52. *Studies in the Polyene Series. Part XVI. The Condensation of αβ-Unsaturated Ketones with 1-Hexyne.*

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Condensations between hexynylmagnesium bromide and methyl vinyl ketone, ethylideneacetone, and mesityl oxide give 60% yields of the expected tertiary carbinols (I). The experimental conditions are somewhat critical, as rearrangement and dehydration may ensue, but low reaction temperatures and low concentrations of reactants in general favour formation of the normal products. Anionotropic rearrangements of the tertiary carbinols (I) to the conjugated vinylacetylenylcarbinols (II) are considerably more facile than those of closely related secondary carbinols and an obvious explanation is suggested. The isomerisation products (II) all exhibit the anticipated light-absorption characteristic of the vinylacetylene chromophore, and their structures have been rigidly proved by complete hydrogenation.

Although the literature abounds with references to the condensation of carbonyl compounds with acetylene, very few condensations involving αβ-unsaturated ketones have been described. We have found that such condensations are by no means easy to effect, the yields obtainable by the standard methods being usually poor and often negligible. Work on this problem is still proceeding; however, considerable progress has been made and the results will be published in due course. Since we were at least equally interested (J., 1942, 727) in the interaction of substituted acetylenes with αβ-unsaturated ketones, and since rather more favourable indications were obtained from a perusal of the literature, we have studied the condensation of a substituted acetylene, 1-hexyne, with three simple unsaturated ketones.

The most satisfactory method of effecting condensations with alkylacetylenes is by means of their Grignard complexes. Reactions between Grignard reagents and αβ-unsaturated ketones, however, may take place by either 1 : 2- or 1 : 4-addition (Kohler *et al.*, *Amer. Chem. J.*, 1909, **42**, 375; 1907, **38**, 5; 1904, **31**, 642), but with hexynylmagnesium bromide and the three simple ketones chosen for this study, no indication of the formation of 1 : 4-addition products was ever obtained.

As far as we are aware, Grignard reactions have not hitherto been performed with the simplest αβ-unsaturated ketone, methyl vinyl ketone. [While this paper was being prepared for publication, Smith and Sprung (*J. Amer. Chem. Soc.*, 1943, **65**, 1276) reported failure to make it react with laurylmagnesium bromide, owing to polymerisation of the ketone.] Nevertheless, when it was allowed to react with hexynylmagnesium bromide at room temperature, 3-*methylnon*-1-*en*-4-*yn*-3-*ol* (I; $R_1 = R_2 = H$) was obtained without difficulty in 55% yield. (Smith and Sprung may have carried out their experiments in boiling ethereal solutions.) As evidence that normal 1 : 2-addition had occurred, the following facts may be cited. The product contained one active hydrogen atom (Zerewitinoff), it exhibited no appreciable absorption in the ultra-violet, and failed to react even after long standing with phenyl or α-naphthyl *iso*cyanate. Since the tertiary carbinol obtainable on complete hydrogenation would not readily be characterised, such evidence for the structure assigned was not sought, but it is to be noted that the facile anionotropic rearrangement (described later) to a product whose constitution has been rigidly proved provides ample confirmation of the correctness of the formulation of the original condensation product.

A similar condensation with ethylideneacetone gave 4-*methyldec*-2-*en*-5-*yn*-4-*ol* (I; $R_1 = H$; $R_2 = Me$) in 55% yield, this carbinol possessing properties closely akin to those of the methyl vinyl ketone product. The greater accessibility of the parent ketone permitted a more detailed study of this reaction from which valuable information was gained. When the condensation between the hexynylmagnesium bromide and the $\alpha\beta$-unsaturated ketone was carried out in boiling ethereal solution, the product obtained corresponded closely

$$CH_3{\cdot}[CH_2]_3{\cdot}C{\vdots}C{\cdot}C(OH)Me{\cdot}CH{:}CR_1R_2 \quad (I.)$$
$$CH_3{\cdot}[CH_2]_3{\cdot}C{\vdots}C{\cdot}CMe{:}CH{\cdot}C(OH)R_1R_2 \quad (II.)$$
$$CH_3{\cdot}[CH_2]_3{\cdot}C{\vdots}C{\cdot}CMe{:}CH{\cdot}CH{:}CH_2 \quad (III.)$$

