Acetylenic Compounds related to "Agropyrene."

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1-Phenyloct-3-yn-2-ol was dehydrated to 1-phenyloct-1-en-3-yne. Sodium acetylide and β-phenylpropaldehyde gave 5-phenylpent-1-yn-3-ol (accompanied by 2-benzyl-5-phenylpent-2-enal). Attempted *C*-methylation of the pentynol gave only 3-methoxy-5-phenylpent-1-yne. Propynylmagnesium bromide and β-phenylpropaldehyde afforded 1-phenylhex-4-yn-3-ol, converted (either *via* 4-bromo-6-phenylhex-2-yne or directly) into 1-phenylhex-2-en-4-yne. This exhibits the properties of a conjugated vinylacetylene, and differs from " agropyrene."

Only one naturally occurring propyne derivative (" carlina oxide," 1-2′-furyl-3-phenylprop-1-yne; Rupe, Pfau, and Plattner, *Helv. Chim. Acta*, 1934, **17**, 372) was known up to 1947, when the discovery of an acetylenic hydrocarbon (" agropyrene ") in the roots of *Agropyrum repens* was announced by Treibs (*Chem. Ber.*, 1947, **80**, 97) who assigned to it the structure 1-phenylhex-2-en-4-yne (I) on the basis of oxidative degradation and hydrogenation.

As a model substance 1-phenyloct-3-yn-2-ol (II) was prepared from phenylacetaldehyde and hexynylmagnesium bromide. In the ultra-violet it showed end-absorption at 2140 Å and a low-intensity maximum at 2600 Å, similar to the spectra of substituted benzyl alcohols (Braude, Jones, and Stern, *J.*, 1947, 1087).

$CH_3{\cdot}C{\vdots}C{\cdot}CH{:}CH{\cdot}CH_2Ph$ (I) $Bu^n{\cdot}C{\vdots}C{\cdot}CH(OH){\cdot}CH_2Ph$ (II) $Bu^n{\cdot}C{\vdots}C{\cdot}CH{:}CHPh$ (III)

Dehydration by potassium hydrogen sulphate (Kuhn and Wallenfels, *Ber.*, 1938, **71**, 1889) gave 1-phenyloct-1-en-3-yne (III) which showed ultra-violet absorption maxima at 2200 and 2830 Å, at the same positions as, but with lower intensities than, the phenylbutadiene chromophore (Braude, Jones, and Stern, *loc. cit.*). Catalytic hydrogenation (platinum) afforded 1-phenyloctane, while semihydrogenation (palladium) gave 1-phenylocta-1 : 3-diene. This exhibited high-intensity absorption at 2240 and 2820 Å, in agreement with the behaviour recorded for phenylbutadiene (*idem, ibid.*); its instability was noted and, in common with these authors' experience, difficulty was encountered in obtaining correct analyses for carbon.

Condensation of sodium acetylide with β-phenylpropaldehyde was next examined. This aldehyde has been prepared in unstated yield from calcium β-phenylpropionate and calcium formate (Miller and Rohde, *Ber.*, 1890, **23**, 1080); use of the barium salts, not previously reported, gave a 7% yield only. Oxidation of 3-phenylpropan-1-ol by chromic–sulphuric acid between 20° and 50° gave 10—20% of aldehyde, accompanied by 3-phenylpropyl β-phenylpropionate, which was the main product (53%) at 10—15°. Preparation of esters by oxidation of alcohols is well known (*e.g.*, Reilly and Hickinbottom, *Proc. Roy. Soc. Dublin*, 1921, **16**, 246) but under the mild conditions employed the mechanism is probably oxidation of an intermediate hemiacetal rather than formation and subsequent esterification of the acid, as postulated by these authors.

The action of ethyl orthoformate on phenethylmagnesium bromide gave the desired aldehyde (41%) which with sodium acetylide in liquid ammonia afforded 5-phenylpent-1-yn-3-ol (IV) by steam-distillation from the bisulphite compound of the unchanged aldehyde, fractional distillation having failed to separate aldehyde and alcohol; distillation of the involatile residue gave 2-benzyl-5-phenylpent-2-enal (V), formed by aldol condensation.

