

589. *Researches on Acetylenic Compounds. Part XXXII.* Dehydration of Acetylphenyl- and Vinylacetylenyl-alcohols derived from cyclohexanone, and the Hydration of the Resultant Hydrocarbons.*

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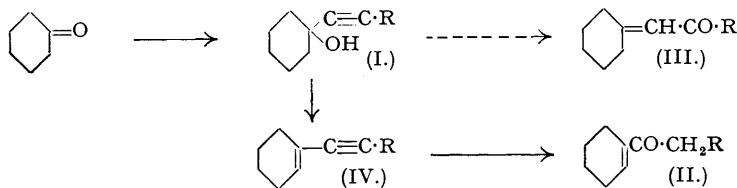
Tertiary alcohols obtained by condensing *cyclohexanone* with mono-substituted acetylenes or vinylacetylenes can be dehydrated with phosphorus oxychloride in pyridine to compounds containing the conjugated systems C:C:C and C:C:C:C respectively in excellent yields. 1-Ethynyl*cyclohexanol* itself gives 1-ethynyl*cyclohexene* in 80% yield, representing a considerable improvement over previous procedures.

The ethynyl*cyclohexenes* are readily hydrated to yield $\alpha\beta$ -unsaturated ketones, whereas vinyllogues are hydrated with greater difficulty and then tend to afford cyclised products (derivatives of 4 : 5 : 6 : 7-tetrahydroindan-1-one). Some experiments with alcohols prepared from 2 : 2-dimethyl- and 2 : 2 : 6-trimethyl-*cyclohexanone* are also described.

MUCH evidence (cf. Chanley, *J. Amer. Chem. Soc.*, 1948, **70**, 244) has indicated that the formic acid-induced isomerisation of ethynylcarbinols leads almost entirely to $\alpha\beta$ -unsaturated methyl

* Part XXXI, *J.*, 1951, 766.

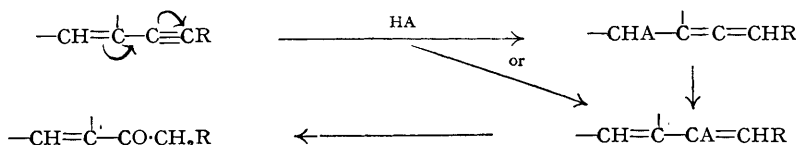
ketones, and that only minor amounts of $\alpha\beta$ -unsaturated aldehydes (as first suggested by Rupe, *Helv. Chim. Acta*, 1926, **9**, 672) are produced. Furthermore, Hennion, Davis, and Maloney (*J. Amer. Chem. Soc.*, 1949, **71**, 2813) have shown that this "isomerisation" reaction proceeds by dehydration, followed by hydration of the conjugated unsaturated hydrocarbon.



No examples of the isomerisation of alcohols prepared from monosubstituted acetylenes have as yet been described. In the present work, this extension was studied first with the alcohol (I; R = Buⁿ), prepared from *cyclohexanone* and hex-1-ynylmagnesium bromide in 80% yield. Heating this alcohol with formic acid for ten minutes gave a mixture of the hydrocarbon (IV; R = Buⁿ) and the unsaturated ketone (II; R = Buⁿ). Longer periods of reaction (45 minutes) increased the yield of the ketone at the expense of the hydrocarbon, indicating that the latter was the intermediate, and this was confirmed by heating the hydrocarbon (see below) with formic acid, the ketone being produced in good yield. The ketone was also formed from the unsaturated hydrocarbon by the boron trifluoride-methanol hydration method of Hennion and Zoss (*J. Amer. Chem. Soc.*, 1941, **63**, 1151). The structure of this ketone was confirmed by ozonolysis, *n*-hexanoic acid being isolated in 65% yield, and also by synthesis from *cyclohexene* and *n*-hexanoyl chloride (cf. Nightingale, Milberger, and Tomisek, *J. Org. Chem.*, 1948, **13**, 357).

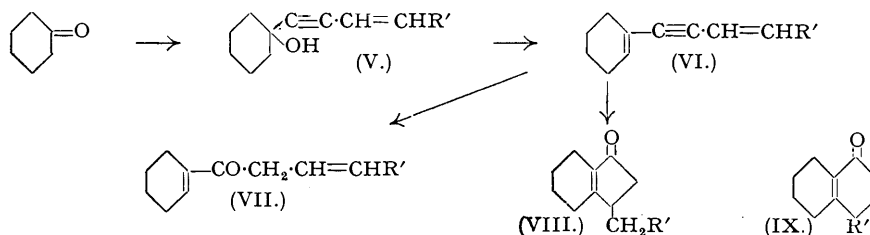
Dehydration of the alcohol (I; R = Buⁿ) to the ethynylcyclohexene was first accomplished by conversion into the tertiary chloro-compound by means of phosphorus pentachloride, followed by dehydrochlorination with pyridine. Phosphorus oxychloride in pyridine was then found to effect the dehydration in one operation in 75% yield. This method has been found to be of general applicability for conversion of alcohols of formula (I) into unsaturated hydrocarbons. 1-Ethynylcyclohexene can thus be obtained from 1-ethynylcyclohexanol in 80% yield, by a process far more convenient than those described previously (cf. Eglinton and Whiting, *J.*, 1950, 3650, where previous references are given).

