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Studies Related to Naturally Occurring Acetylene Compounds. XVIII. The Synthesis of Some Phenylacetylenes Related to *Compositae* Compounds

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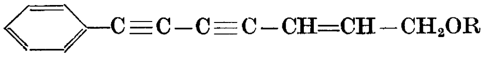
1-Phenyl-hept-5-ene-1:3-diyn-7-yl acetate (I), methyl 1-phenyl-hept-5-ene-1:3-diyn-7-oate (II) and 1-phenyl-octa-1:3:5-triyne (VII) were synthesised according to known procedures. (I) turned out to be identical with one of the acetylenic components of the essential oils of some *Coreopsis* species. (VII) showed an U.V. absorption spectrum so close to those of ene-triynes that qualitative spectroscopical separations of these chromophores are obliterated.

Some of the acetylenic compounds which occur in *Compositae* plants are present in very small amounts and so it is sometimes difficult to obtain sufficient amounts of the pure compounds for degradational experiments to establish their structure. There has in recent years accumulated a rather large body of material concerning the ultra-violet as well as the infra-red spectra of synthetic and naturally occurring acetylenic compounds which sometimes makes it possible to predict a very restricted number of possible structures from the spectroscopical data.

J. S. Sörensen and N. A. Sörensen[1] in their work on the polyacetylenes of some *Coreopsis* species isolated small amounts of a substance, m.p. 43°, which they assumed to be 1-phenyl-hept-5-ene-1 : 3-diyn-7-yl acetate (I, R = $COCH_3$)



(I)

Since this compound should be readily available by a Glaser coupling[2] of phenylacetylene with the pent-2-en-4-yn-1-ol of Heilbron *et al*[3]. this synthesis was supposed to be the easiest way to get a confirmation of the structure and at the same time to establish the unknown configuration at the double bond. As described in the experimental part the synthesis of (I, R = $COCH_3$) through the corresponding free alcohol (I, R = H) was successful. The m.p. of synthetic

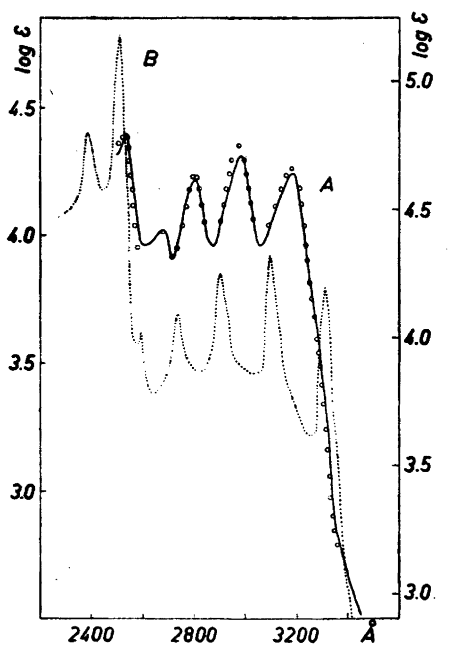
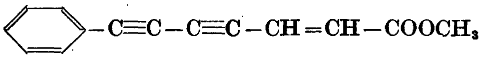


Fig. 1. Ultraviolet absorption in hexane of
A: ○ ○ ○ ○ *1-phenyl-hept-5-ene-1:3-diyne-7-ol (I), synthetic, scale left side.*
A: ———— *1-phenyl-hept-5-ene-1:3-diyne-7-ol (I), from Coreopsis, scale left side.*
B: ·········· *1-phenyl-octa-1:3:5-triyne, scale right side.*

(I, R = $COCH_3$) was found at 45—46°, mixed m.p. with the ester from *Coreopsis* 42—45°. As is seen from Fig. 1 the U.V. spectra were identical. The identity was further confirmed by mixed m.p. determination with the saponification product of the *Coreopsis* ester.