Treatment of the dimagnesium bromide complex of (IV) with methyl iodide or toluene-*p*-sulphonate did not achieve the desired *C*-methylation, and the action of methyl sulphate on the disodium salt gave 3-methoxy-5-phenylpent-1-yne. No reaction occurred between (IV) and hydrochloric acid (Campbell, Campbell, and Eby, *J. Amer. Chem. Soc.*, 1938, **60**, 2882) at room temperature. Thionyl chloride afforded 77·5% of 3-chloro-5-phenylpent-1-yne, which was dehydrohalogenated in hot pyridine, estimation of chloride ion produced showing elimination of 75% of the chlorine in 3 hours. Distillation, however, gave 25% of chloro-compound as sole product; a similar treatment occupying 4 hours gave 17% of chloro-compound, and in both cases much ether-insoluble tar was produced.

Condensation of β-phenylpropaldehyde with sodiopropyne in liquid ammonia (Vaughn, Hennion, Vogt, and Nieuwland, *J. Org. Chem.*, 1937, **2**, 1) gave the required 1-phenylhex-4-yn-3-ol (VI) in only 7% yield. This alcohol showed light absorption of low intensity at

$CH{\vdots}C\cdot CH(OH)\cdot CH_2\cdot CH_2Ph$ (IV) $CH_2Ph\cdot CH_2\cdot CH{:}C(CH_2Ph)\cdot CHO$ (V) $CH_3\cdot C{\vdots}C\cdot CH(OH)\cdot CH_2\cdot CH_2Ph$ (VI)

$CH_3\cdot C{\vdots}C\cdot CHCl\cdot CH_2\cdot CH_2Ph$ (VII) $[CH_3\cdot C{\vdots}C\cdot CH(CH_2\cdot CH_2Ph)\cdot]_2O$ (VIII)

2550 Å and end-absorption at 2170 Å. Other products obtained were (V) and 1 : 8-diphenyloct-4-yn-3 : 5-diol, which was partly dehydrated at its boiling point (200—220°/0·15 mm.) as shown by analysis.

The Grignard method readily gave 1-phenylhex-4-yn-3-ol (VI) in 53% yield. This failed to react with hydrochloric acid but thionyl chloride gave 4-chloro-6-phenylhex-2-yne (VII), accompanied by an equal quantity of di-(1-phenethylbut-2-ynyl) ether (VIII), produced either by self-etherification during the reaction with thionyl chloride (cf. Heilbron, Jones, and Weedon, *J.*, 1945, 81) or during the distillation from chloro-compound and unchanged alcohol. As attempted dehydrochlorination of the chloro-compound was unsuccessful, 4-bromo-6-phenylhex-2-yne (cf. VII) was prepared by the method of Henbest, Jones, and Walls (*J.*, 1949, 2690). It showed only end-absorption in the ultra-violet. Dehydrobromination with diethylaniline resulted in a 44% yield of 1-phenylhex-2-en-4-yne (I), which exhibited light absorption in accordance with the conjugated vinylacetylene chromophore, and on hydrogenation gave 1-phenylhexane, identified by analysis and physical constants.

The physical constants obtained for (I) ($n_{\mathrm{D}}^{26\cdot5}$ 1·5510, $d^{26\cdot5}$ 0·9450) differed considerably from those reported (n_{D}^{20} 1·5695, d^{20} 0·9744) by Treibs (*loc. cit.*) for " agropyrene." Treibs states that the molecular refraction (calc. 52·6; found 52·4) shows an absence of exaltation, and therefore excludes the structure of a conjugated phenylhexa-1 : 3 : 5-triene but not that of (I), which he accordingly assigns to " agropyrene."

Vinylacetylene compounds do, however, show an exaltation of the molecular refraction, ranging from 1·1 to 1·6 units (see Johnson, " The Chemistry of the Acetylenic Compounds," Vol. I, E. Arnold, London, 1946) when refractions are calculated by using for the carbon–carbon triple bond either Eisenlohr's value (2·398; *Z. physikal. Chem.*, 1910, **75**, 604) or that of Auwers (2·325 for terminal and 2·573 for non-terminal acetylenes; *Ber.*, 1935, **68**, 1635). However, re-calculation of the molecular refractivities of 17 vinylacetylenes (Anzilotti and Vogt, *J. Amer. Chem. Soc.*, 1939, **61**, 572) from the recent data of Jeffery and Vogel (*J.*, 1948, 674) and Vogel (*J.*, 1948, 1842) employing the values of 2·35 for non-terminal and 1·977 for terminal acetylenic bonds, gave the figures shown in Table 1; the exaltation produced by the vinylacetylene grouping thus has an average magnitude of 1 unit.