In the formic acid isomerisation described above, it was noteworthy that only one ketone was apparently formed, as judged by careful chromatography of the total 2 : 4-dinitrophenylhydrazone. This observation signifies that the dehydration takes place much more rapidly than the alternative 1 : 3-anionotropic shift of the hydroxyl group, which would lead to the isomeric ketone (III; R = Buⁿ) or its $\beta\gamma$ -isomer. The production of the small amounts of $\alpha\beta$ -unsaturated aldehydes from unsubstituted ethynyl-alcohols (Chanley, *loc. cit.*) must involve this type of anionotropic rearrangement. Formation of the ketone (II; R = Buⁿ) is in accord with the direction of polarisation in vinylacetylenic systems as shown, for instance, by the addition of hydrogen halides (Carothers and Berchet, *J. Amer. Chem. Soc.*, 1933, **55**, 2807) :



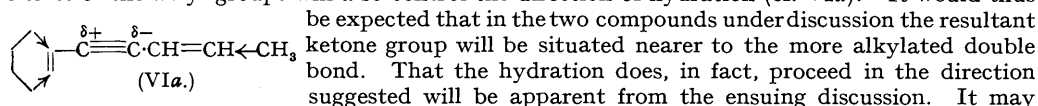
The formation, dehydration, and subsequent hydration of vinylacetylenic alcohols derived from *cyclohexanone* were next investigated. Nazarov and Pinkina (*Chem. Abs.*, 1948, **42**, 7732) have recently dehydrated (with 50% sulphuric acid) the alcohol (V; R' = H) to obtain the hydrocarbon (VI; R' = H). Hydration of the latter with mercuric sulphate in methanol containing a little sulphuric acid yielded a ketone, believed to be (VII; R' = H), which was cyclised by heating it with a mixture of formic and phosphoric acids to give an isomeric ketone, formulated as (VIII; R' = H). Repetition of their experiments gave essentially similar results, except that it seems probable that the cyclisation actually occurs during the hydration stage, and that the subsequent treatment with acid effects no appreciable change. This conclusion is supported by the similarity of the physical constants

of the two materials as reported by Nazarov and Pinkina, and confirmed in the present work, and also by the fact that they both afford the same 2 : 4-dinitrophenylhydrazone. No proof of structure was advanced by the Russian workers for their products; it is believed that the cyclised compound does in fact contain a five-membered ring, as suggested by Nazarov and Pinkina, for reasons that will be discussed later.



The homologous alcohol (V; $\text{R}' = \text{Me}$) was prepared from the Grignard derivative of pent-2-en-4-yne (Eglinton and Whiting, *loc. cit.*) in 70% yield, and was dehydrated by phosphorus oxychloride to the corresponding hydrocarbon (VI; $\text{R}' = \text{Me}$) in 85% yield. Heating the alcohol with formic acid under the normal isomerisation conditions gave no ketonic products, but, instead, a good yield of hydrocarbon was obtained. Longer periods of reaction, or heating the hydrocarbon itself with formic acid, gave no appreciable amounts of ketone. Hydration of the hydrocarbon was then attempted by Nazarov and Pinkina's procedure, but here a striking difference from the lower homologue was observed, for little reaction took place, the greater part of the hydrocarbon being recovered unchanged.

The difficulties encountered in hydrating this $\cdot\text{C}\cdot\text{C}\cdot\text{C}\cdot\text{C}\cdot\text{C}\cdot$ system, compared with the ease with which the mild hydrating reagent, formic acid, reacts with the $\cdot\text{C}\cdot\text{C}\cdot\text{C}\cdot\text{C}\cdot$ compound, can be attributed to the relatively great "electronic symmetry" of the triple bond (or the $\cdot\text{C}\cdot\text{C}\cdot\text{C}\cdot\text{C}\cdot\text{C}\cdot$ system), leading to only a weak polarisation in any one direction. The marked difference in reactivity of the triple bond in the two compounds (VI; $\text{R}' = \text{H}$ and Me) towards mercuric-catalysed hydration may then be explained by the difference in the degree of alkyl substitution of the double bonds on either side of the triple bond, the former with two (ring-)alkyl groups on one double bond and none on the other being less symmetrical than the latter with two and one alkyl groups respectively. In these compounds, the inductive effects of the alkyl groups will also control the direction of hydration (cf. VIa). It would thus



be expected that in the two compounds under discussion the resultant ketone group will be situated nearer to the more alkylated double bond. That the hydration does, in fact, proceed in the direction suggested will be apparent from the ensuing discussion. It may be noted that the direction of hydration of unsymmetrically substituted triple bonds should provide a useful method of comparing the electronic effects of various types of substituents (cf., Robinson and Robinson, *J.*, 1926, 2204).

The action of the more powerful hydration reagent, boron trifluoride-mercuric oxide in methanol, on the hydrocarbon (VI; $\text{R}' = \text{Me}$) was next examined. From the first experiment a 30% yield of a semicarbazone was obtained. This, however, was a mixture, for, although not easily resolved by crystallisation, two 2 : 4-dinitrophenylhydrazones (m. p. 123° and 193° respectively), were easily separated by chromatography. The light absorption of the lower-melting, less easily eluted derivative agrees very closely with that of the ketone (II; $\text{R} = \text{Bu}^n$). It is therefore believed to be the derivative of the open-chain compound (VII; $\text{R}' = \text{Me}$), this being confirmed by phosphoric acid-formic acid cyclisation to give the higher-melting derivative, shown to be derived from (VIII; $\text{R}' = \text{Me}$) (see below).

