

## Studies Related to Naturally Occurring Acetylene Compounds

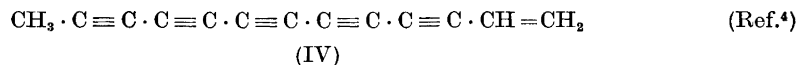
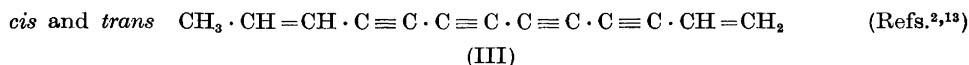
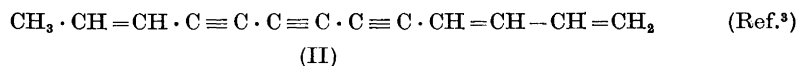
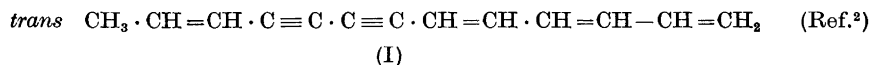
XXVII. The Synthesis of a Mixture of Trideca-1:3:11-triene-5:7:9-triyne (II) and *trans* 1-phenylhepta-1:3-diyn-5-ene (V). A Novel Cyclisation Reaction

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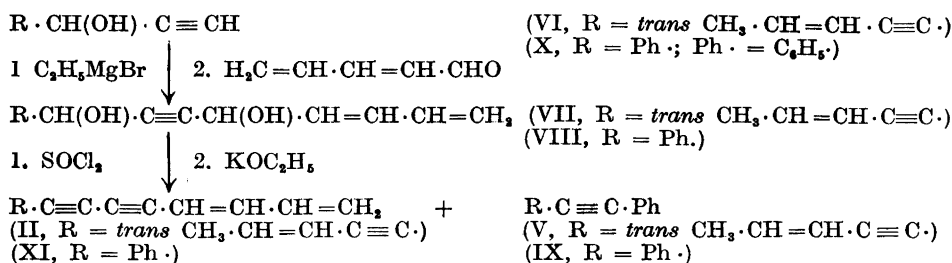
A synthesis of (II) is described which unexpectedly also yielded some (V). The cyclisation leading to (V) was confirmed by the isolation of diphenylacetylene (IX) from a similar reaction starting with 1-phenylocta-5:7-dien-2-yne-1:4-diol (VIII). A mechanism for this novel cyclisation reaction is briefly discussed.

A number of aliphatic and aromatic polyacetylenic hydrocarbons have been isolated from higher plants<sup>1</sup>. Among these are a series of straight chain C<sub>13</sub> compounds, isolated from some members of the family *Compositae*:



The structures of (I)<sup>5</sup>, (II)<sup>6</sup>, (III)<sup>7</sup> and (IV)<sup>7</sup> have been confirmed by synthesis but the preparation of (II) has only been reported since the present work was started. This paper describes a different approach to the synthesis of this compound which resulted in a mixture of (II) and *trans* 1-phenylhepta-1:3-diyn-5-ene (V). The latter also occurs naturally<sup>3</sup>, accompanying (II) in a number of *Coreopsis* species.

The following sequence of reactions was expected to yield (II):



2:4-Pentadienal was prepared from 2:3-dihydropyran \* according to Woods and Sanders <sup>8</sup>, and the aldehyde was shown to be the *trans* isomer by infrared spectroscopy. *trans* Octa-6-ene-1:4-diyne-3-ol (VI) was prepared according to Jones, Skatteböl and Whiting <sup>7</sup>. The Grignard reaction between these compounds gave the corresponding glycol (VII) as a crystalline compound in 27 % yield, m.p. 65—67°. The yield of crude material was considerably higher but losses occurred during the careful purification. The ultraviolet absorption maximum at 2 260 Å showed that no anionotropic rearrangement had taken place, and that structure (VII) was correct. This was confirmed by infrared measurements which also indicated that the double bonds had the *trans* configuration.