Calculation of the molecular refraction of (1) with the same figures gave a value of 52·02; the molecular refraction of synthetic (I) was 52·82, corresponding to an exaltation of 0·8 unit, in reasonable agreement with that observed for other vinylacetylene compounds. Treibs's value (52·4) for " agropyrene " implies an exaltation of 0·38 unit; no spectrographic data were published by him, nor has it so far been possible to obtain details of the ultra-violet spectrum of natural " agropyrene."

Dehydration of 1-phenylhex-4-yn-3-ol with potassium hydrogen sulphate gave a 36% yield of (I), possessing properties in excellent agreement with those of the material obtained from the bromo-compound. In the preparation of (1) by dehydration or dehydrobromination, the normal reaction is one of *trans*-elimination requiring hydroxyl or bromine, the two carbon atoms, and hydrogen to lie in one plane for elimination to take place (Dhar, Hughes, Ingold, Mandour, Maw, and Woolf, *J.*, 1948, 2093). The synthetic product (which can in this case possess either a *cis*- or a *trans*-ethylenic structure) is, from stability considerations, probably the *trans*-olefin. Irradiation of a solution of synthetic (I) with ultra-violet light caused a 33% diminution in the intensity of the absorption maxima at 2280 and

2340 Å, with the simultaneous appearance of a new low intensity maximum at 2850 Å. On storage of the irradiated solution in the dark partial reversion was noted, the intensities of these maxima reaching 75% of the original values. This behaviour is characteristic of photo-conversion of the *trans-* into *cis*-isomer, which then reverts to the *trans*-form (cf., *inter al.*, Cook, Jones, and Polya, *J.*, 1939, 1315; Sandoval and Zechmeister, *J. Amer. Chem. Soc.*, 1947, **69**, 553.) Many naturally occurring compounds possess a *cis*-ethylenic structure and it is possible that " agropyrene " is the *cis*-isomer of (I). The molecular refractions observed by Campbell and Eby (*J. Amer. Chem. Soc.*, 1941, **63**, 2684) for seven pairs of *cis-* and *trans*-olefins show the *trans*-isomer, in every case, to have a value for $[R_L]_D$ (on the average) 0·14 unit higher than that of the corresponding *cis*-compound. The effect of *cis–trans*-isomerism on the magnitude of the exaltation in a vinylacetylene system does not appear to have been investigated.

TABLE 1.—*Ultra-violet absorption in 95% ethanol.*

Substance	$\lambda_{max.}$ (Å)	$\varepsilon_{max.}$
1-Phenyloct-3-yn-2-ol (II)	2600	250
	2150 *	2,950
1-Phenylhex-4-yn-3-ol (VI)	2490	500
	2540	550
	2590	550
	2170 *	3,100
1-Phenylbut-2-en-1-ol [1]	2510	450
	2580	450
4-Bromo-6-phenylhex-2-yne (cf. VII)	2220 *	3,400
1-Phenylhex-2-en-4-yne (I)	2280	15,200
	2350 †	14,500
	2550 †	800
Dec-3-en-5-yn-2-ol [2]	2260	16,000
	2350 †	15,000

Substance	$\lambda_{max.}$ (Å)	$\varepsilon_{max.}$
1-Phenyloct-1-en-3-yne (III)	2200	15,750
	2230 †	15,250
	2830	16,250
	2950	11,500
	2150 *	16,000
1-Phenylocta-1 : 3-diene	2240	14,500
	2330	9,000
	2710	19,000
	2820	25,000
	2860	20,000
	3030	6,000
1-Phenylbuta-1 : 3-diene [1]	2230	12,000
	2330	8,500
	2710	28,000
	2800	28,300
	2900	27,000
	3050	6,000

* End absorption. † Inflexion.

