}CH{\cdot}CHO$ (XII)

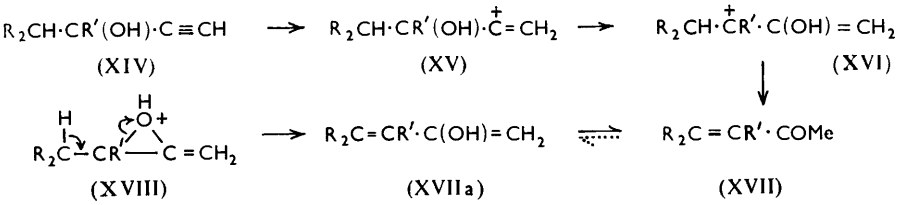
(XIII) $MeO{\cdot}C_6H_4{\cdot}CHR{\cdot}C(=C{=}CHCl){\cdot}C_6H_4{\cdot}OMe$

With phosphorus trichloride in pyridine at 20° the alcohol (I; R = Me, R′ = H) gave the chloro-allene (XIII; R = Me), showing intense absorption at 1920 cm.$^{-1}$ characteristic of the allene group, in agreement with the known lowering of the frequency of the allenic absorption band from its normal position (1950 cm.$^{-1}$) to 1900—1930 cm.$^{-1}$ when conjugated.[14,15] The formation of the chloro-allene (XIII; R = Me) provides a further example of the ready rearrangement of the system (IX; X = Cl or OH) to the allene (XI; X = Cl);[16] and similar allenic halides have recently been isolated.[17] The αβ-unsaturated aldehyde (VIII; R = Me) was not found, but a second product was the αβ-unsaturated ketone (VII; R = Me), previously obtained from the alcohol (I; R = Me, R′ = H) by use of phosphorus tribromide and formed by a Meyer–Schuster rearrangement.

This reaction[11] had been earlier postulated to proceed by a dehydration-hydration mechanism,[18] but this suggestion is made untenable by Newman's demonstration[19] that conversion of the system (XIV) into (XVII) may be carried out at room temperature in the presence of sulphonated polystyrene (Dowex 50) as source of hydrogen ions, in conditions under which neither hydration of the triple bond nor dehydration of tertiary alcohols occurred.

[11] Meyer and Schuster, *Ber.*, 1922, **55**, 819.
[12] Rupe, *Helv. Chim. Acta*, 1926, **9**, 672; 1928, **11**, 449, 656, 965; 1931, **14**, 708.
[13] MacGregor, *J. Amer. Chem. Soc.*, 1948, **70**, 3953.
[14] Celmer and Solomons, *J. Amer. Chem. Soc.*, 1953, **75**, 1372.
[15] Oroshnik, Mebane, and Karmas, *J. Amer. Chem. Soc.*, 1953, **75**, 1050.
[16] Favorski and Favorskaya, *Compt. rend.*, 1935, **200**, 839; Favorskaya, *J. Gen. Chem.* (*U.S.S.R.*), 1939, **9**, 386, 1237; 1942, **12**, 638; 1948, **18**, 52; Favorskaya and Favorskaya, *ibid.*, 1940, **10**, 451; Favorskaya and Zakharova, *ibid.*, 1940, **10**, 446; Nagibina, *ibid.*, 1940, **10**, 427; Hennion, Sheehan, and Maloney, *J. Amer. Chem. Soc.*, 1950, **72**, 3542; Hennion and Maloney, *ibid.*, 1951, **73**, 4735.
[17] Ford, Thompson, and Marvel, *J. Amer. Chem. Soc.*, 1935, **57**, 2619; Favorskaya, *J. Gen. Chem.* (*U.S.S.R.*), 1940, **10**, 461; Jacobs and Brill, *J. Amer. Chem. Soc.*, 1953, **75**, 1314; Jacobs, Teach, and Weiss, *ibid.*, 1955, **77**, 6254.
[18] Hennion, Davis, and Maloney, *J. Amer. Chem. Soc.*, 1949, **71**, 2813.
[19] Newman, *J. Amer. Chem. Soc.*, 1953, **75**, 4740.

Newman [19] proposed a mechanism involving a 1,2-hydroxyl shift in an initially formed conjugate acid (XV) to the enolic carbonium ion (XVI), which eliminates a proton from the adjacent carbon atom and ketonises to yield the product (XVII). Such 1,2-hydroxyl shifts are, however, unknown, and we prefer to formulate this step as occurring through an intermediate epoxide oxonium salt (XVIII), readily formed by nucleophilic attack of the hydroxyl group in (XV) on the adjacent carbonium carbon atom; the oxide undergoes ring-fission with simultaneous loss of a proton directly to furnish the enolic form (XVIIa) of (XVII).



The alcohol (I; R = Et, R′ = H) was unchanged in refluxing acetic anhydride for 2 hr., but with phosphorus trichloride in pyridine at 0° gave the chloro-allene (XIII; R = Et), showing infrared absorption at 1920 cm.$^{-1}$, and the αβ-unsaturated ketone (VII; R = Et), previously obtained by Hofstetter and Wilder Smith [10] on attempted dehydration of the alcohol (I; R = Et, R′ = H) under acidic conditions (the 2,4-dinitrophenylhydrazones were identical).

When the chloro-allene (XIII; R = Et) was treated with a suspension of sodamide in liquid ammonia which still contained unchanged sodium, dehydrohalogenation was accompanied by reduction to give the known *meso*- and racemic isomers [20] of 3,4-di-*p*-methoxyphenylhexane, and the partially reduced 3,4-di-*p*-methoxyphenylhex-1-yne, showing light absorption in agreement with this structure. From its m. p. range the latter is probably a mixture of the two possible diastereoisomeric racemates.

Repetition of the experiment with precautions to ensure the absence of unconverted sodium gave an excellent yield of the stilbene (II; R = Et), m. p. 125°, $\lambda_{max.}$ 223 mμ (ε 14,600) and 284 mμ (ε 12,200). The slight bathochromic shift of the former, and the very marked hypsochromic shift and reduced intensity of the latter, maximum, compared with those of the compound (II; R = H), are characteristic of αβ-dialkyl-substituted stilbenes,[8,21] in which steric repulsions largely destroy the coplanarity of the chromophoric system.