The subsequent chlorination with thionyl chloride and dehydrochlorination with potassium ethoxide at —40° gave a small amount of a liquid product, which was purified by chromatography on alumina. The ultraviolet spectrum of the petroleum-ether eluate was practically identical with that of (II) <sup>3,6</sup> as far as the long wavelength maxima were concerned (Fig. 1). The infrared spectrum, however, showed some bands at 1 493, 753 and 687 cm<sup>-1</sup> which indicated the presence of some aromatic contaminant. The product was distilled under high-vacuum and the distillate gave surprisingly an absorption in ultraviolet light (Fig. 1) similar to that of *trans* 1-phenylhepta-1:3-diyne-5-ene (V) <sup>3</sup>. The infrared spectrum was also very similar to that of (V). It seemed probable that a cyclisation had taken place in the dehydrochlorination step.

Chromatography of the distillation residue eventually gave a liquid which, from ultraviolet and infrared spectra, consisted mainly of (II). Because of the very small amounts available, a serious attempt to separate this mixture was not made. The mixture did not give an adduct with maleic anhydride in benzene and illumination with daylight, in the presence of iodine, produced small hypsochromic shift (25—30 Å) of the ultraviolet absorption maxima. These results together with a band at 716 cm<sup>-1</sup> in the infrared spectrum are in accordance with a *cis* configuration about the double bond at the 3-position in (II). However, the presence of the *trans* isomer was not excluded, and the mixture consisted probably of these two isomers and some (V). The start-

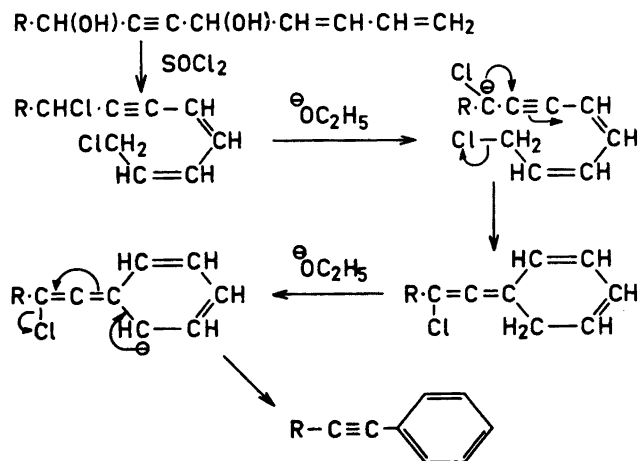
\* We are indebted to Dr. R. D. Smith and E. I. duPont de Nemours and Company for a generous gift of 2:3-dihydropyran.



to separate diphenylacetylene from the mixture by chromatography were not wholly successful, as only enriched fractions were obtained. However, when a sample was left in air at room temperature for some hours, chromatography gave a small amount of a colourless crystalline substance, m.p. 57°, in all respects identical with an authentic sample of diphenylacetylene<sup>9</sup>.


Isolation of the second main product, *viz.* 1-phenylocta-1:3-diyne-5:7-diene (XI), was not attempted as it was expected to be rather tedious and was little interest to this work.

The mechanism of this cyclisation reaction can be visualized in the following way:



The anionotropic rearrangement in the chlorination step would be expected to give a mixture of *cis* and *trans* isomers, by analogy with previous results obtained with similar compounds<sup>11</sup>. The *cis* isomer is sterically favourable for a cyclisation, which would subsequently lead to the formation of a benzene derivative. The scheme given here for the actual dehydrochlorination step is certainly dubious, as the general mechanism for this very fast elimination reaction is not known.

This cyclisation is the more interesting as the two compounds (II) and (V) have been isolated from the same plants, *viz.* some *Coreopsis* species. One cannot exclude the possibility that the benzene derivative (V) is formed by cyclisation of the dienyne system of (II), but it seems more reasonable that they both derive from a common precursor. The resemblance between the

two substances  $\text{Ph} \cdot \text{CH}_2\text{C} \equiv \text{C} \cdot$   and



isolated<sup>12</sup> from *Carlina vulgaris*, and



isolated<sup>2</sup> from some *Coreopsis* species, is also of considerable interest in this connection.