[1] Braude, Jones, and Stern, *J.*, 1947, 1087. [2] Heilbron, Jones, and Raphael, *J.*, 1943, 264.

TABLE 2.—*Molecular refraction of vinylacetylenic compounds.*

Substance	$[R_L]_D$ Found	$[R_L]_D$ Calc.	Exaltation
Hex-5-en-3-yn-2-ol	30·20	29·21	0·99
5-Methylhex-5-en-3-yn-1-ol	34·73	33·86	0·87
Hept-6-en-4-yn-3-ol	34·31	,,	0·45
5-Methylhex-5-en-3-yn-2-ol	34·85	,,	0·99
2-Methylhex-5-en-3-yn-2-ol	34·96	,,	1·10
Oct-7-en-5-yn-4-ol	39·32	38·51	0·81
3-Ethylhept-6-en-4-yn-3-ol	44·17	43·15	1·02
1-(But-3-en-1-ynyl)*cyclo*hexanol	46·57	45·59	0·98
3-*n*-Propyloct-7-en-5-yn-4-ol	53·44	52·45	0·99
5-Methyltridec-1-en-3-yn-5-ol	67·36	66·40	0·86

Substance	$[R_L]_D$ Found	$[R_L]_D$ Calc.	Exaltation
Hept-1-en-3-yne	33·04	32·28	0·76
Oct-1-en-3-yne	38·33	36·93	1·40
Non-1-en-3-yne	42·97	41·58	1·39
Dec-1-en-3-yne	47·02	46·22	0·80
Dodec-1-en-3-yne	56·18	55·52	0·66
Non-2-en-4-yne	42·67	41·58	1·09
Dec-2-en-4-yne	47·57	46·22	1·35

Average exaltation : 0·97

It is evident that (I) and " agropyrene " differ appreciably and further work is necessary before a structure can be assigned with certainty to the natural hydrocarbon.

EXPERIMENTAL

1-*Phenyloct*-3-*yn*-2-*ol*.—A solution of hexynylmagnesium bromide, prepared from hex-1-yne (18 g.) and ethylmagnesium bromide (from 4·5 g. of magnesium) in ether (200 c.c.) by the method of Cymerman, Heilbron, and Jones (*J.*, 1944, 146), was treated gradually with a solution of phenylacetaldehyde (15 g.) in ether (100 c.c.) at 0° with vigorous stirring. After 5 hours' refluxing, the complex was worked up with ice-cold ammonium chloride solution and ether. Distillation of the dried (Na_2SO_4) extracts gave 1-*phenyloct*-3-*yn*-2-*ol* (21 g., 84%) as a pleasant-smelling liquid, b. p. 145—148°/1·6 mm., 150—151°/2·3 mm., n_D^{25} 1·5184 (Found : C, 83·3; H, 9·0%; active H, 1·05. $C_{14}H_{18}O$ requires C, 83·15; H, 8·95%). Light absorption : See

Table 1. The α-*naphthylurethane*, formed after 1 week at 20°, crystallised from light petroleum (b. p. 60—80°) in needles, m. p. 71—72° (Found : N, 4·05. $C_{25}H_{25}O_2N$ requires N, 3·8%).

1-*Phenyloct*-1-*en*-3-*yne*.—A mixture of 1-phenyloct-3-yn-2-ol (3 g.) and freshly powdered anhydrous potassium hydrogen sulphate (2·2 g.) was heated at 190° (bath) for 1 hr. at 35 mm. Dehydration set in at 175°, and distillation of the residue afforded 1-*phenyloct*-1-*en*-3-*yne* (1·5 g., 56%) as a pale yellow mobile liquid, b. p. 144—146°/2 mm., 130—134°/1 mm., $n_D^{20.5}$ 1·5613 (Found : C, 90·9; H, 8·8. $C_{14}H_{16}$ requires C, 91·25; H, 8·75%). Light absorption : See Table 1. Quantitative hydrogenation : A solution of 1-phenyloct-1-en-3-yne (1·15 g.) in methanol (50 c.c.) was shaken with platinic oxide (10 mg.) and hydrogen till absorption ceased, 448 c.c. (21°/763 mm.), of hydrogen were absorbed, equiv. to 3·0 double bonds. Removal of catalyst and distillation of the residue afforded 1-phenyloctane (1 g., 90%) as a pleasant-smelling mobile liquid, b. p. 260—261°/759 mm., n_D^{20} 1·4889 (Eisenlohr and Schulz, *Ber.*, 1924, **57**, 1815, give b. p. 264°, and Schmidt, Hopp, and Schoeller, *ibid.*, 1939, **72**, *B*, 1893, give n_D^{20} 1·4851).