After having been kept in sunlight for several weeks, a dilute ethanolic solution of the compound (II; R = Et) showed $\lambda_{max.}$ 226, 242, and 277 mμ (ε 21,300, 24,700, and 9900 respectively). The displacement of the long- and short-wavelength maxima are in agreement with the known *trans* ⟶ *cis* conversion.[1,8,9] The new maximum at 242 mμ, however, is reminiscent of the peak (247 mμ) reported by Buckles [22] to result from the irradiation of dilute ethanolic solutions of *cis*- and *trans*-stilbene and ascribed by him to the formation of phenanthrene, which was isolated and identified. Similar absorption maxima in the 250 mμ region were observed for *cis*-stilbene derivatives by Braude.[21] Such a cyclisation may occur, in the sterically favourable *cis*-isomer, by a photochemical reaction resulting in the loss of two hydrogen atoms to produce a diradical which stabilises itself by bond formation between the two adjacent aromatic rings.

The stilbene (II; R = Et) was also obtained as an amorphous hydrate, m. p. 90—92°, showing infrared absorption characteristic of a hydrogen-bonded hydroxyl group. When the chloro-allene was prepared from Hofstetter and Wilder Smith's isomer,[7] m. p. 95°,

[20] Buu-Hoï, Ng, and Hoán, *J. Org. Chem.*, 1949, **14**, 1023; Schmelkes, U.S.P. 2,385,472/1945; *Chem. Abs.*, 1946, **40**, 176.

[21] Braude, *J.*, 1949, 1902; Oki, *Bull. Chem. Soc. Japan*, 1953, **26**, 37, 161, 331; Grundy, *Chem. Rev.*, 1957, **57**, 281; Miquel, *Tetrahedron*, 1960, **8**, 205.

[22] Buckles, *J. Amer. Chem. Soc.*, 1955, **77**, 1040.

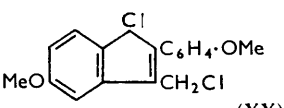
of the alcohol (I; R = Et, R′ = H) (for which we are indebted to Dr. E. Hofstetter) and treated with sodamide in liquid ammonia, the same hydrate, m. p. 90—93°, was obtained. Its ultraviolet absorption ($\lambda_{max.}$ 228, 275 mμ; ε = 21,000 and 8000) was essentially that of the irradiation product of the *trans*-stilbene (II; R = Et), m. p. 125°; the hydrate, m. p. 90—92°, is therefore regarded as the *cis*-isomer of this stilbene. It is clear that if the formation of the stilbene proceeds *via* the intermediate chloro-allene (XIII; R = Et), then both diastereoisomeric racemates of the alcohol (I; R = Et, R′ = H) are capable of furnishing the same form of the dehydration product (II; R = Et), as observed. Catalytic hydrogenation of the stilbene (II; R = Et) gave the known mixture of isomers of 3,4-di-*p*-methoxyphenylhexane, identical with that previously obtained and with an authentic sample.

The ethynyldiol (I; R = OH, R′ = H) from anisoin was unchanged on prolonged treatment with an excess of methylmagnesium iodide, known to act as a dehydrating agent.[23] It was converted by phosphorus trichloride in pyridine into a colourless substance possessing no hydroxylic, acetylenic, or ketonic function in its infrared spectrum; analysis showed this to contain two chlorine atoms, and it is presumably a cyclisation product of the intermediate dichloro-allene (XIX). Its ultraviolet spectrum ($\lambda_{max.}$ 254, 322 mμ; ε = 12,500 and 26,000) does not agree with the naphthalene structure (IV; R = R′ = Cl)

(XIX) MeO·C$_6$H$_4$·CHCl·C(=C=CHCl)·C$_6$H$_4$·OMe

(XXI) MeO·C$_6$H$_4$·CO·CH(COMe)·C$_6$H$_4$·OMe

(XXII) MeO·C$_6$H$_4$·C(OH)=C[C(OH)=CH$_2$]·C$_6$H$_4$·OMe



(XX)

which would show absorption resembling that of its parent compound (IV; R = R′ = H) with the expected bathochromic shift due to the halogen. The long-wavelength maximum indicates a conjugated system resembling that of a *trans*-stilbene, and from its stability and lack of colour it may be the indene derivative (XX), produced by migration into conjugation of the exocyclic double-bond first formed on cyclisation of the dichloro-allene (XIX). Similar indene derivatives, exhibiting ready migration of the central ethylenic linkage,[10] have been obtained from dienœstrol [24] and shown to have light absorption resembling that of *trans*-stilbene.[25] The observed bathochromic shift of the low-wavelength maximum in (XX) may be due to hyperconjugation by the two allylic chlorine atoms. A second product was the β-diketone (XXI), $\nu_{max.}$ 1720 (CO) and 1650 cm.$^{-1}$ (C=C–C=O), previously obtained [2] by reaction of α-bromodeoxyanisoin with sodium acetylide in ammonia, giving a bis-2,4-dinitrophenylhydrazone and with hydroxylamine yielding deoxyanisoin oxime; the diketone arises by Meyer–Schuster rearrangement of the diol (I; R = OH, R′ = H), and subsequent ketonisation of the dienol (XXII).

Experimental

Ultraviolet absorption spectra were determined for 95% EtOH solutions on a Hilger " Unispek " instrument; infrared spectra were measured on a Perkin–Elmer " Infracord " spectrophotometer, and m. p.s on a Kofler block.

1,2-*Di*-p-*methoxyphenylbut*-3-*yn*-2-*ol* (I; R = R′ = H).—(*a*) A solution of ethylmagnesium bromide, prepared from magnesium (4·8 g.) in tetrahydrofuran (140 c.c.), was added in 1 hr. to a saturated solution of acetylene in tetrahydrofuran (80 c.c.) at 0° (Jones, Skatteböl, and

[23] Jacquemain, *Compt. rend.*, 1934, **198**, 483; Brachin, *Bull. Soc. chim. France*, 1906, **35**, 1177; Wilson and Hyslop, *J.*, 1923, 2612.