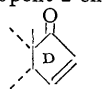
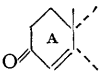
Modification of this hydration procedure led to a 40% yield of a homogeneous semicarbazone, convertible into the higher-melting 2 : 4-dinitrophenylhydrazone and by hydrolysis into a ketone which, although $\alpha\beta$ -unsaturated, resisted hydrogenation in acetic acid with a palladium catalyst and also mild ozonolysis. These facts, together with the ease of elution of the 2 : 4-dinitrophenylhydrazone and the high melting points of the derivatives, suggested that cyclisation had occurred to give most probably (VIII; $\text{R}' = \text{Me}$) or (IX; $\text{R}' = \text{Me}$). Analogously, Nazarov and Pinkina's cyclised compound would be (VIII; $\text{R}' = \text{H}$) or (IX; $\text{R}' = \text{H}$). The presence of a cyclopentenone ring in both ketones was indicated by the carbonyl stretching frequency in the infra-red absorption spectrum (determined by the late Dr. H. P. Koch), and by the ultra-violet absorption spectrum of the ketone and its semicarbazone, characteristic of

cyclopentenones (cf. Gillam and West, *J.*, 1942, 486). Further there was close agreement (see Table) of the light absorption of the semicarbazones and 2 : 4-dinitrophenylhydrazones of (VIII; R' = H and Me) with those of the corresponding derivatives of the parent ketone of the series (VIII; CH₂R' replaced by H), these derivatives being kindly supplied by Dr. D. W. Mathieson (cf. Mathieson, *J.*, 1951, 177). Since hydration of the triple bond in the diolefinic acetylenes must precede cyclisation, the cyclic ketones are presumably formed by way of an open-chain ketone, but, whatever the precise mechanism of the cyclisation reaction, the formation of products such as (VIII) shows that the direction of the initial hydration is in accord with the simple electronic effects referred to above.

	$\lambda_{\max.}$ (Å)	$\epsilon_{\max.}$		$\lambda_{\max.}$ (Å)	$\epsilon_{\max.}$
<i>Compounds containing C=C—C≡C.</i>					
(IV; R = H)	2235	10,500	(V; R' = Me)	2260	14,500
(IV; R = Bu ⁿ)	2270	10,500		2340 *	12,000
	2300 *	10,000	2 : 2-Dimethyl derivative of	2275	15,500
2-Hex-1'-ynyl-3 : 3-dimethyl-	2280	12,500	(V; R' = Me)		
cyclohexene			(V; R' = CH ₂ ·OH)	2260	12,500
(V; R' = H)	2240	13,500	2 : 2-Dimethyl derivative of	2290	16,000
	2340	11,500	(V; R' = CH ₂ ·OH)		

	$\lambda_{\max.}$ (Å)	$\epsilon_{\max.}$		$\lambda_{\max.}$ (Å)	$\epsilon_{\max.}$
<i>Compounds containing C=C—C≡C—C=CH₂.</i>					
(VI; R' = H)	2610	14,500	(VI; R' = Me)	2640	13,000
(VI; R' = CH ₂ ·OH)	2645	13,000	2 : 2-Dimethyl derivative of	2700	13,000
			(VI; R' = Me)		

<i>cycloHex-1-enyl ketones, C₆H₉·COR.</i>					2 : 4-Dinitrophenyl- hydrazone †	
R	Ketone		Semicarbazone		$\lambda_{\max.}$ (Å)	$\epsilon_{\max.}$
	$\lambda_{\max.}$ (Å)	$\epsilon_{\max.}$ (Å)	$\lambda_{\max.}$ (Å)	$\epsilon_{\max.}$		
Me	2320	12,500	2605	24,500	2550	16,500
<i>n</i> -C ₅ H ₁₁	2340	12,000	2615	23,500	3850	27,000
CH ₃ ·CH·CHMe	—	—	—	—	2570	16,500
					3870	28,000
					2570	17,500
					3870	28,500

<i>Cyclised compounds, etc.</i>							
	Ketone			Semicarbazone †		2 : 4-Dinitrophenyl- hydrazone †	
	Infra-red § (cm. ⁻¹)	$\lambda_{\max.}$ (Å)	$\epsilon_{\max.}$	$\lambda_{\max.}$ (Å)	$\epsilon_{\max.}$	$\lambda_{\max.}$ (Å)	$\epsilon_{\max.}$
(VII; H replaces CH ₂ R)	—	—	—	2650	26,500	2600	17,500
(VIII; R = H)	1705	2380	12,500	2650	26,500	3970	27,000
(VIII; R = Me)	1710	2380	12,500	2650	26,000	2590	17,500
						3950	27,500
2- <i>n</i> -Amyl-3-methyl- cyclopent-2-enone ‡	—	2370	12,200	2665	20,400	2605	18,500
	1716					3980	28,500
	1675						

* Inflexion.

† Determined in chloroform solution.

‡ Gillam and West, *loc. cit.*

§ C=O frequency.

<i>p</i> -Phenylazobenzoates.						
Derivative of	$\lambda_{\max.}$ (Å)	$\epsilon_{\max.}$	Derivative of	$\lambda_{\max.}$ (Å)	$\epsilon_{\max.}$	
(V; R' = CH ₂ ·OH)	2300	27,000	(VI; R' = CH ₂ ·OH)	2320	17,000	
	3245	25,000		2685	21,000	
2 : 2-Dimethyl derivative of	2280	30,500		3245	23,000	
(V; R' = CH ₂ ·OH)	3245	27,000	2 : 2-Dimethyl derivative of	2335	18,000	
Ph·N ₂ ·C ₆ H ₄ ·CO ₂ Me- <i>p</i>	2290	11,500	(VI; R' = CH ₂ ·OH)	2710	21,500	
	3230	23,500		3255	26,000	