1-*Phenylocta*-1 : 3-*diene*.—A solution of 1-phenyloct-1-en-3-yne (2·25 g.) in methanol (50 c.c.) was shaken with 10% palladised charcoal (0·5 g.) and hydrogen until 1 mol. had been absorbed. Filtration and distillation gave 1-*phenylocta*-1 : 3-*diene* as a mobile sweet-smelling liquid (2 g., 89%), b. p. 126—130°/0·9 mm., $n_D^{27.5}$ 1·5430, which rapidly darkened and resinified (Found : C, 88·7; H, 9·75. $C_{14}H_{18}$ requires C, 90·15; H, 9·85%). Light absorption : See Table 1.

β-*Phenylpropaldehyde*.—(*a*) Ethyl orthoformate (72·5 g.) was added slowly with stirring to a solution of phenethylmagnesium bromide (from 14·9 g. of magnesium) in ether (100 c.c.) and the mixture then refluxed for 6 hr. Working-up by Bachman's method (*J. Amer. Chem. Soc.*, 1933, **55**, 4281) gave β-phenylpropaldehyde (27 g., 41%), b. p. 106—107°/12 mm., $n_D^{17.5}$ 1·5280. Steam-distillation of the aldehyde bisulphite solution before addition of sodium hydrogen carbonate gave ethylbenzene (3·4 g., 6%), b. p. 136°/760 mm., n_D^{19} 1·4956 (lit., b. p. 136°, n_D^{20} 1·4951).

(*b*) Dry distillation of an intimate mixture of finely powdered barium β-phenylpropionate (97 g.) and barium formate (76 g.), finally *in vacuo*, afforded a yellow oil which was shaken with saturated sodium hydrogen sulphite solution. Isolation as described above gave the aldehyde (2·2 g., 7% yield on acid which reacted), b. p. 113—115°/23 mm., n_D^{18} 1·5275. The residue from the dry distillation gave recovered β-phenylpropionic acid (14·2 g., 28%), m. p. 47°.

3-*Phenylpropyl* β-*Phenylpropionate*.—A solution of chromium trioxide (33 g.) in sulphuric acid (100 c.c., 50% v/v) was added to a solution of 3-phenylpropanol (68 g.) in acetone (100 c.c.) with stirring, the temperature being kept at 10—15°. After a further 15 minutes' stirring, water (500 c.c.) and ether were added. Evaporation of the washed (water and sodium hydrogen carbonate solution) and dried (Na_2SO_4) ethereal extracts and distillation through a column packed (15 cm.) with single-turn helices gave β-phenylpropaldehyde (2·7 g., 4%), b. p. 45°/0·01 mm., n_D^{22} 1·5240, and 3-*phenylpropyl* β-*phenylpropionate* (35·5 g., 53%) as a pleasant-smelling oil, b. p. 132—135°/0·01 mm., n_D^{20} 1·5408 (Found : C, 80·3; H, 7·65. $C_{18}H_{20}O_2$ requires C, 80·55; H, 7·5%). Alkaline hydrolysis gave β-phenylpropionic acid, m. p. and mixed m. p. 47·5—48·5°, and 3-phenylpropanol, b. p. 119°/12 mm., n_D^{25} 1·5357 (lit., b. p. 119°/12 mm., n_D^{20} 1·5356).