## EXPERIMENTAL

All melting points are uncorrected. The ultraviolet absorption data were obtained in ethanol, unless otherwise stated, using a Beckman, Model DK recording spectrophotometer. A Perkin Elmer instrument, Model 21, was used for the infrared measurements. The carbon and hydrogen determinations were carried out by Alfred Bernhardt, Mülheim, Ruhr, Germany.

*trans Octa-6-ene-1:4-diyne-3-ol (VI)* was prepared in Manchester<sup>7</sup> from hex-4-en-2-yn-1-ol and ethynylmagnesium bromide.

*Penta-2:4-dienal* was prepared according to Wooes and Sanders<sup>8</sup>, in 25 % overall yield from 2:3-dihydropyran.

*trans Trideca-1:3:11-triene-6:9-diyne-5:8-diol (VII)*. A solution of *trans octa-6-ene-1:4-diyne-3-ol (VI)*, 5.8 g in tetrahydrofuran (10 ml), was added during 30 min to an ice-cooled solution of ethylmagnesium bromide, prepared from magnesium (2.4 g) in tetrahydrofuran (60 ml). After 1.5 h at room temperature, freshly distilled pentadienal (1.5 g) in tetrahydrofuran (5 ml) was added with stirring and ice-cooling. The reaction mixture was then left with stirring at room temperature for 4 h and decomposed with a saturated aqueous solution of ammonium chloride. Extraction with ether, and evaporation of the solvents gave a dark-coloured liquid which was purified by chromatography on deactivated alumina (5 % of 10 % acetic acid). The glycol was eluted with ether and rechromatographed under the same conditions. The light yellow liquid obtained, was dissolved in ether-petroleum-ether, and after standing at  $-25^{\circ}$  gave some crystals. Recrystallisation from the same solvent yielded the glycol (970 mg, 27 %), m.p. 65–67° (Found: C 76.7; H 6.8. Calc. for  $C_{13}H_{14}O_2$ ; C 77.20; H 6.98). Ultraviolet absorption:  $\lambda_{\max}$  2 260 Å,  $\epsilon = 43\ 000$ . The infrared spectrum (in nujol): 3 300 (O–H), 2 210 (C≡C), 1 605 (C=C), 948 (C=C–H), 983 and 923  $cm^{-1}$  (C=CH–H).

*Trideca-1:3:11-trien-5:7:9-triyn-5-ene (II)* and *trans 1-phenylhepta-1:3-diyne-5-ene (V)*. The glycol (VII, 880 mg) was dissolved in dry ether (3 ml) and cooled in an ice-bath. Thionyl chloride (1 ml) was added with stirring and the reaction mixture left for 2 h. Ether and excess thionyl chloride were evaporated off under vacuum, and the residue dissolved in 10 ml of dry ether. This solution was added with stirring to potassium ethoxide, prepared from potassium (1.5 g) in dry ethanol (25 ml), and cooled to  $-40^{\circ}$ . The reaction mixture was left while the temperature rose to  $-10^{\circ}$  (30 min). Addition of water and isolation with ether gave a dark-coloured liquid which was purified by chromatography on alumina. With petroleum ether a product was eluted, which after further chromatography was obtained as a light yellow oil with the following absorption maxima in ultraviolet light: 3 665, 3 525, 3 410, 3 275, 3 190 and 2 995 Å (Fig. 1). The infrared spectrum (liq.) showed bands at 752 and 688  $cm^{-1}$ , characteristic of a substituted benzene ring, in addition to bands expected for the aliphatic hydrocarbon (II).