A few related experiments were carried out with carbinols prepared from 2 : 2-dimethyl- and 2 : 2 : 6-trimethyl-cyclohexanone. Reaction between the former ketone and hex-1-ynylmagnesium bromide gave the tertiary alcohol in 75% yield. Dehydration of this compound by phosphorus oxychloride in pyridine was markedly slower than that of the unsubstituted cyclohexanone analogue, but an 80% yield of hydrocarbon was obtained by using a longer reaction period. The Grignard derivative of pent-2-en-4-yne condensed with 2 : 2 : 6-trimethylcyclohexanone to furnish the alcohol in 50% yield. Very long periods of heating with phosphorus oxychloride in pyridine were necessary to dehydrate this compound, presumably owing to steric factors, but the final yield was 60%. Attempted hydration of this hydrocarbon by the boron trifluoride-methanol method gave mainly unchanged starting material, even under moderately vigorous conditions. The presence of the three ring-methyl groups clearly introduces steric factors that prevent or inhibit the approach of the hydration catalysts.

As a potential model substance for forming polyene alcohol side chains, the glycol (V; $R' = CH_2 \cdot OH$) was prepared from cyclohexanone and pent-2-en-4-yn-1-ol (Haynes, Heilbron, Jones, and Sondheimer, *J.*, 1947, 1583). The primary hydroxyl group was protected by formation of the crystalline *p*-phenylazobenzoate; dehydration with formic acid or with phosphorus oxychloride in pyridine then gave the crystalline dehydrated ester, converted by hydrolysis into the carbinol (VI; $R' = CH_2 \cdot OH$). A similar series of compounds was obtained starting from 2 : 2-dimethylcyclohexanone. No hydration was attempted with these alcohols or their derivatives.

The light-absorption properties of the compounds described in this paper are presented in the tables on p. 2655.

EXPERIMENTAL.

Some m. p.s [designated m. p. (K)] were taken on a Kofler block and are corrected; the remainder were taken (uncorrected) in capillary tubes. Light-absorption data were determined in ethanol solutions with a Beckman spectrophotometer unless stated otherwise.

1-Ethynylcyclohexene (I; $R = H$).—A solution of phosphorus oxychloride (55 c.c.) in dry pyridine (55 c.c.) was added slowly to a solution of 1-ethynylcyclohexanol (100 g.) in dry pyridine (150 c.c.), in a flask fitted with a stirrer and a reflux condenser, at such a rate that the mixture just boiled. After being gently heated on a steam-bath for 1 hour (internal temp., 85°), the reaction mixture was poured on ice and the product isolated with pentane. Distillation gave 1-ethynylcyclohexene (69 g., 80%) b. p. 53–56°/40 mm., n_D^{25} 1.4978. For material regenerated from the silver derivative, Milas, MacDonald, and Black (*J. Amer. Chem. Soc.*, 1948, **70**, 1829) give b. p. 52–53°/30 mm., n_D^{25} 1.4934. Material prepared by the above method did not deteriorate (in refractive index or colour) when stored over a little calcium chloride at 0° for many months.

1-1'-Hydroxycyclohexylhex-1-yne (I; $R = Bu^a$).—A solution of hex-1-yne (45 g.) in ether (45 c.c.) was added with stirring to an ethereal solution of ethylmagnesium bromide (from magnesium, 13.5 g.) during 30 minutes. Rapid evolution of ethane occurred after a brief induction period. Dry benzene (50 c.c.) was added to dissolve the Grignard complex, the clear solution then being stirred for 30 minutes. Purified cyclohexanone (48 g.) in ether (50 c.c.) was added during 30 minutes, the flask being externally cooled with ice. After the mixture had been stirred overnight, ice and ammonium nitrate were added and the carbinol was isolated with ether. The carbinol (71 g., 80%) had b. p. 90–92°/1 mm., n_D^{18} 1.4836 (Found: C, 79.9; H, 11.3. $C_{12}H_{20}O$ requires C, 79.95; H, 11.2%).

Dehydration of 1-1'-Hydroxycyclohexylhex-1-yne.—(a) *With phosphorus oxychloride.* Phosphorus oxychloride (20 c.c.) in dry pyridine (50 c.c.) was added slowly with stirring to the alcohol (10 g.) in dry pyridine (20 c.c.), the mixture being kept at 20–25° by external cooling. After being kept at 25° for 30 minutes, the mixture was heated on the steam-bath for 30 minutes and then poured on excess of ice. Isolation with pentane gave 1-cyclohex-1'-enylhex-1-yne (IV; $R = Bu^a$) (6.9 g., 80%), b. p. 68°/0.6 mm., n_D^{14} 1.5000 (Found: C, 88.7; H, 11.2. $C_{12}H_{18}$ requires C, 88.8; H, 11.2%).

(b) *With phosphorus pentachloride.* Powdered phosphorus pentachloride (14 g.) was added slowly with stirring to the alcohol (10 g.) in dry ether (70 c.c.). Stirring was continued overnight, the clear solution was then poured on ice, and the chloro-compound isolated with ether. Removal of the ether by distillation gave a residue that was heated under reflux with pyridine (50 c.c.) for 3 hours. Isolation with pentane gave the hydrocarbon (6.7 g.), b. p. 77°/0.5 mm., n_D^{17} 1.4988—1.4999.

1-n-Hexanoylcyclohexene (II; $R = Bu^a$).—(a) *By isomerisation of (I; $R = Bu^a$).* A mixture of the alcohol (5 g.) and formic acid (22 c.c.; *d* 1.20) was gently heated under reflux for 45 minutes. The deep green solution was poured into ice-water, and the ketone isolated with pentane. Distillation gave the nearly pure ketone (4.3 g.), b. p. 78–80°/0.5 mm., n_D^{14} 1.4843.