5-*Phenylpent*-1-*yn*-3-*ol*.—A stirred solution of sodium acetylide (from 9·2 g. of sodium) in liquid ammonia (500 c.c.), prepared by Jones and McCombie's method (*J.*, 1942, 733), was treated with β-phenylpropaldehyde (26·8 g.) in ether (25 c.c.) during ¾ hr. and the mixture stirred and cooled for a further 4¾ hr. After addition of ammonium chloride (14·7 g.), the ammonia was allowed to evaporate overnight, and the mixture decomposed with 2N-sulphuric acid and ice, and extracted with ether. The residue on evaporation of the washed (sodium hydrogen carbonate) ethereal extracts was shaken with a solution of sodium hydrogen sulphite (21 g.) in water (50 c.c.). Steam-distillation and ether-extraction of the distillate afforded 5-*phenylpent*-1-*yn*-3-*ol* (11·8 g., 38%) as a sweet-smelling oil, b. p. 92—94°/0·4 mm., n_D^{17} 1·5344 (Found : C, 82·15; H, 7·6%; active H, 1·9. $C_{11}H_{12}O$ requires C, 82·45; H, 7·55%). The α-*naphthylurethane* crystallised from light petroleum (b. p. 90—100°) as prisms, m. p. 97—97·5° (Found : N, 4·65. $C_{22}H_{19}O_2N$ requires N, 4·25%). Quantitative hydrogenation : The alcohol (0·8 g.) in methyl acetate (50 c.c.), shaken with platinic oxide (25 mg.) and hydrogen until absorption ceased, absorbed 223 c.c. of hydrogen at 15°/747 mm. (1·95 double bonds). Removal of catalyst gave 1-phenylpentan-3-ol, b. p. 52—56°/0·08 mm., n_D^{16} 1·5165.

Steam-distillation of the residual aldehyde bisulphite compound after addition of sodium hydrogen carbonate gave recovered β-phenylpropaldehyde (0·6 g., 2%), b. p. 117—119°/28 mm., n_D^{18} 1·5275. Ether-extraction of the residue not volatile in steam afforded 2-*benzyl*-5-*phenylpent*-2-*enal* as a viscous oil (1 g., 2%), b. p. 175—180°/0·5 mm., n_D^{18} 1·5761 (Found : C, 86·0; H, 7·6. $C_{18}H_{18}O$ requires C, 86·35; H, 7·25%). It gave a positive reaction with Schiff's reagent and the 2 : 4-*dinitrophenylhydrazone* crystallised from ethanol as red needles, m. p. 165·5—166·5° (Found : N, 13·15. $C_{24}H_{22}O_4N_4$ requires N, 13·05%).

3-*Methoxy*-5-*phenylpent*-1-*yne*.—A solution of 5-phenylpent-1-yn-3-ol (4 g.) in ether (5 c.c.) was added dropwise with stirring to sodamide (2·2 g.) and ether (50 c.c.), and the mixture refluxed until evolution of ammonia had ceased (3½ hr.). Methyl sulphate (3·2 g.) in ether (10 c.c.) was added to the cooled mixture, which was refluxed for 1 hr. After addition of water, removal of solvent from the washed (dilute aqueous ammonia and water) and dried (Na_2SO_4) ethereal extracts gave 3-*methoxy*-5-*phenylpent*-1-*yne* (3 g., 68%) as a sweet-smelling mobile liquid, b. p. 66°/0·3 mm., $n_{D}^{23\cdot5}$ 1·5031 (Found : C, 82·2; H, 8·4%; active H at 90°, 1·05. $C_{12}H_{14}O$ requires C, 82·65; H, 8·15%). It gave a positive test with Tollens's reagent.

3-*Chloro*-5-*phenylpent*-1-*yne*.—Freshly distilled thionyl chloride (6·7 g.) was added to a stirred solution of 5-phenylpent-1-yn-1-ol (8 g.) in pyridine (4·4 g.) at 50—60°, which temperature was maintained for a further 3 hr. The mixture was poured on ice (100 g.) and extracted with ether. Removal of solvent from the washed (dilute sulphuric acid, water, and sodium hydrogen carbonate) and dried (Na_2SO_4) extracts afforded 3-*chloro*-5-*phenylpent*-1-*yne* (6·9 g., 77·5%) as a pleasant-smelling liquid, b. p. 73—75°/0·25 mm., n_{D}^{24} 1·5292 (Found : C, 73·6; H, 6·5. $C_{11}H_{11}Cl$ requires C, 73·95; H, 6·2%).