Part of the mixture was high-vacuum distilled, and a light yellow liquid was obtained at 40–45° (bath temperature)/ $10^{-5}$  mm. The ultraviolet spectrum resembled that of the naturally occurring substance (V)<sup>9</sup> (Fig. 1). The infrared spectrum (liq.) had the following main absorption maxima: 3 060 (ar. C–H), 2 870 (C–H), 2 190 (C≡C), 1 630 (C=C), 1 600, 1 493, (ar. C=C), 1 445 (–CH<sub>3</sub>), 995, 940, 922 (C=C–H), 753, 687 (ar. C–H), 716  $cm^{-1}$  (C=C–H). Except for the fairly weak band at 716  $cm^{-1}$  the spectrum was almost identical with that of (V).

*Isomerisation*. Part of the mixture, dissolved in hexane with a few crystals of iodine, was placed in daylight for some hours. The ultraviolet maxima were shifted 25–30 Å to shorter wavelengths.

*trans 1-Phenylocta-5:7-diene-2-yne-1:4-diol (VIII)* was prepared in the same way as for (II) above, by condensing 1-phenylprop-2-yne-1-ol (X, 13.2 g) with pentadienal (8.2 g). The reaction time in this experiment was 13 h. Chromatography and recrystallisation from ether-petroleum-ether yielded the glycol, (2.90 g, 14 %), m.p. 75–76°. (Found: C 78.61; H 6.66. Calc. for  $C_{14}H_{14}O_2$ ; C 78.48; H 6.59). Ultraviolet absorption:  $\lambda_{\max}$  2 245, 2 220 (infl.) Å.  $\epsilon = 36\ 000$  and 35 300. The infrared spectrum (in CHCl<sub>3</sub>): 3 360 (–H), 1 615 (C=C), 1 500 (ar. C=C), 1 000, 953, 905 (C=C–H), 690  $cm^{-1}$  (ar. C–H).

*Diphenylacetylene (IX)*. The glycol (VIII, 2.0 g) was dissolved in dry ether (6 ml) and cooled in an ice-bath. Thionyl chloride (2 ml) was added with stirring, and the reaction mixture left for 1 h at room temperature. Ether and excess thionyl chloride were then evapo-

rated off under vacuum, and the residue dissolved in dry ether (10 ml). Ultraviolet absorption:  $\lambda_{\max}$  2 705 Å. The solution was added dropwise to a stirred solution of potassium ethoxide, prepared from potassium (2.0 g) in ethanol (25 ml.) and cooled to  $-40^\circ$ . The mixture was stirred for 30 min, the bath-temperature being allowed to rise to  $-10^\circ$ . Addition of water and isolation with ether gave a viscous liquid which was chromatographed on alumina. A light yellow-coloured liquid was eluted with petroleum-ether 10–20 % benzene. Ultraviolet absorption:  $\lambda_{\max}$  3 665, 2 975, 2 865, 2 770, 2 625, 2 570 Å. The last fraction, presumed to be enriched in diphenyl-acetylene, was evaporated and left at room temperature for some hours. Chromatography yielded a small amount ( $\sim 3$  mg) of a crystalline substance, eluted with petroleum-ether, 20 % benzene. The compound was recrystallised from ethanol-water, m.p.  $57^\circ$ . Ultraviolet absorption  $\lambda_{\max}$  2 960, 2 870, 2 785, 2 715, 2 640 and 2 360 Å.  $\epsilon = 29\ 000, 23\ 000, 33\ 500, 25\ 500, 23\ 000$  and  $9\ 500$ , respectively. Infrared absorption (in  $\text{CCl}_4$ ): 3 100 [ar. C—H]. 1 610, 1 505, 1 450 (ar. C=C), 1 405, 1 025, 910 and  $687\ \text{cm}^{-1}$  (ar. C—H).

Authentic diphenylacetylene<sup>9</sup>, m.p.  $60^\circ$ , had the following maxima in ultraviolet light:  $\lambda_{\max}$  2 960, 2 870, 2 785, 2 715, 2 640 and 2 360 Å.  $\epsilon = 31\ 700, 23\ 600, 38\ 000, 25\ 600, 23\ 100, 8\ 600$ , respectively. The two compounds, mixed 1:1, melted at  $57-58^\circ$  and their infrared spectra were identical.

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Received August 17, 1959.