The methyl ester of the acid corresponding to the alcohol (I, R = H) was also prepared by an asymmetric Glaser coupling. This ester (II) may be regarded as a phenyl analogue of the matricaria ester (III)


(II)

$$H_3C-CH=CH-C\equiv C-C\equiv C-CH=CH-COOCH_3 \qquad \text{(III)}$$

As will be seen from Fig. 2, the similarity of the two U.V. absorption curves is rather striking. The agreement of the maxima in the long-wave band group is good; curiously enough (II) has the most pronounced fine structure. In the short-wave band group (II) has maxima at about 50 ÅU longer wavelengths than (III).

Sörensen *et al.* in the cited paper[1] transferred a liquid hydrocarbon, known to contain a monosubstituted benzene ring, into a maleic anhydride adduct with a beautiful fine structure in the UV spectrum, with maxima occurring in positions close to those of ene-triynes, represented by one of the compounds of the oil from the root of *Artemisia vulgaris*[4] (Table 1).

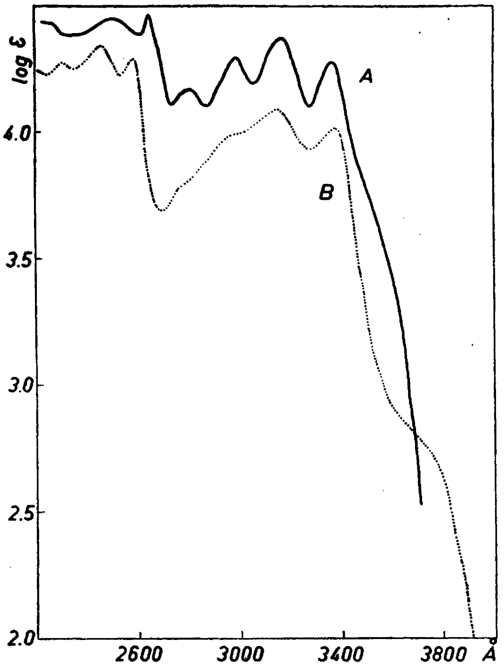


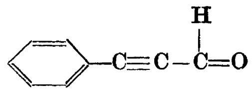
Fig. 2. Ultraviolet absorption in hexane of A: methyl 1-phenyl-hept-5-ene-1:3-diyn-7-oate (II). B: methyl deca-2:8-diene-4:6-diyn-1-oate (III).

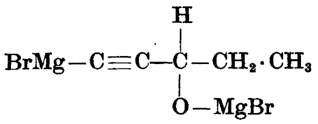
Table 1.

Found in adduct	3 317	3 105	2 920	2 750	2 605	2 450	2 327
Found in $R-(C\equiv C)_3-CH=CH-R'$	3 286	3 081	2 890	2 725	2 577	2 425	2 310
Found in $Ph-(C\equiv C)_3-CH_2-CH_3$	3 315	3 100	2 905	2 735	2 595	2 510	2 387

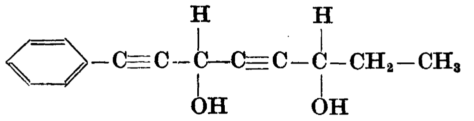
In this connection it was desired to obtain information about the UV spectrum of phenyltriynes of the type Ph—$(C\equiv C)_3$—R with R = alkyl. Since amyldiacetylene was at hand from another synthesis[5], we first tried a Glaser coupling with this substance and phenylacetylene. From the reaction mixture fractions could be isolated with UV maxima in the expected position as far as regards the weak long-wave band group. The strong short-wave band group was, however, mixed up with very sharp peaks corresponding to diamyl tetra-acetylene[5], and our efforts to separate this mixture have been without success.

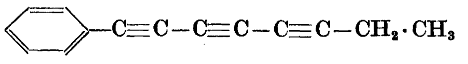
1-Phenyl-octa-1 : 3 : 5-triyne (VII) was then synthesised according to reactions worked out in Manchester for analogous reactions[6]. Phenylpropargyl aldehyde (IV) was reacted with the Grignard complex of pent-1-yn-3-ol (V) to 1-phenyl-octa-1 : 4-diyne-3 : 6-diol (VI). The dichloride of (VI) was dehydrohalogenated with potassium ethoxide according to Bohlmann[7].