1-*Phenylhex*-4-*yn*-3-*ol*.—(*a*) A solution of sodium acetylide (from 25 g. of sodium) in liquid ammonia (1 l.) was treated with methyl iodide (142 g.) in ether (150 c.c.) during 45 min. with further stirring and cooling for 4 hr. The prop-1-yne was converted into the sodium salt by addition of a suspension of sodamide (from 25 g. of sodium; Vaughn, Vogt, and Nieuwland, *J. Amer. Chem. Soc.*, 1934, **56**, 2120) in liquid ammonia (700 c.c.). After a further hour's stirring, β-phenylpropaldehyde (147 g.) was added and the mixture stirred and cooled for 24 hr. Working-up with ammonium chloride (50 g.) and ether gave, on distillation, 2 fractions : (i) 1-*Phenylhex*-4-*yn*-3-*ol* (12 g., 7%) as a pleasant-smelling oil, b. p. 74—76°/0·05 mm., n_{D}^{22} 1·5349 (Found: C, 82·3; H, 8·0. $C_{12}H_{14}O$ requires C, 82·65; H, 8·15%). Light absorption : See Table 1. The α-*naphthylurethane* crystallised from light petroleum (b. p. 90—100°) as prisms, m. p. 103·5—105° (Found : C, 80·35; H, 6·1; N, 4·6. $C_{23}H_{21}O_2N$ requires C, 80·45; H, 6·1; N, 4·15%). (ii) 2-Benzyl-5-phenylpent-2-enal (25 g., 15%), as a viscous oil, b. p. 135—138°/0·05 mm., $n_{D}^{26\cdot5}$ 1·5724. The 2 : 4-dinitrophenylhydrazone had m. p. 164—166°, undepressed on admixture with the sample (m. p. 165·5—166·5°) described above.

(*b*) A stream of prop-1-yne, prepared from 1 : 2-dibromopropane (395 g.), *n*-butanol (900 c.c.), and potassium hydroxide (450 g.) by the method of Heisig and Davis (*J. Amer. Chem. Soc.*, 1935, **57**, 339), was passed into a solution of ethylmagnesium bromide (from 12 g. of magnesium) in ether (200 c.c.) at 0°, and the mixture stirred for 6 hr. under a reflux condenser cooled to −40°. A solution of β-phenylpropaldehyde (67 g.) in ether (100 c.c.) was then added and the solution refluxed for 3 hr. The complex was decomposed (ammonium chloride solution) and acidified (10% sulphuric acid), and the ethereal extracts were washed with sodium hydrogen sulphite and sodium hydrogen carbonate solutions and dried (Na_2SO_4). Distillation gave 1-phenylhex-4-yn-3-ol (46 g., 53%), b. p. 88—90°/0·06 mm., n_{D}^{22} 1·5350.

4-*Chloro*-6-*phenylhex*-2-*yne*.—Addition of thionyl chloride (6·7 g.) to a solution of 1-phenylhex-4-yn-3-ol (8·5 g.) in pyridine (4·4 g.) at 40—50° and working up by the method described above gave 4-*chloro*-6-*phenylhex*-1-*yne* (2·5 g., 26%), as a sweet-smelling mobile liquid, b. p. 31—32°/0·05 mm., n_{D}^{25} 1·5230 (Found : C, 74·35; H, 6·9. $C_{12}H_{13}Cl$ requires C, 74·75; H, 6·75%), and *di*-(1-*phenethylbut*-2-*ynyl*) *ether* (2·5 g.) as a colourless oil, b. p. 114—118°/0·05 mm., $n_{D}^{25\cdot5}$ 1·5407 (Found : C, 86·85; H, 7·9. $C_{24}H_{26}O$ requires C, 87·3; H, 7·9%).

4-*Bromo*-6-*phenylhex*-2-*yne*.—Freshly distilled phosphorus tribromide (30 g.,) in ether (30 c.c.) was added dropwise with stirring to a mixture of 1-phenylhex-4-yn-3-ol (17·4 g.) in ether (50 c.c.) and pyridine (1 g.) at −20° during 0·5 hr. The solution was allowed to come to room temperature and stirred for a further hour. Working up gave 4-*bromo*-6-*phenylhex*-2-*yne* (15 g., 65%), b. p. 78—80°/0·04 mm., n_{D}^{25} 1·5613 (Found : C, 61·1; 5·65. $C_{12}H_{13}Br$ requires C, 60·8; H, 5·5%). Light absorption : See Table 1.