Treatment with semicarbazide acetate in methanol solution gave the semicarbazone, forming needles, m. p. (K) 173°, from aqueous methanol (Found: C, 66.1; H, 9.6. $C_{13}H_{22}ON_3$ requires C, 65.8; H, 9.8%). The 2 : 4-dinitrophenylhydrazone formed red needles (from ethanol), m. p. (K) 119° (Found: C, 60.15; H, 7.0. Calc. for $C_{13}H_{20}O_4N_4$: C, 60.0; H, 6.7%).

Hydrolysis of the semicarbazone by the method of Heilbron, Johnson, Jones, and Spinks (*J.*, 1942, 727) gave the pure ketone, b. p. 83°/0.5 mm., n_D^{18} 1.4825 (Found: C, 79.85; H, 11.2. Calc. for $C_{12}H_{20}O$:

C, 79.95; H, 11.2%). Nightingale *et al.* (*loc. cit.*) give b. p. 121—123°/18 mm., for the ketone and m. p. 118—119° for the 2 : 4-dinitrophenylhydrazone. When this isomerisation was carried out with only 10 minutes' heating the product (4.6 g.) had n_D^{17} 1.4910; treatment with semicarbazide acetate gave the foregoing semicarbazone (5.0 g.), m. p. 168° (without recrystallisation). The non-ketonic product was isolated and distilled, to yield hydrocarbon (IV; R = Bu^a) (0.5 g.), b. p. 80°/0.5 mm., n_D^{16} 1.4987.

(b) *By hydration of 1-cyclohex-1'-enylhex-1-yne* (IV; R = Bu^a). (i) A solution of the hydrocarbon (5 g.) in methanol (10 c.c.) was added to a catalyst solution prepared by warming together mercuric oxide (0.3 g.), boron trifluoride-ether complex (0.1 c.c.), trichloroacetic acid (0.05 g.), and methanol (0.3 c.c.). The mixture became very warm and was then stirred for 1 hour. Isolation with ether gave the ketone (4.5 g.), n_D^{18} 1.4821. The 2 : 4-dinitrophenylhydrazone had m. p. 119°. (ii) A mixture of the hydrocarbon (2 g.), mercuric acetate (0.5 g.), ethanol (15 c.c.), water (2 c.c.), and acetic acid (2 c.c.) was heated under reflux for 3 hours. Isolation with pentane followed by distillation gave a product (0.6 g.), n_D^{17} 1.4870—1.4931, an incompletely separated mixture of starting material and the ketone. The 2 : 4-dinitrophenylhydrazone, prepared from the mixture, had m. p. 118—119°. (iii) A mixture of the hydrocarbon (1.49 g.) and formic acid (8 c.c.; *d* 1.20) was heated under reflux for 30 minutes. Isolation with pentane and distillation gave nearly pure ketone (1.41 g.), n_D^{14} 1.4848. Conversion into the 2 : 4-dinitrophenylhydrazone, purified by chromatography and crystallisation, gave the derivative (2.6 g.), m. p. 118—119°.

(c) *By condensation of cyclohexene with n-hexanoyl chloride.* A solution of stannic chloride (62.5 g.) in redistilled carbon disulphide (150 c.c.) was cooled to -10° in a flask fitted with stirrer, thermometer, and dropping funnel. A mixture of freshly distilled *n*-hexanoyl chloride (33 g.) and cyclohexene (20 g.) was added slowly with stirring, the temperature being kept below -5°. Stirring was continued at -5° for 3 hours and then at 20° for 3 hours. Ice (200 g.) was added, and the carbon disulphide removed by distillation from a steam-bath. The chloro-compound, isolated with ether, was heated under reflux with diethylaniline (38 c.c.) for 3 hours. Isolation of the product with ether, followed by two distillations, gave the ketone (18.3 g.), n_D^{17} 1.4790. The semicarbazone (m. p. 170°) and the 2 : 4-dinitrophenylhydrazone (m. p. 119°) proved to be identical with those obtained by the previous methods.

Ozonolysis of the ketone (II; R = Bu^a) by Asinger's method (*Ber.*, 1942, 75, 656) gave a 65% yield of *n*-hexanoic acid, isolated as its *p*-phenylphenacyl ester, m. p. and mixed m. p. with an authentic sample, 67—68°.

5-1'-Hydroxycyclohexylpent-2-en-4-yne (V; R' = Me).—Pent-2-en-4-yne (22 g.) in dry ether (50 c.c.) was added during 30 minutes to a solution of ethylmagnesium bromide (from magnesium, 9 g.). After a further 30 minutes' stirring, the solution was treated slowly (1 hour) with cyclohexanone (33 g.) in ether (50 c.c.). Stirring was continued overnight, the solid complex then being decomposed with ice and ammonium nitrate, and the alcohol isolated with ether. Distillation gave the alcohol (40 g., 70%), b. p. 95—97°/1 mm., n_D^{17} 1.5173 (Found: C, 80.3; H, 9.7. C₁₁H₁₆O requires C, 80.45; H, 9.8%).