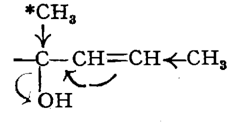
in its constants to that of the isomeric carbinol (II; $R_1 = H$; $R_2 = Me$) which, as will be seen later, is normally produced by the action of acids on the original condensation product. It would thus appear that at quite moderate temperatures the –OMgBr group participates in an anionotropic rearrangement. When hexynylmagnesium iodide was employed in place of the bromide in an experiment in which the reaction mixture was refluxed for some hours, a mixture consisting entirely of hydrocarbons (no active hydrogen) was obtained. One fraction, which showed intense and complex light absorption (maxima at 2360, 2620, and an inflexion at 2740 A.; $E^{1\%}_{1\,\mathrm{cm.}}$ 720, 480, and 370, respectively) obviously contained an appreciable quantity of a triply unsaturated hydrocarbon such as (III). It is obvious that the intermediate organometallic complexes (particularly the magnesium iodide) in these Grignard condensations are somewhat labile, and in this connection it has also been observed that normal condensation products can only be isolated provided the reactions are effected in moderately dilute solutions. Jacquemain (*Compt. rend.*, 1934, **198**, 483) found that the use of alkylmagnesium iodides in Grignard reactions with mesityl oxide resulted in extensive dehydration of the tertiary carbinols.

The nature of the product isolated from condensations between mesityl oxide and hexynylmagnesium bromide was even more dependent upon the experimental conditions. In warm concentrated solutions the product consisted entirely of hydrocarbon, whereas in cold dilute solutions, a 66% yield of 2 : 4-*dimethyldec*-2-*en*-5-*yn*-4-*ol* (I; $R_1 = R_2 = Me$) was readily achieved, the carbinol exhibiting properties in accord with the formulation given. This ease of dehydration may explain why Nazarov and Elizarova (*Chem. Abstracts*, 1942, **36**, 742) obtained only a hydrocarbon on condensing mesityl oxide with vinylacetylenylmagnesium bromide.

The rearrangement in the presence of acids of numerous acetylenic carbinols and glycols derived from unsaturated aldehydes has been thoroughly described in the preceding papers in this series (Parts VIII—XV),

$$CH_3{\cdot}[CH_2]_3{\cdot}C{\vdots}C{\cdot}CH(OH){\cdot}CH{:}CH{\cdot}CH_3 \quad (IV.)$$
$$CH_3{\cdot}[CH_2]_3{\cdot}C{\vdots}C{\cdot}CH{:}CH{\cdot}CH(OH){\cdot}CH_3 \quad (V.)$$

the condensation product (IV) between 1-hexyne and crotonaldehyde, for example, isomerising to the conjugated vinylacetylenylcarbinol (V) on shaking with 25% sulphuric acid for 24 hours. In the cases of the carbinols (I) derived from hexyne and $\alpha\beta$-unsaturated ketones, the rearrangement is much more facile, shaking with 0·5% sulphuric acid for 3—5 hours sufficing to give practically quantitative yields of the isomeric carbinols (II). Solubility differences between (IV) and (I; $R_1 = H$; $R_2 = Me$) can only be of a low order, and the increased mobility of the anionotropic system must be occasioned mainly by the inductive effect of the additional methyl group (* in inset), which would naturally tend to facilitate the separation of the hydroxylic anion.



Isomerisation of the carbinol (I; $R_1 = R_2 = H$) from methyl vinyl ketone by shaking for 4 hours with 0·5% sulphuric acid gave an excellent yield of 3-*methylnon*-2-*en*-4-*yn*-1-*ol* (II; $R_1 = R_2 = H$) which, being a primary alcohol, formed an α-*naphthylurethane* very readily. Its constitution was proved by hydrogenation to 3-methylnonan-1-ol (α-*naphthylurethane*) which was oxidised to 2-*n*-hexylbutyric acid. Since no solid derivatives of this acid are described in the literature, it was synthesised from methyl hexyl ketone by

$$HC{\vdots}C{\cdot}CH(OH){\cdot}CH{:}CH_2 \quad (VI.)$$

means of a Reformatsky reaction and dehydration of the resultant hydroxy-ester followed by hydrogenation and hydrolysis. The p-*toluidides* prepared from the two specimens were identical. The facile rearrangement of the carbinol (I; $R_1 = R_2 = H$) is in striking contrast to the immobility of the hydroxyl group in the similarly constituted vinylethynylcarbinol (VI) (Jones and McCombie, J., 1943, 261) and phenylvinylcarbinol (Burton and Ingold, J., 1928, 904), indicating the surprisingly powerful influence of the tertiary methyl group.