[24] Lane and Spialter, *J. Amer. Chem. Soc.*, 1951, **73**, 4408; Hausmann and Wilder Smith, *Nature*, 1948, **161**, 892; *J.*, 1949, 1030.

[25] Solmssen, *J. Amer. Chem. Soc.*, 1943, **65**, 2370.

Whiting [4]). Deoxyanisoin [3] (25·6 g.) was added and the mixture was heated under reflux for 18 hr. After addition of saturated ammonium chloride solution and acidification with sulphuric acid, the product was extracted into ether. On evaporation of the solvent, 1,2,5,6-tetra-*p*-methoxyphenylhexa-1,5-dien-3-yne separated as yellow prisms, m. p. 226° (1·63 g.), mixed m. p. with authentic sample [1] 226°. To remove unchanged deoxyanisoin the residual red oil was treated with Girard P reagent (24 g.) in absolute alcohol (240 c.c.) and acetic acid (24 g.) for 1 hr. at 100°, poured on ice (2·5 l.) containing potassium carbonate (24·84 g.), and extracted into benzene. The resulting oil was adsorbed from hexane on to aluminium oxide (500 g.). Elution with hexane (5 × 500 c.c.) gave 3-*ethoxy*-3,4-*di*-p-*methoxyphenylbut*-1-*yne* (I; R = H, R′ = Et) (9·76 g.), m. p. 70° [Found (after drying at 20°/0·5 mm. for 5 hr.): C, 77·6; H, 7·3; O, 15·7; active H, 0·3%; *M*, 310. $C_{20}H_{22}O_3$ requires C, 77·4; H, 7·15; O, 15·5; 1 active H, 0·3%; *M*, 289], $\nu_{max.}$ 3260 (C≡CH), 2115 (C≡C) cm.$^{-1}$, $\lambda_{max.}$ 230, 275 mμ (ε 19,500 and 3300 respectively).

Further elution with 1 : 4 benzene–hexane (8 × 500 c.c.) gave 1,2-*di*-p-*methoxyphenylbut*-1-*en*-3-*yne* (II; R = H), m. p. 85° (from hexane) (7·8 g.) [Found (after drying at 20°/0·5 mm. for 3 hr.): C, 81·6; H, 6·2; O, 12·2; active H, 0·37%; *M* (Rast), 567; *M* (depression of f. p. of benzene) 262. $C_{18}H_{16}O_2$ requires C, 81·8; H, 6·1; O, 12·1; 1 active H, 0·37%; *M*, 264], $\nu_{max.}$ 3240 (C≡CH), 2080 (C≡C) cm.$^{-1}$, $\lambda_{max.}$ 219, 329 mμ (ε 19,500 and 28,800 respectively). After the solution had been in the sun for several hr. it had $\lambda_{max.}$ 221, 308 mμ (ε 25,700 and 20,800 respectively).

Elution with ether (3 × 500 c.c.) gave 1,2-di-*p*-methoxyphenylbut-3-yn-2-ol (I; R = R′ = H) (7·64 g.), m. p. 95° (from benzene–hexane) (lit.,[1] 95°) [Found (after drying at 20°/0·5 mm. for 3 hr.): C, 76·5; H, 6·4; O, 16·7; active H, 0·68%; *M* (Rast), 267. Calc. for $C_{18}H_{18}O_3$: C, 76·55; H, 6·4; O, 17·0; 2 active H, 0·71%; *M*, 282], $\nu_{max.}$ 3440 (OH), 3230 (C≡CH), 2115 (C≡C) cm.$^{-1}$, $\lambda_{max.}$ 230, 275 mμ (ε 20,450 and 3225 respectively).

(*b*) A second experiment carried out by refluxing the Grignard reactants for 6 hr., decomposing the complex with ammonium chloride, acidifying the mixture with sulphuric acid, and extracting it with ether gave a red oil. This was dissolved in a little methanol, leaving a white insoluble material, m. p. 180—184°. Recrystallisation from acetone gave 1,2,5,6-*tetra*-p-*methoxyphenylhex*-3-*yne*-2,5-*diol* (III; R = H), m. p. 194—195° (5·63 g.) [Found (after drying at 20°/0·5 mm. for 3 hr.): C, 75·7; H, 6·3; active H, 0·37; OMe, 22·0. $C_{34}H_{34}O_6$ requires C, 75·8; H, 6·35; 2 active H, 0·37; OMe, 23·2%], $\nu_{max.}$ 3480 (OH), 2050 (C≡C) cm.$^{-1}$, $\lambda_{max.}$ 228, 275 mμ (ε = 18,100 and 3030 respectively). After removal of the methanol, the residual oil was adsorbed on a column of aluminium oxide (500 g.). Elution with pentane (200 c.c.) gave 3-*methoxy*-3,4-*di*-p-*methoxyphenylbut*-1-*yne* (I; R = H, R′ = Me) (3·0 g.), m. p. 62° (from pentane) [Found (after drying at 20°/0·5 mm. for 3 hr.): C, 76·8; H, 6·6; O, 16·1; OMe, 28·7; active H, 0·27. $C_{19}H_{20}O_3$ requires C, 77·0; H, 6·8; O, 16·2; OMe, 31·2; 1 active H, 0·3%], $\nu_{max.}$ 3230 (C≡CH), 2110 (C≡C) cm.$^{-1}$, $\lambda_{max.}$ 230, 275 mμ (ε 19,800 and 2780 respectively). Further elution with 1 : 4 hexane–benzene gave deoxyanisoin (10·5 g.), m. p. and mixed m. p. 111°. Elution with ether gave 1,2-di-*p*-methoxyphenylbut-3-yn-2-ol (I; R = R′ = H) (2·4 g.), m. p. 95° undepressed with the sample prepared as in (*a*) above.

3-*Ethoxy*-3,4-*di*-p-*methoxyphenylbut*-1-*yne* (I; R = H, R′ = Et).—1,2-Di-*p*-methoxyphenylbut-3-yn-2-ol (I; R = R′ = H) (500 mg.) and ethanol (10 c.c.) were treated with conc. sulphuric acid (2 drops) for 1 hr. at 80°. After neutralisation of the acid and evaporation the residual oil was adsorbed from hexane on aluminium oxide (10 g.). Elution with pentane gave 3-ethoxy-3,4-di-*p*-methoxyphenylbut-3-yne (I; R = H, R′ = Et) (120 mg.), m. p. and mixed m. p. 68—69°.