5-cycloHex-1'-enylpent-2-en-4-yne (VI; R' = Me).—A solution of the foregoing alcohol (17.1 g.) in pyridine (20 c.c.) was added cautiously with gentle agitation to phosphorus oxychloride (15 c.c.) in pyridine (15 c.c.) in a flask fitted with an air condenser. When the exothermic reaction had gone to completion, the mixture was allowed to cool to 20°, and the product was isolated with pentane. Distillation gave the hydrocarbon (13 g., 85%), b. p. 67°/1 mm., n_D^{23} 1.5468 (Found: C, 90.1; H, 9.6. C₁₁H₁₄ requires C, 90.35; H, 9.65%).

When a solution of the alcohol (5 g.) in formic acid (22 c.c.; *d* 1.20) was heated under reflux for 45 minutes, a mixture of the hydrocarbon and unchanged alcohol was obtained. None of the distillation fractions gave a positive ketone test with 2 : 4-dinitrophenylhydrazine.

Hydration of 5-cycloHex-1'-enylpent-2-en-4-yne.—(a) Mercuric oxide (0.6 g.) was dissolved by gentle warming in a mixture of methanol (0.6 c.c.), boron trifluoride-ether complex (0.2 c.c.), and trichloroacetic acid (0.05 g.). Methanol (5 c.c.), followed by a solution of the hydrocarbon (4.4 g.) in absolute methanol (10 c.c.), was added to the catalyst solution at 20°. The temperature of the mixture rose to ca. 50°, and a dark brown colour developed. After the mixture had been allowed to cool to 25°, it was filtered into sodium hydrogen carbonate solution and extracted with ether. Distillation gave a mixture (3.0 g.), b. p. 60—90°/0.4 mm., n_D^{19} 1.5361—1.5128. The total distillate was treated with semicarbazide acetate reagent, to yield a solid (1.4 g.), m. p. 170—175°, which was separated into two (still impure) components (m. p.s 163—164° and 182—183°) by recrystallisation from 80% methanol. The combined semicarbazones (1 g.) were converted directly into the mixed 2 : 4-dinitrophenylhydrazones, which were separated by chromatography on alumina. The more easily eluted 3-ethyl-4 : 5 : 6 : 7-tetrahydroindan-1-one (VIII; R' = Me) 2 : 4-dinitrophenylhydrazone (0.96 g.) formed dark red needles (from ethanol), m. p. (K) 193° (Found: C, 59.25; H, 5.8. C₁₇H₂₀O₄N₄ requires C, 59.3; H, 5.85%). Further elution gave 1-pent-3'-enoylcyclohex-1-ene* (VII; R' = Me) 2 : 4-dinitrophenylhydrazone (0.42 g.) as vermilion plates (from ethanol), m. p. (K) 123° (Found: C, 59.2; H, 5.9. C₁₇H₂₀O₄N₄ requires C, 59.3; H, 5.85%).

(b) The hydrocarbon (3 g.), dissolved in methanol (30 c.c.) and water (1 c.c.), was added at 20° to a catalyst solution, prepared as above from mercuric oxide (0.4 g.). The temperature slowly rose to 23°; after 5 hours at room temperature the solution was filtered into sodium hydrogen carbonate solution, and the organic products were isolated with ether. Distillation gave two major products, (i) (0.75 g.), n_D^{20} 1.5349, mainly unchanged hydrocarbon, and (ii) (1.6 g.), n_D^{20} 1.5292—1.5093, which contained ketonic material. The latter product was treated with semicarbazide acetate in methanol, to yield 3-ethyl-4 : 5 : 6 : 7-tetrahydroindan-1-one semicarbazone. This derivative (1.1 g.) formed needles, m. p. (K) 200—202°, from 80% methanol (Found: C, 65.15; H, 8.9. C₁₂H₁₈ON₃ requires

* Geneva nomenclature of the acid (CO₂H = 1).

C, 65.15; H, 8.65%). Conversion of a portion of the semicarbazone into the 2 : 4-dinitrophenylhydrazone gave a product, m. p. (K) 193°, undepressed on admixture with that obtained in the previous hydration experiment.

Hydrolysis of the semicarbazone (1 g.) gave the pure *ketone* (VIII; R' = Me) (0.66 g.), b. p. 79—80°/0.1 mm., n_D^{19} 1.5120 (Found: C, 80.35; H, 9.75. $C_{11}H_{16}O$ requires C, 80.45; H, 9.8%).

Attempted hydration of the hydrocarbon in the presence of mercuric sulphate (cf. Nazarov and Pinkina, *loc. cit.*) or mercuric acetate led to inappreciable amounts of ketonic product, most of the starting material being recovered unchanged.

Cyclisation of the foregoing 2 : 4-dinitrophenylhydrazone (52 mg.) was effected by heating its solution in formic acid (2.5 c.c. of 90%) and phosphoric acid (0.9 g.) at 100° for 6 hours. Chromatographic purification gave one main band containing 40 mg. of material, which after recrystallisation yielded 3-ethyl-4 : 5 : 6 : 7-tetrahydroindanone 2 : 4-dinitrophenylhydrazone (32 mg.), m. p. (K) 192—193°, undepressed on admixture with an authentic specimen. Light absorption in chloroform: Maxima, 2600 and 3970 Å; $\epsilon = 18,000$ and 28,000 respectively.

4-1'-Hydroxycyclohexylbut-1-en-3-yne (V; R' = H).—Vinylacetylene (17.5 g.), prepared from but-3-yn-1-ol as described by Eglinton and Whiting (*loc. cit.*), was slowly distilled from a trap containing a piece of calcium chloride (for drying and to promote ebullition) into a solution of ethylmagnesium bromide (from magnesium, 7 g.) in benzene (100 c.c.). After 1 hour, cyclohexanone (33 g.) in benzene (50 c.c.) was added during 30 minutes, the mixture being kept at 10°. After being stirred overnight, the resultant complex was decomposed in the usual way. Distillation gave the alcohol (30.3 g., 60%), b. p. 80—81°/2 mm., n_D^{15} 1.5170 (Nazarov *et al.* give n_D^{15} 1.5168). On cooling, the alcohol solidified; it could be recrystallised from light petroleum (b. p. 40—60°) to yield cubes, m. p. (K) 33—34°.