(IV) 

 (V)

$$\mathrm{BrMg{-}C{\equiv}C{-}\underset{\displaystyle O{-}MgBr}{\overset{\displaystyle H}{C}}{-}CH_2{\cdot}CH_3}$$

 (VI)

 (VII)

(VII) was purified by chromatography on alumina and carefully distilled at 0.0005 mm and 60°. (VII) decomposed readily on superheating and elementary analyses were quite unsatisfactory. The constitution of the synthesised hydrocarbon, therefore, was proved by catalytical hydrogenation to 1-phenyl-*n*-octane, identical in the infra-red spectrum with authentic material.

The UV spectrum of (VII) is given in Fig. 1, curve B. The maxima come very close — as can be seen from the compilation of the data in Table 1 — to those of ene-triynes. In diacetylenes the phenyl group is spectroscopically somewhat more active than one double bond; in the tri-yne series the difference is too small for qualitative spectroscopical examinations.

EXPERIMENTAL

1-Phenyl-hept-5-ene-1:3-diyn-7-ol. Air was passed through a mixture of phenylacetylene (5 g), pent-2-en-4-yn-1-ol (4.1 g) and a solution of ammonium chloride (112.4 g), copper(I) chloride (72.5 g) and iron(III) chloride (5.9 g) in water (280 ml) for 6 ½ hours at room temperature. The reaction product was isolated with ether. The residue left after the ether had been removed was extracted with three times 100 ml of petroleum b.r. 40/70°. The material which had been extracted by the petroleum was chromatographed on de-alkalised alumina[8]. Diphenyl-diacetylene was removed by petroleum and petroleum-benzene mixtures. Elution with ether furnished an oil (0.7 g), which from petroleum afforded long, thin, colourless needles of 1-phenyl-hept-5-ene-1:3-diyne-7-ol, m.p. 71—72° (0.3 g). Light absorption maxima: 3 180, 2 980, 2 810 and 2 530 Å, ε 18 000, 24 000, 18 000 and 24 000, respectively. (Found: C 86.05; H 5.55. $C_{13}H_{10}O$ requires C 85.65; H 5.55). A mixture with the saponified compound from *Coreopsis*[1] (m. p. 71—72°) melted at 71—72°, all three samples taken at the same time. The substance was acetylated in pyridine with a large excess of acetic anhydride with standing in the refrigerator for 2 days and then 3 hours at room temperature. The *acetate* was isolated with ether and crystallised from petroleum, m. p. 45—46°, colourless plates, light abs.max. 3 185, 2 975, 2 810, 2 660, 2 535, 2 435, 2 390 and 2 320 Å, ε 15 000, 19 000, 15 500, 10 000, 31 500, 42 500, 43 000, 43 000, respectively. (Found: C 80.25; H 5.35. $C_{15}H_{12}O_2$ requires C 80.35; H 5.4.) A mixture with the *Coreopsis* compound[1] (m. p. 40—43°) melted at 42—45°, all three taken at the same time.

Methyl 1-phenyl-hept-5-ene-1:3-diyn-7-oate. The ester was prepared by oxidative coupling of phenylacetylene (8.0 g, impure) with methyl pentenynoate[3] (3.75 g) by passing air for 6 hours through a solution of ammonium chloride (76 g), copper(I) chloride (49 g) and iron(III) chloride (4.0 g) in water (190 ml). The reaction product was isolated with ether and chromatographed on de-alkalised[8] alumina. The fractions eluted with petroleum ether-benzene (1:1) and benzene were combined and crystallised from petroleum ether. The deposited yellow crystals, m. p. 42—43°, were rechromatographed carefully to remove the last traces of diphenyl diacetylene. The purest material was crystallised twice from petroleum ether. The methyl 1-phenyl-hept-5-ene-1:3-diyn-1-oate formed nearly colourless, hard crystals, m. p. 44—45° (Found: C 80.15; H 4.8. $C_{14}H_{10}O_2$ (210.2) requires C 80.0; H 4.8). Light abs. max. in hexane: 3 365, 3 150, 2 980, 2 800, 2 640, and 2 500 ÅU, ε 18 500, 22 000, 19 500, 14 000, 28 500 and 28 000, respectively.