3-Methoxy-3,4-di-*p*-methoxyphenylbut-1-yne, similarly prepared by reaction in methanol at 65°, had m. p. and mixed m. p. 59—61°.

α-*Methyldeoxyanisoin.*—α-Methyldeoxyanisoin was prepared in 68·5% yield by the method of Dodds, Golberg, Lawson, and Robinson,[5] from deoxyanisoin (25·6 g.), methyl iodide (14·2 g.), and sodium (2·3 g.) in alcohol (50 c.c.), followed by further sodium (2·3 g.) in alcohol (50 c.c.). It formed prisms (from hexane), m. p. 43° [Found (after drying at 20°/0·5 mm. for 3 hr.): C, 75·3; H, 6·7. Calc. for $C_{17}H_{18}O_3$: C, 75·5; H, 6·7%]. The infrared spectrum for this material was essentially identical with that of a sample of m. p. 52—53°, kindly provided by Dr. R. I. Cox. Dodds *et al.*[5] report m. p. 53—57°.

3,4-*Di*-p-*methoxyphenylpent*-1-*yn*-3-*ol* (I; R = Me, R′ = H).—A solution of ethylmagnesium bromide (from magnesium, 2·43 g.) in dry tetrahydrofuran (60 c.c.) was added in 1 hr. to a

saturated solution of acetylene in tetrahydrofuran (50 c.c.) at 0°. α-Methyldeoxyanisoin (13·6 g.) was then added and the mixture was refluxed for 18 hr. The Grignard complex was extracted with ether, decomposed with ammonium chloride, acidified with sulphuric acid, and washed with sodium hydrogen carbonate solution. On partial evaporation of the solvent a white solid, m. p. 204—209°, separated; recrystallisation from acetone gave 2,3,6,7-*tetra*-p-*methoxyphenyloct*-4-*yne*-3,6-*diol* (III; R = Me) (2·68 g.), m. p. 217° [Found (after drying at 20°/0·5 mm. for 3 hr.): C, 76·15; H, 6·8; O, 17·1; active H, 0·4%; *M* (Rast), 656. $C_{36}H_{38}O_6$ requires C, 76·30; H, 6·8; O, 16·95; 2 active H, 0·35%; *M*, 567], $\nu_{max.}$ 3500 (OH), 2040 (C≡C) cm.$^{-1}$, $\lambda_{max.}$ 230, 275 mμ (ε 18,300 and 3120 respectively). Complete removal of the solvent from the filtrate gave a yellow solid which was adsorbed on aluminium oxide (200 g.) from hexane. Elution with benzene (3 × 250 c.c.) and ether (4 × 250 c.c.) gave 3,4-*di*-p-*methoxyphenylpent*-1-*yn*-3-*ol* (I; R = Me, R′ = H), m. p. 112—113° (from benzene–hexane) (9·74 g.) [Found (after drying at 20°/0·5 mm. for 3 hr.): C, 77·0; H, 6·8; O, 15·9; active H, 0·65%; *M* (Rast), 283. $C_{19}H_{20}O_3$ requires C, 77·0; H, 6·8; O, 16·2; 2 active H, 0·67%; *M*, 296], $\nu_{max.}$ 3470 (OH), 3220 (C≡H), 2105 (C≡C) cm.$^{-1}$, $\lambda_{max.}$ 230, 275 mμ (ε 21,950, 3020 respectively).

α-*Ethyldeoxyanisoin*.—Interaction of deoxyanisoin (90 g.), ethyl iodide (54·8 g.), sodium 8·1 g.), and alcohol (150 c.c.) by the method of Dodds, Golberg, Lawson, and Robinson [5] gave, on cooling, unchanged deoxyanisoin (47·0 g.), m. p. and mixed m. p. 111°. The filtrate was extracted with ether and the resulting oil was adsorbed on aluminium oxide (1 kg.). Elution with hexane (6 × 500 c.c.) gave α-ethyldeoxyanisoin (48 g.), m. p. 47—48°, previously given by Wilds and Biggerstaff,[6] although Dodds, Golberg, Lawson, and Robinson [5] reported it as an oil [Found (after drying at 20°/0·5 mm. for 3 hr.): C, 75·9; H, 7·05. Calc. for $C_{18}H_{20}O_3$: C, 76·05; H, 7·0%].

3,4-*Di*-p-*methoxyphenylhex*-1-*yn*-3-*ol* (I; R = Et, R′ = H).—(*a*) A solution of ethylmagnesium bromide (from magnesium, 3·66 g.) in dry tetrahydrofuran (150 c.c.) was added in 1 hr. to a saturated solution of acetylene in tetrahydrofuran (80 c.c.) at 0°. α-Ethyldeoxyanisoin (21·3 g.) was added and the mixture heated under reflux for 18 hr. Working up as above gave an oil that was adsorbed on aluminium oxide (600 g.). Successive elution with hexane (6 × 250 c.c.), 1 : 4 benzene–hexane (250 c.c.), and benzene (3 × 200 c.c.) gave amorphous 3,4-*di*-p-*methoxyphenylhex*-1-*yn*-3-*ol* (I; R = Et, R′ = H) (16·4 g.) [Found (after drying at 50°/0·5 mm. for 24 hr.): C, 77·3; H, 7·2; O, 15·6; active H, 0·62. $C_{20}H_{22}O_3$ requires C, 77·4; H, 7·1; O, 15·5; 2 active H, 0·65%], $\nu_{max.}$ 3460, 3530 (OH), 3230, 3275 (C≡CH), 2110 (C≡C) cm.$^{-1}$. This crystallised from hexane as a *hydrate*, m. p. 43° [Found (after drying at 20°/760 mm. for 48 hr.): C, 73·3; H, 7·32; active H, 0·89%; *M*, 265. $C_{20}H_{22}O_3,H_2O$ requires C, 73·2; H, 7·35; 2 active H, 0·89%; *M*, 328], $\nu_{max.}$ 3535, 3460 (OH), 3225 (C≡CH), 2110 (C≡C) cm.$^{-1}$, $\lambda_{max.}$ 230, 275 mμ (ε 20,700 and 3020 respectively). The infrared spectrum (OH bands) was unaffected by the concentrations of carbon tetrachloride solutions, indicating the hydrate to be intramolecularly bonded. Further elution with ether (3 × 500 c.c.) gave 3,4,7,8-*tetra*-p-*methoxyphenyldec*-5-*yne*-4,7-*diol* (III; R = Et), m. p. 204—205° (from acetone) [Found (after drying at 20°/0·5 mm. for 3 hr.): C, 76·4; H, 7·0; O, 16·1; active H, 0·37%; *M*, 558. $C_{38}H_{42}O_6$ requires C, 76·7; H, 7·1; O, 16·1; 2 active H, 0·34%; *M*, 594], $\nu_{max.}$ 3570 (OH) 2060 (C≡C) cm.$^{-1}$, $\lambda_{max.}$ 229, 275 mμ, (ε 22,200 and 3420 respectively).