4-cycloHex-1'-enylbut-1-en-3-yne (VI; R' = H) and its Hydration.—This hydrocarbon was prepared as described by Nazarov and Pinkina; it had b. p. 77—79°/12 mm., n_D^{16} 1.5492 (*idem*, n_D^{15} 1.5490). Hydration by Nazarov and Pinkina's procedure gave a ketonic product, essentially (VIII; R' = H), b. p. 83—85°/1 mm., n_D^{15} 1.5135 (*idem*, n_D^{15} 1.5155). Light absorption: Maximum, 2400 Å; $\epsilon = 11,000$. The 2 : 4-dinitrophenylhydrazone, purified by chromatography, had m. p. (K) 246° (Found: C, 57.95; H, 5.7. $C_{16}H_{18}O_4N_4$ requires C, 58.15; H, 5.5%). Subjecting this ketone to Nazarov and Pinkina's cyclisation procedure effected little alteration in the properties of the material; it then had b. p. 84—86°/1 mm., n_D^{16} 1.5150 (*idem*, n_D^{15} 1.5146). Light absorption: see Table. The same 2 : 4-dinitrophenylhydrazone, m. p. (K) and mixed m. p. (K) 246°, was obtained. The semicarbazone crystallised from methanol as needles, m. p. (K) 210—212° (*idem*, m. p. 210°).

5-1'-Hydroxycyclohexylpent-2-en-4-yn-1-ol (V; R' = CH₂OH).—A solution of pent-2-en-4-yn-1-ol (10.2 g.) in benzene (100 c.c.) was added with stirring and cooling to ethylmagnesium bromide solution [from magnesium, 6.75 g., the ether being replaced by benzene (100 c.c.) after formation of the reagent]. When the exothermic reaction was complete, stirring was continued for 90 minutes, whereupon the complex had separated as a jelly. The mixture was warmed to 60° for 5 minutes with stirring, causing the complex to become a greyish-white suspension. After cooling to 20°, the stirred mixture was treated slowly with cyclohexanone (12.5 g.) with external cooling. After overnight stirring, the product was isolated with ether. A viscous brown oil (18 g., 80%) was obtained: light absorption: Maximum, 2290 Å; $\epsilon = 9500$. A portion was distilled at 110—130° (bath-temp., short-path still)/10⁻⁴ mm. giving a pale yellow liquid, n_D^{15} 1.5402.

Treatment of the glycol (0.33 g.) in pyridine (0.5 c.c.) and benzene (5 c.c.) with *p*-phenylazobenzoyl chloride (0.43 g.) gave the *mono-p*-phenylazobenzoate, which after recrystallisation from isopropanol formed orange plates (0.58 g.), m. p. 116° (Found: C, 73.95; H, 6.4. $C_{24}H_{24}O_3N_2$ requires C, 74.2; H, 6.2%).

Alkaline hydrolysis of the ester gave the pure *glycol*, b. p. 110—120° (bath-temp., short-path still)/10⁻⁵ mm., n_D^{17} 1.5410 (Found: C, 73.0; H, 8.8. $C_{11}H_{16}O_2$ requires C, 73.3; H, 8.95%).

5-cycloHex-1'-enylpent-2-en-4-yn-1-ol (VI; R' = CH₂OH).—A solution of the glycol *mono-p*-phenylazobenzoate (0.37 g.) in benzene (5 c.c.) and formic acid (3 c.c.; *d* 1.20) was heated under reflux for 30 minutes. After addition of water, the benzene layer was separated and chromatographed on alumina. Elution with benzene-ether (1 : 3) gave a product (0.29 g.), m. p. 97°, which when recrystallised from isopropanol gave 5-cyclohex-1'-enylpent-2-en-4-yn-1-yl *p*-phenylazobenzoate as orange-red plates, m. p. 98—99° (Found: C, 77.55; H, 5.7. $C_{24}H_{22}O_3N_2$ requires C, 77.8; H, 6.0%). The dehydration was also readily accomplished with phosphorus oxychloride in pyridine at 70°.

Hydrolysis of this ester gave the parent *carbinol*, b. p. 60—70° (bath-temp., short-path still)/5 × 10⁻⁵ mm., n_D^{17} 1.5732 (Found: C, 81.15; H, 8.5. $C_{11}H_{14}O$ requires C, 81.4; H, 8.7%).

1-1'-Hydroxy-2' : 2'-dimethylcyclohexylhex-1-yne (this and subsequent experiments which describe the preparation of compounds starting from 2 : 2-dimethylcyclohexanone were carried out by Mrs. A. Mende).—Hex-1-yne (9 g.) in ether-benzene (1 : 1; 20 c.c.) was added slowly at room temperature to a solution of ethylmagnesium bromide in ether (40 c.c.) (prepared from magnesium, 2.67 g.). This solution was kept for 1 hour at room temperature, whereafter 2 : 2-dimethylcyclohexanone (12.6 g.) in ether (10 c.c.) was added; a slight exothermic reaction took place and the solution became milky. After the mixture had been kept at room temperature overnight, the *alcohol* (15.5 g., 75%) was isolated in the usual way; it had b. p. 116°/2.5 mm., n_D^{19} 1.4810 (Found: C, 80.4; H, 11.4. $C_{14}H_{24}O$ requires C, 80.7; H, 11.6%).