1-*Phenylhex*-2-*en*-4-*yne*.—(*a*) A mixture of 4-bromo-6-phenylhex-2-yne (5 g.) and diethylaniline (15 c.c.) was heated at 160—170° (bath) for 15 min. under nitrogen and immediately cooled to 0°. The mixture was taken up in ether, washed with 2N-nitric acid, aqueous sodium hydrogen carbonate, and water, and dried (Na_2SO_4). Distillation of the ethereal extracts gave 1-*phenylhex*-2-*en*-4-*yne* (1·4 g., 44%) as a sweet-smelling mobile liquid, b. p. 40°/0·04 mm., $n_{D}^{26\cdot5}$ 1·5510, $d^{26\cdot5}$ 0·9450 (Found: C, 91·85; H, 8·1; $[R_L]_D$ 52·82. $C_{12}H_{12}$ requires C, 92·25; H, 7·75%; $[R_L]_D$ 52·02). Light absorption : See Table 1. Addition of silver nitrate to the aqueous layer gave 3·1 g. (82%) of silver bromide. 1-Phenylhex-2-en-4-yne (0·425 g.) in methanol

(30 c.c.) was shaken with platinic oxide (20 mg.) and hydrogen until absorption ceased, 201 c.c. of hydrogen being absorbed at 26°/756 mm., equiv. to 3·0 double bonds. The catalyst was filtered off and the filtrate on distillation gave 1-phenylhexane (0·4 g., 94%) as a sweet-smelling liquid, b. p. 80—83°/1 mm., n_D^{22} 1·4880, d^{22} 0·8600 (Found: C, 89·1; H, 11·4; $[R_L]_D$ 54·28. Calc. for $C_{12}H_{18}$: C, 88·9; H, 11·1%; $[R_L]_D$ 54·25). Schmidt, Hopp, and Schoeller, *loc. cit.*, give b. p. 97·5—101°/12 mm., n_D^{20} 1·4868, d^{20} 0·8592, and Vogel (*J.*, 1948, 607) gives b. p. 222·5°/766 mm., n_D^{20} 1·4874, d^{20} 0·8602.

(*b*) A mixture of 1-phenylhex-4-yn-3-ol (6·2 g.) and powdered potassium hydrogen sulphate (5·3 g.) was heated at 190° (bath) for 30 min. at 45 mm. in a slow stream of nitrogen. Distillation gave the crude hydrocarbon (3 g.) still containing a trace of alcohol. Fractionation through a Vigreux column (10 cm.) gave 1-phenylhex-2-en-4-yne (2 g., 36%), b. p. 78—82°/0·3 mm., n_D^{16} 1·5532 (Found: C, 91·95; H, 8·0. Calc. for $C_{12}H_{12}$: C, 92·25; H, 7·75%). Light absorption: Max. at 2280 (ε 14,800), infl. at 2340 (ε 14,000) and 2550 Å (ε 600). The hydrocarbon (0·907 g.) in methanol (50 c.c.) was shaken with platinic oxide (30 mg.) and hydrogen until absorption ceased, 413 c.c. being absorbed at 18°/755 mm., corresponding to 2·95 double bonds. Filtration and distillation of the filtrate gave 1-phenylhexane (0·85 g., 94%), b. p. 104°/13 mm., n_D^{20} 1·4877, as a sweet-smelling liquid.

An alcoholic solution of the hydrocarbon containing 0·001 g./100 c.c. was irradiated in a quartz cell with ultra-violet light from a mercury-vapour lamp for 0·5 hr., and the spectrum then re-determined. The solution was then left in the dark for 0·5 hr. and the absorption again measured. The results are tabulated.

	Intensity (ε) at maxima (Å)		
Solution	2280	2340	2850
Original solution	14,900	14,250	—
After irradiation	9,500	10,000	1250
After storage in dark	11,250	11,000	1250

Absorption spectra were determined in 95% alcoholic solution by means of a Beckman quartz spectrophotometer, model DU. We are indebted to the late Mrs. E. Bielski for microanalyses.

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