(*b*) A second preparation on the same scale was carried out when the laboratory temperature was 39—42° with ~15% humidity. After isolation in the usual manner the product was adsorbed on aluminium oxide (600 g.). Elution with hexane (8 × 200 c.c.) gave unchanged α-ethyldeoxyanisoin (7·55 g.), m. p. 45—46°. Further elution with benzene and ether gave 3,4-*di*-p-*methoxyphenylhex*-1-*yn*-3-*ol* (I; R = Et, R′ = H), m. p. 105° (12·5 g.) [Found (after drying at 80°/0·5 mm. for 72 hr.): C, 77·1; H, 7·2; O, 16·0; active H, 0·65. $C_{20}H_{22}O_3$ requires C, 77·4; H, 7·14; O, 15·5; 2 active H, 0·65%], $\nu_{max.}$ 3500 (OH) 3275 (C≡CH), 2110 (C≡C) cm.$^{-1}$, $\lambda_{max.}$ 230, 275 mμ (ε = 19,500, 3250 respectively).

Hydrogenation of 3,4-*Di*-p-*methoxyphenylhex*-3-*yn*-2-*ol*.—(*a*) A solution of 3,4-di-*p*-methoxyphenylhex-1-yn-3-ol hydrate (200 mg.) in methanol (10 c.c.) was shaken with pre-reduced platinum oxide (40 mg.) in methanol (10 c.c.) under hydrogen (absorption, 27 c.c.). Filtration and evaporation gave 3,4-di-*p*-methoxyphenylhexan-3-ol, m. p. 83° [Found (after drying at 20°/0·5 mm. for 3 hr.): C, 76·4; H, 8·0. Calc. for $C_{20}H_{26}O_3$: C, 76·4; H, 8·3%], $\nu_{max.}$ 3570 (OH) cm.$^{-1}$, $\lambda_{max.}$ 230, 275 mμ (ε 19,000 and 3100 respectively).

(*b*) A solution of 3,4-di-*p*-methoxyphenylhex-1-yn-3-ol, m. p. 95° (100 mg.) (prepared by Hofstetter and Wilder Smith [7]), in methanol (10 c.c.) was added to a suspension of pre-reduced

platinum and hydrogenated as above (absorption, 13 c.c.). It gave 3,4-di-*p*-methoxyphenylhexan-3-ol, m. p. 115° [Found (after drying at 20°/0·5 mm. for 3 hr.): C, 76·5; H, 8·0%], $\nu_{max.}$ 3570 (OH) cm.$^{-1}$, $\lambda_{max.}$ 230, 275 mμ (ε 18,900 and 3100 respectively). The infrared absorption curves of these two diastereoisomers were almost identical. Wilds and Biggerstaff [6] isolated both isomers (*a*), m. p. 83—85° and (*b*), m. p. 114—117° after treating α-ethyldeoxyanisoin with ethylmagnesium bromide in ether.

1,2-*Di*-p-*methoxyphenylbut*-3-*yne*-1,2-*diol* (I; R = OH, R′ = H).—Ethylmagnesium bromide (from magnesium, 3·63 g.) in tetrahydrofuran (140 c.c.) was added in 1 hr. to a saturated solution of acetylene in tetrahydrofuran (80 c.c.) at 0°. Anisoin (13·6 g.) was added and the mixture was heated under reflux for 18 hr. After the usual working up, a white solid separated from the ether solution. Recrystallisation from acetone gave 1,2,5,6-*tetra*-p-*methoxyphenylhex*-3-*yne*-1,2,5,6-*tetraol* (III; R = OH), m. p. 217° (4·95 g.) [Found (after drying at 20°/5 mm. for 12 hr.): C, 71·43; H, 6·0; O, 22·1; active H, 0·69. $C_{34}H_{34}O_8$ requires C, 71·55; H, 6·0; O, 22·4; 2 active H, 0·7%], $\nu_{max.}$ 3390 (OH), 2060 (C≡C) cm.$^{-1}$, $\lambda_{max.}$ 237, 274, 280 mμ (ε 19,000, 2975, and 2550 respectively). Evaporation of the ether gave a brown oil which was adsorbed on aluminium oxide (300 g.). Elution with benzene–hexane (1 : 1; 4 × 150 c.c.) gave unchanged anisoin, m. p. and mixed m. p. 111° (5·3 g.). Further elution with benzene (2 × 75 c.c.) and ether (100 c.c.) gave 1,2-*di*-p-*methoxyphenylbut*-3-*yne*-1,2-*diol* (I; R = OH, R′ = H), m. p. 107° [Found (after drying at 20°/0·5 mm. for 8 hr.): C, 72·4; H, 6·15; O, 21·2; active H, 1·0. $C_{18}H_{18}O_4$ requires C, 72·45; H, 6·1; O, 21·45; 3 active H, 1·0%], $\nu_{max.}$ 3495, 3590 (OH), 3260 (C≡CH), 2110 (C≡C) cm.$^{-1}$, $\lambda_{max.}$ 234, 274, 280 mμ (ε 19,000, 3000, 2680 respectively).