Treatment of the carbinol (I; $R_1 = H$; $R_2 = Me$) from ethylideneacetone with either 0·5 or 5% sulphuric acid for 3 hours gave 4-*methyldec*-3-*en*-5-*yn*-2-*ol* (II; $R_1 = H$; $R_2 = Me$), characterised by the preparation of the α-*naphthylurethane*, in practically theoretical yield. Hydrogenation gave 4-*methyldecan*-2-*ol* (α-*naphthylurethane*), oxidised to 4-methyldecan-2-one, the semicarbazone of which had a somewhat higher m. p. than that given in the literature. Further structural proof was afforded by the hypobromite oxidation of the latter ketone to 2-*n*-hexylbutyric acid.

The conditions for the successful isomerisation of the carbinol (I; $R_1 = R_2 = Me$) from mesityl oxide were highly critical. With 0·5% sulphuric acid for 3 hours, conversion was incomplete, but after a further 2 hours an excellent yield of 2 : 4-*dimethyldec*-3-*en*-5-*yn*-2-*ol* (II; $R_1 = R_2 = Me$) was obtained. No crystalline derivatives could be prepared from this tertiary carbinol. Treatment of the original carbinol with 1% sulphuric acid for 24 hours gave a product (maximum at 2620 A.; $E^{1\%}_{1\,\mathrm{cm.}}$ 410) which had undergone rearrangement followed by dehydration, and with 5% acid for the same time the product had a more complex absorption spectrum (maxima at 2640 and 2400 A.; $E^{1\%}_{1\,\mathrm{cm.}}$ 360 and 320, respectively) indicating some dehydration of the rearranged carbinol and also some dehydration of the starting material

Further evidence of the lability of the anionotropic system present in carbinol (I; $R_1 = R_2 = Me$) was obtained when mesityl oxide was condensed with hex-3-en-5-yn-2-ol (VII; cf. previous paper) by the Grignard method. The glycol (VIII), 2 : 4-*dimethyldeca*-2 : 7-*dien*-5-*yn*-4 : 9-*diol*, produced in 25% yield, underwent

$$HC\vdots C{\cdot}CH{:}CH{\cdot}CH(OH){\cdot}CH_3 \quad \text{(VII.)}$$
$$CMe_2{:}CH{\cdot}C(OH)Me{\cdot}C\vdots C{\cdot}CH{:}CH{\cdot}CH(OH){\cdot}CH_3 \quad \text{(VIII.)}$$

some rearrangement (as indicated by the appearance of an inflexion at 2630 A. in its absorption spectrum) even on distillation at 10^{-4} mm.

The absorption spectra (table) of the three pure isomerised carbinols (II), containing the conjugated vinyl-acetylene chromophore, are all closely analogous both amongst themselves and when compared with similar carbinols previously examined (*see* Parts VIII, IX, X, XIV, and XV).

	$\lambda_{max.}$, A.	$\varepsilon_{max.}$	$\lambda_{infl.}$, A.	$\varepsilon_{infl.}$
3-Methylnon-2-en-4-yn-1-ol (II; $R_1 = R_2 = H$)	2275	14,000	2350	11,000
4-Methyldec-3-en-5-yn-2-ol (II; $R_1 = H$; $R_2 = Me$)	2275	14,500	2320	8,000
2 : 4-Dimethyldec-3-en-5-yn-2-ol (II; $R_1 = R_2 = Me$) ...	2280	12,500	2400	7,500