2-Hex-1'-ynyl-3 : 3-dimethylcyclohexene.—1-1'-Hydroxy-2' : 2'-dimethylcyclohexylhex-1-yne (2 g.) in dry pyridine (3 c.c.) was treated with phosphorus oxychloride (3.5 c.c.) in dry pyridine (10 c.c.), and then kept at 20° for 30 minutes. The solution was heated on the steam-bath for 3 hours and, after cooling, treated with ice, and the product isolated in pentane. Distillation gave a nearly pure product

(1.49 g., 80%), b. p. 77°/0.9 mm., n_D^{18} 1.4898. A portion of this material in pentane was chromatographed on a short column of alumina, which removed small quantities of unchanged alcohol. The pentane eluate on evaporation gave 1-6': 6'-dimethylcyclohex-1'-enylhex-1-yne, b. p. 77°/0.9 mm., n_D^{15} 1.4912 (Found: C, 88.1; H, 11.45. $C_{14}H_{22}$ requires C, 88.35; H, 11.65%).

5-1'-Hydroxy-2': 2'-dimethylcyclohexylpent-2-en-4-yn-1-ol.—A solution of ethylmagnesium bromide was prepared from magnesium (5.35 g.) in ether; dry benzene (80 c.c.) was then added and the ether removed by distillation. A solution of freshly distilled pent-2-en-4-yn-1-ol (8.2 g.) in benzene (40 c.c.) was added at 0° and the solution was stirred at this temperature for 2 hours. 2: 2-Dimethylcyclohexanone (12.6 g.) in benzene (16 c.c.) was added at 0° during 30 minutes, and finally stirred at room temperature overnight (18 hours). Isolation in the usual way gave a partly crystalline product consisting of the required glycol contaminated with 2: 2-dimethylcyclohexanone and pent-2-en-4-yn-1-ol. Most of the latter two products were removed at 80°/2 mm., and the solid residue was recrystallised from light petroleum (b. p. 60—80°) to give the glycol (4.0 g.), m. p. 87—88°. Further recrystallisation from benzene-light petroleum (b. p. 60—80°) gave the glycol as plates, m. p. 95° (Found: C, 75.1; H, 9.5. $C_{13}H_{20}O_2$ requires C, 74.95; H, 9.65%).

The *mono-p-phenylazobenzoate* of the above glycol was prepared by adding *p*-phenylazobenzoyl chloride (0.73 g.) to the glycol (0.5 g.) in benzene (10 c.c.) and pyridine (1 c.c.). After the mixture had been kept overnight at room temperature, water (3 c.c.) was added and the whole kept at 60° for 5 minutes with intermittent shaking. The solid (*p*-phenylazobenzoic anhydride) was filtered off, and the required ester isolated in the usual way. The pure ester (0.8 g.) crystallised from methanol as plates, m. p. 62—63° (Found: C, 75.1; H, 7.1. $C_{26}H_{28}O_3N_2$ requires C, 74.95; H, 6.75%).

Dehydration of this *p*-phenylazobenzoate (0.2 g.) was accomplished by dissolving it in pyridine (1 c.c.) and adding phosphorus oxychloride (0.4 c.c.) in pyridine (2 c.c.). The solution was heated on a steam-bath for 1½ hours, when the product was isolated with ether. Recrystallisation from methanol gave the *p*-phenylazobenzoate of 5-6': 6'-dimethylcyclohex-1'-enylpent-2-en-4-yn-1-ol (0.13 g.) as plates, m. p. 84—85° (Found: C, 78.55; H, 6.85. $C_{26}H_{26}O_2N_2$ requires C, 78.35; H, 6.55%).

5-1'-Hydroxy-2': 2': 6'-trimethylcyclohexylpent-2-en-4-yne.—Pent-2-en-4-yne (11.3 g.) in dry ether (100 c.c.) was added during 30 minutes to ethylmagnesium bromide (from magnesium, 4.5 g.). The solution was then stirred at 20° for 90 minutes. 2: 2: 6-Trimethylcyclohexanone (23 g.) in ether (30 c.c.) was added slowly, the mixture then being stirred overnight. Isolation in the usual way gave the alcohol (14.8 g., 50%), b. p. 94°/0.5 mm., n_D^{17} 1.5075 (Found: C, 81.1; H, 10.55. $C_{14}H_{22}O$ requires C, 81.4; H, 10.7%).

5-2': 6': 6'-Trimethylcyclohex-1'-enylpent-2-en-4-yne.—A mixture of the above alcohol (8.5 g.), phosphorus oxychloride (10 c.c.), and dry pyridine (15 c.c.) was heated at 70° for 24 hours. The product was isolated with pentane, the extract being passed through a column of alumina, which retained unchanged carbinol. Elution with pentane gave the hydrocarbon (4.4 g., 60%), b. p. 80°/0.3 mm., n_D^{18} 1.5311 (Found: C, 89.05; H, 10.5. $C_{14}H_{20}$ requires C, 89.3; H, 10.7%).

Attempted hydration of this hydrocarbon by the boron trifluoride-methanol method (50° for 2 hours) gave mainly unchanged hydrocarbon together with 20% of material, b. p. 80—83°/0.3 mm., n_D^{15} 1.5125—1.5292. Light absorption: Maximum, 2280 Å; $E_{1\%}^{1\text{cm}}$ 430. No 2: 4-dinitrophenylhydrazone could be obtained.

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