1,2-*Di*-p-*methoxyphenylbut*-1-*en*-3-*yne* (II; R = H).—(*a*) Phosphorus trichloride (1·5 c.c.) was added to 1,2-di-*p*-methoxyphenylbut-3-yn-2-ol (500 mg.) in dry pyridine (10 c.c.) at 0°. After 15 hr. at 20° the mixture was added dropwise to ice and water (50 c.c.). Ether-extraction afforded an oil which was adsorbed from hexane on aluminium oxide (15 g.). Successive elution with hexane (2 × 50 c.c.), hexane–benzene (1 : 1; 2 × 100 c.c.), and benzene (100 c.c.) gave 1,2-di-*p*-methoxyphenylbut-1-en-3-yne (415 mg.), m. p. 82—84° (from hexane). The infrared absorption curve was identical with, and the m. p. did not depress that of, an authentic sample.

(*b*) Treatment of 1,2-di-*p*-methoxyphenylbut-3-yn-2-ol (200 mg.) with acetic anhydride (10 c.c.) at 130° for 0·75 hr. gave a yellow oil after ether-extraction; adsorption from hexane on to aluminium oxide (10 g.) and elution with hexane (100 c.c.) gave 1,2-di-*p*-methoxybut-1-en-3-yne, m. p. and mixed m. p. 85° (100 mg.).

(*c*) Treatment of 1,2-di-*p*-methoxyphenylbut-3-yn-2-ol (1·1 g.) with acetic anhydride (30 c.c.) at 130° for 1·5 hr. under nitrogen gave a brown oil after ether-extraction. This was adsorbed from hexane on aluminium oxide (30 g.). Elution with hexane (3 × 50 c.c.) gave 1,2-di-*p*-methoxyphenylbut-1-en-3-yne (684 mg.), m. p. and mixed m. p. 84°. Further elution with benzene (2 × 50 c.c.) gave a dark polymer (220 mg.); elution with ether (3 × 50 c.c.) afforded unchanged alcohol, m. p. 94° (231 mg.).

(*d*) When experiment (*c*) was repeated with a reaction time of 3 hr., the yield of stilbene was 370 mg., whilst that of the polymer increased to 455 mg. No unchanged alcohol was isolated.

Attempted Preparation of 2,3-*Di*-p-*methoxyphenylpent*-2-*en*-4-*yne* (II; R = Me).—(*a*) 3,4-Di-*p*-methoxyphenylpent-1-yn-3-ol (8·0 g.) in chloroform (10 c.c.) was treated with phosphorus tribromide (8 g.) in chloroform (10 c.c.) at 0°. After 4 hr. at 20° the mixture was cooled to 0° and poured into ice-cold ethanol, diluted with water, and extracted with ether. Evaporation of the dried ether extracts at 20° gave a yellow oil which was adsorbed from pentane on aluminium oxide (250 g.). Elution with pentane gave 6-*methoxy*-2-p-*methoxyphenyl*-3-*methyl*-1-*methyleneindene* (V) (3·87 g.), m. p. 85°, as yellow needles from methanol [Found (after drying at 20°/1 mm. for 24 hr.): C, 81·3; H, 6·6; OMe, 21·5%; *M* (f. p. in benzene), 242. $C_{19}H_{18}O_2$ requires C, 82·0; H, 6·5; OMe, 22·3%; *M*, 278], $\lambda_{max.}$ 221, 267 mμ (ε 23,000 and 37,300 respectively), no further absorption up to 350 mμ. The infrared absorption curve showed an absence of bands in the OH, C=O, C≡CH and C≡C regions but included $\nu_{max.}$ 905 cm.$^{-1}$ (C=CH$_2$). This compound would not form a 2,4-dinitrophenylhydrazone, gave a negative test with Tollens's reagent, and showed a negative iodoform reaction. Recrystallisation from methanol gave a white insoluble *substance*, m. p. 141°. After drying at 40°/0·5 mm. for 12 hr., the m. p. had increased to 245° (Found: C, 81·0; H, 6·7. $C_{19}H_{18}O_2$ requires C, 82·0; H, 6·5%), and the infrared absorption curve had no band in the region corresponding to OH, C=O, C≡CH, C≡C, and C=CH$_2$.

Further elution with benzene (3 × 150 c.c.) gave an αβ-unsaturated ketone, $\nu_{max.}$ 1650 cm.$^{-1}$ (2·5 g.), which gave the 2,4-*dinitrophenylhydrazone*, m. p. 75°, of 3,4-di-*p*-methoxyphenylpent-3-en-2-one (VII; R = Me) [Found (after drying at 20°/0·5 mm. for 24 hr.): C, 62·6; H, 5·15. $C_{25}H_{24}O_6N_4$ requires C, 63·0; H, 5·1%].

(*b*) 3,4-Di-*p*-methoxyphenylpent-1-yn-3-ol (1 g.) in dry methanol (10 c.c.) was treated with 20% sulphuric acid (2 c.c.) for 0·25 hr. at 70°. The acid was neutralised with sodium hydrogen carbonate and the product extracted into ether. The resulting oil was adsorbed from pentane on aluminium oxide (30 g.). Elution with pentane (4 × 20 c.c.) gave 3-*methoxy*-3,4-*di*-p-*methoxyphenylpent*-1-*yne* (I; R = R′ = Me) (200 mg.) as a colourless oil [Found (after drying at 20°/0·5 mm. for 24 hr.): C, 77·1; H, 7·35. $C_{20}H_{22}O_3$ requires C, 77·4; H, 7·15%], $\nu_{max.}$ 3200s (C≡CH), 2115w cm.$^{-1}$ (C≡C), $\lambda_{max.}$ 230, 275 mμ (ε 20,400 and 3450 respectively). Further elution with benzene–hexane (1 : 20; 20 c.c.) and (1 : 10; 2 × 20 c.c.) afforded a yellow oil (735 mg.), $\nu_{max.}$ 1670s cm.$^{-1}$ (C=C–C=O). This gave a positive test with Schiff's reagent, showed a negative iodoform reaction, and readily formed the 2,4-*dinitrophenylhydrazone*, m. p. 185°, of 3,4-di-*p*-methoxyphenylpent-2-enal (VIII; R = Me) as red needles from ethanol–ethyl acetate [Found (after drying at 60°/0·5 mm. for 8 hr.): C, 62·8; H, 5·0. $C_{25}H_{24}N_4O_6$ requires C, 63·0; H, 5·1%].