Phenylpropargyl aldehyde. This aldehyde was prepared according to[9], with the exception that the cyclic ethylene acetal of α-bromocinnamic aldehyde was used as an intermediate instead of the diethyl acetal. It was prepared in the following way (compare[10]. We are indebted to B. Löken, Assistant Director of Development, Syntex S/A, for the details of the procedure): α-Bromocinnamic aldehyde (105 g) and ethylene glycol (25.4 g) in toluene (150 ml) were refluxed in a water determination apparatus with addition of *p*-toluenesulphonic acid (100 mg) until the theoretical amount of water (7.4 ml) had been collected. The *cyclic acetal* boiled at 168—172° at 16 mm (Found: C 74.6; H 6.1. $C_{11}H_{11}O_2Br$ (256.2) requires C 74.4; H 6.1).

1-Phenyl-octa-1:4-diyne-3:6-diol. Ethyl magnesium bromide was prepared in the customary manner from 8 g of magnesium in 100 ml of tetrahydrofuran. To the filtered solution of the Grignard compound pent-1-yn-3-ol (15 g)[11] in tetrahydrofuran (30 ml) was added drop-wise with stirring and cooling during 1 hour. The solution was refluxed for another hour. Freshly distilled phenylpropargyl aldehyde (15 g) was added to the refluxed solution, drop-wise, with stirring and cooling during one hour, heated for another hour and decomposed, whilst still warm, with ice-water and diluted sulphuric acid. The tetrahydrofuran and water layers were separated and the water solution extracted with ether (200 ml). The combined ether and tetrahydrofuran solutions were dried over sodium sulphate. Removal of the solvents, finally in a vacuum, left a viscous, orange liquid (20 g), b. p. 100° at 0.005 mm.

1-Phenyl-3:6-dichlorocta-1:4-diyne. The diol (above) (17 g) was dissolved in pyridine (15 ml) and thionyl chloride (15 ml) was added drop-wise with stirring and cooling to keep the temperature below —15°. The stirring was continued for 4 hours at room temperature, and then the reaction mixture was decomposed by addition of water. Organic material was extracted with 3 × 100 ml ether. The combined ether extracts were washed with 100 ml of 2 *N* hydrochloric acid and then with a 5 % sodium carbonate solution until neutral reaction. The ether solution was dried with magnesium sulphate. The crude reaction product (12 g) was not purified but used straight away for the following reaction.

1-phenyl-octa-1:3:5-triyne. Potassium ethoxide (from 4 g of potassium) in ethanol (100 ml) was cooled to —15 to —20° and the crude dichloride above (12 g) was added drop-wise during ½ hour (nitrogen) with stirring. Stirring was continued for 1 ½ hours, when water was added and the reaction product extracted with ether. The ether solution was dried with magnesium sulphate. The extracted material was purified by repeated chromatography on alumina. The pure *1-phenyl-octa-1:3:5-triyne* distilled at 60° and 0.0005 mm as a faintly yellow liquid (1.3 g). Light abs. max. 3 315, 3 100, 2 905, 2 735, 2 595, 2 510 and 2 385 Å, ε 16 000, 21 000, 18 000, 13 000, 10 000, 155 000, 63 000, respectively. On hydrogenation in ethanol with a palladium-on-barium sulphate catalyst 5.9 moles of hydrogen were consumed. The hydrogenation product had n_D^{20} 1.4850 (given for *n*-octylbenzene n_D^{20} 1.4851). Infra-red spectra of the hydrogenation product and of synthetic *n*-octylbenzene were identical in the 2—15 μ range.

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