(*c*) Phosphorus trichloride (1·5 c.c.) in pyridine (10 c.c.) was added to 3,4-di-*p*-methoxyphenylpent-1-yn-3-ol (500 mg.) in pyridine (10 c.c.) at 0°. After 3 hr. at 20°, the mixture was added dropwise to ice and water (50 c.c.), extracted with ether, and washed with dilute sulphuric acid and sodium hydrogen carbonate solution. Evaporation afforded an oil which was adsorbed from pentane on aluminium oxide (15 g.). Elution with pentane (3 × 20 c.c.) yielded 1-chloro-3,4-di-*p*-methoxyphenylpenta-1,2-diene (XIII; R = Me) as a colourless oil (250 mg.) giving a positive Beilstein test, $\nu_{max.}$ 1920s, 1890w cm.$^{-1}$ (C=C=C), $\lambda_{max.}$ 224, 278 mμ (ε 18,100 and 14,900 respectively). Further elution with benzene (3 × 50 c.c.) gave a yellow oil (120 mg.) containing a mixture of the chloro-allene and an αβ-unsaturated carbonyl compound, $\nu_{max.}$ 1920m, 1890w, 1650m cm.$^{-1}$. This oil formed the 2,4-dinitrophenylhydrazone, m. p. 75°, of 3,4-di-*p*-methoxyphenylpent-3-en-2-one (VII; R = Me) which did not depress the m. p. of the sample described in (*a*).

3,4-*Di*-p-*methoxyphenylhex*-3-*en*-1-*yne* (II; R = Et).—(*a*) Phosphorus trichloride (30 c.c.) in pyridine (20 c.c.) was added dropwise to 3,4-di-*p*-methoxyphenylhex-1-yn-3-ol (m. p. 105°) (10 g.) in pyridine (200 c.c.) at −40°. After 4 hr. at 0° the mixture was poured slowly on ice and water (1 l.). Ether-extraction afforded a product which was adsorbed from pentane on neutral aluminium oxide (300 g.). Elution with pentane (8 × 50 c.c.) and pentane–ether (1 : 20; 5 × 50 c.c.) gave 1-chloro-3,4-di-*p*-methoxyphenylhexa-1,2-diene (XIII; R = Et) (5·92 g.), $\nu_{max.}$ 1920s, 1890s cm.$^{-1}$ (C=C=C), n_D^{25} 1·607, which was not further purified before use in the following experiment. Further elution with ether (6 × 50 c.c.) gave an oil (3·2 g.) consisting of a mixture of the chloro-allene and an αβ-unsaturated carbonyl compound, $\nu_{max.}$ 1920m, 1890w, 1650m cm.$^{-1}$, that formed the 2,4-dinitrophenylhydrazone, m. p. 80—82°, of 3,4-di-*p*-methoxyphenylhex-3-en-2-one [Found (after drying at 20°/0·5 mm. for 24 hr.): C, 63·5; H, 5·4. Calc. for $C_{26}H_{26}N_4O_6$: C, 63·7; H, 5·35%]. This sample did not depress the m. p. of a sample, m. p. 75—80°, obtained from Hofstetter and Wilder Smith.[10]

(*b*) Finely powdered ferric nitrate (50 mg.) and sodium (0·25 g.) were added to a stirred solution of ammonia (200 c.c.) at −35°. Further sodium (3 g.) was added in small pieces followed after 0·5 hr. by 1-chloro-3,4-di-*p*-methoxyphenylhexa-1,2-diene (4·0 g.) in dry ether (10 c.c.). After the mixture had been stirred at −35° for 1 hr., ether (50 c.c.) and ammonium chloride)3 g.) were added. Evaporation of the ammonia and extraction into ether gave a yellow product which was adsorbed from hexane on aluminium oxide (100 g.). Elution with hexane (5 × 30 c.c.) and benzene–hexane (1 : 20, 2 × 30 c.c.) gave 3,4-di-*p*-methoxyphenylhexane (3·1 g.), m. p. 133—145° [Found (after drying at 60°/0·5 mm. for 4 hr.): C, 80·35; H, 8·6. Calc. for $C_{20}H_{26}O_2$: C, 80·5; H, 8·8%], $\lambda_{max.}$ 230, 275 mμ (ε 21,400 and 3530 respectively). The infrared spectrum showed no band in the OH, C≡CH, C≡C, and C=O regions. Two isomers are reported [20] to have m. p. 133° and 144°. Further elution with ether–hexane (1 : 20; 30 c.c.) gave an oil which crystallised from methanol to give 3,4-*di*-p-*methoxyphenylhex*-1-*yne*, m. p. 25—30° [Found (after drying at 20°/0·5 mm. for 4 hr.): C, 81·3; H, 8·0. $C_{20}H_{22}O_2$ requires C, 81·6; H, 7·6%], $\nu_{max.}$ 3240m (C≡CH), 2080w cm.$^{-1}$ (C≡C), $\lambda_{max.}$ 228, 278 mμ (ε 19,550 and 3420).

(*c*) To stirred ammonia (500 c.c.) at −35° was added ferric nitrate (100 mg.) and sodium

(1·5 g.) in small pieces. No blue colour of dissolved sodium remained after 0·5 hr. but the mixture was stirred for a further 1·5 hr., then 1-chloro-3,4-di-*p*-methoxyphenylhexa-1,2-diene (1·5 g.) in ether (25 c.c.) was added dropwise at −40°. After 0·5 hr. the usual working up gave an oil, $\nu_{max.}$ 3240m (C≡CH) and 2080w cm.$^{-1}$ (C≡C), which was adsorbed from pentane on aluminium oxide (40 g.). The product was not eluted with pentane or benzene but ether–benzene (1 : 20; 7 × 25 c.c.) gave a yellow oil (1·04 g.), $\nu_{max.}$ 3240m (C≡CH), 2080w cm.$^{-1}$ (C≡C). Rechromatography gave 3,4-*di*-p-*methoxyphenylhex*-3-*en*-1-*yne* (II; R = Et) (400 mg.), m. p. 125°, as needles from methanol [Found (after drying at 20°/0·5 mm. for 3 hr.): C, 81·75; H, 6·9. $C_{20}H_{20}O_2$ requires C, 82·15; H, 6·9%], $\nu_{max.}$ 3240m (C≡CH), 2080w cm.$^{-1}$ (C≡C), $\lambda_{max.}$ 223, 284 mμ (ε 14,600 and 12,200 respectively). After 4 weeks in sunlight this absorption had changed to $\lambda_{max.}$ 226, 242, 277 mμ (ε 21,320, 24,760, and 9900 respectively). The oily fractions of the stilbene gradually crystallised and had m. p. 125° after several days.

(*d*) In a preliminary experiment, 1-chloro-3,4-di-*p*-methoxyphenylhexa-1,2-diene (500 mg.) was added to sodamide prepared from sodium (1 g.) and ammonia (100 c.c.) as described in (*c*). Ether-extraction gave a reddish-brown oil, giving a negative Beilstein test, which was absorbed from pentane on aluminium oxide (10 g.). Elution with pentane and benzene gave only oils (130 mg.), $\nu_{max.}$ 3250w (C≡CH) and 1650m cm.$^{-1}$ (C=C–C=O); further elution, with ether–benzene (1 : 5; 2 × 20 c.c.), gave a yellow oil (300 mg.), $\nu_{max.}$ 3250s (C≡CH), 2115w cm.$^{-1}$ (C≡C). Addition of pentane to its solution in ether precipitated cis-3,4-*di*-p-*methoxyphenylhex*-3-*en*-1-*yne hydrate*, m. p. 90—92° as a yellow amorphous solid [Found (after drying at 20°/0·5 mm. for 2 hr.): C, 77·3; H, 6·95. $C_{20}H_{20}O_2,H_2O$ requires C, 77·4; H, 7·15%], $\nu_{max.}$ 3400m (OH), 3240m (C≡CH), 2080vw cm.$^{-1}$ (C≡C), $\lambda_{max.}$ 228, 275 mμ (ε 20,800 and 8000 respectively). A mixed m. p. with the alcohol,[7] m. p. 95—97° (for which we are indebted to Dr. E. Hofstetter), was depressed to 70—75°.

(*e*) Repetition of the above experiment but with 1-chloro-3,4-di-*p*-methoxyphenylhexa-1,2-diene (500 mg.) prepared from 3,4-di-*p*-methoxyphenylhex-1-yn-3-ol, m. p. 95—97° (Hofstetter and Wilder Smith [7]), gave an identical product, m. p. 90—93°.

Hydrogenation of 3,4-*Di*-p-*methoxyphenylhex*-1-*en*-3-*yne*.—3,4-Di-*p*-methoxyphenylhex-1-en-3-yne (70 mg.), m. p. 125°, in ethyl acetate (20 c.c.) with pre-reduced Adams catalyst (15 mg.) absorbed 18 c.c. of hydrogen at 25°/760 mm. in 40 min. Complete hydrogenation of the stilbene to 3,4-di-*p*-methoxyphenylhexane requires 17·5 c.c. Filtration and evaporation gave a yellow oil which was absorbed from pentane on aluminium oxide (2 g.). Elution with pentane (2 × 25 c.c.) gave 3,4-di-*p*-methoxyphenylhexane (51 mg.), m. p. 133—144°, which did not depress the melting point of an authentic sample.[20]

Attempted Dehydration of 1,2-*Di*-p-*methoxyphenylbut*-3-*yne*-1,2-*diol*.—(*a*) Phosphorus trichloride (2·0 c.c.) was added to 1,2-di-*p*-methoxyphenylbut-3-yne-1,2-diol (500 mg.) in dry pyridine (10 c.c.) at 0°. After 3 hr. at 20° the mixture was added dropwise to ice and water (50 c.c.). Ether-extraction afforded a colourless material crystallising from ethanol to give 1-*chloro*-3-*chloromethyl*-5-*methoxy*-2-p-*methoxyphenylindene* (XX), m. p. 114° (210 mg.) [Found (after drying at 20°/0·5 mm. for 4 hr.): C, 64·75; H, 5·05. $C_{18}H_{16}Cl_2O_2$ requires C, 64·5; H, 4·8%], $\lambda_{max.}$ 254, 322 mμ (ε 12,480 and 26,000 respectively) with end-absorption at 210 mμ (ε 18,000). The infrared spectrum showed no band in the OH, C≡CH, C≡C, and C=O regions. The mother-liquors were evaporated and the resulting oil was adsorbed from pentane on aluminium oxide (10 g.). Elution with pentane (2 × 20 c.c.) gave a further quantity of the indene, m. p. 114° (50 mg.). Further elution with benzene–pentane (1 : 5; 2 × 20 c.c.) and benzene (2 × 20 c.c.) gave an oil (150 mg.), $\nu_{max.}$ 1720 (C=O) and 1650 cm.$^{-1}$ (C=C–C=O), affording the hydrated *bis*-2,4-*dinitrophenylhydrazone* of 1,2-di-*p*-methoxyphenylbutane-1,3-dione as needles (from ethanol), m. p. 254° [Found (after drying at 20°/0·5 mm. for 12 hr.): C, 53·1; H, 4·6. $C_{30}H_{26}O_{10}N_8,H_2O$ requires C, 53·25; H, 4·2%]. Treatment of the oil with hydroxylamine hydrochloride and sodium hydroxide for 1 hr. gave deoxyanisoin oxime, m. p. 120—121° [Found (after drying at 20°/0·5 mm. for 8 hr.): C, 71·0; H, 6·35. Calc. for $C_{16}H_{17}NO_3$: C, 70·8; H, 6·3%]. A mixed m. p. with an authentic specimen [2] was undepressed.

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Organic Chemistry Department,
The University of Sydney.

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