In view of the unsatisfactory results attendant upon attempts to condense acetylene itself with αβ-ethylenic ketones, it was considered of interest to investigate the behaviour of αβ-acetylenic ketones in this respect. Oct-3-yn-2-one (IX) is a fairly readily accessible ketone of this type, having been prepared by Kroeger and Nieuwland (*J. Amer. Chem. Soc.*, 1936, **58**, 1862) by condensation of hexynylmagnesium chloride with acetic anhydride. After this substance (for which we are indebted to Mr. J. T. McCombie) had been kept with sodium acetylide (from sodium) in liquid ammonia, it was recovered almost quantitatively. With hexynylmagnesium bromide, however, it gave a 48% yield of 7-methyltrideca-5 : 8-diyn-7-ol (X), which had previously been

$$CH_3{\cdot}[CH_2]_3{\cdot}C\vdots C{\cdot}CO{\cdot}CH_3 \quad \text{(IX.)}$$
$$CH_3{\cdot}[CH_2]_3{\cdot}C\vdots C{\cdot}C(OH)Me{\cdot}C\vdots C{\cdot}[CH_2]_3{\cdot}CH_3 \quad \text{(X.)}$$

obtained by Kroeger and Nieuwland (*loc. cit.*) as a by-product in the preparation of the ketone (IX). It is evident, therefore, that in condensations with substances containing free ethynyl groups, αβ-acetylenic ketones closely resemble the αβ-ethylenic compounds in that reaction with substituted acetylenes is more facile than with acetylene itself.

EXPERIMENTAL.

(Absorption spectra were determined in alcoholic solutions.)

3-*Methylnon*-1-*en*-4-*yn*-3-*ol* (I; $R_1 = R_2 = H$).—A solution of 1-hexyne (24 g.) in ether (400 c.c.) was added gradually to an ethereal solution of ethylmagnesium bromide (from 6 g. of magnesium), and the mixture refluxed for 3 hours. A solution of methyl vinyl ketone (17·5 g.) in ether (300 c.c.) was now dropped into the cooled reaction mixture in a nitrogen atmosphere, after which it was stirred vigorously for a further 3 hours and then set aside overnight. Subsequent isolation of the product in the usual manner yielded 3-*methylnon*-1-*en*-4-*yn*-3-*ol* (19·5 g.) as a colourless mobile liquid, b. p. 61—61·5°/3·5 mm., $n_D^{17^\circ}$ 1·4593 (Found: C, 78·6; H, 10·5. $C_{10}H_{16}O$ requires C, 78·9; H, 10·6%). *Active hydrogen* (Zerewitinoff): The carbinol (90 mg.) evolved 15·0 c.c. of methane at 22°/756 mm., equivalent to 1·05 active hydrogen atoms per mol.

4-*Methyldec*-2-*en*-5-*yn*-4-*ol* (I; $R_1 = H$; $R_2 = Me$).—Condensation of hexynylmagnesium bromide, from 1-hexyne (22·5 g.) and magnesium (6 g.), with ethylideneacetone (20 g.) in ether (400 c.c.) gave the *carbinol* (20·7 g.) as a colourless mobile liquid, b. p. 62—62·5°/2 mm., $n_D^{19^\circ}$ 1·4641 (Found: C, 79·75; H, 11·1. $C_{11}H_{18}O$ requires C, 79·45; H, 10·9%). *Active hydrogen* (Zerewitinoff): The carbinol (93 mg.) evolved 13·9 c.c. of methane at 25°/760 mm. (1·0 active hydrogen atom per mol.). Neither this nor the preceding compound showed appreciable light absorption in the ultra-violet.

2 : 4-*Dimethyldec*-2-*en*-5-*yn*-4-*ol* (I; $R_1 = R_2 = Me$).—By the method described above, 1-hexyne (11·3 g.), magnesium (3 g.), and mesityl oxide (12 g.) in ether (950 c.c.) afforded the *carbinol* (14·2 g.) as a colourless mobile liquid, b. p. 69—69·5°/3 mm., $n_D^{19^\circ}$ 1·4673 (Found: C, 79·9; H, 11·3. $C_{12}H_{20}O$ requires C, 79·9; H, 11·2%). *Active hydrogen* (Zerewitinoff): The carbinol (102 mg.) gave 13·5 c.c. of methane at 21°/765 mm. (1·0 active hydrogen atom per mol.). It showed no absorption of appreciable intensity in the ultra-violet.

4-*Methyldec*-3-*en*-5-*yn*-2-*ol* (II; $R_1 = H$; $R_2 = Me$).—A mixture of 4-methyldec-2-en-5-yn-4-ol (12 g.) and sulphuric acid (2000 c.c.; 0·5% w/v) was shaken vigorously for 3 hours at 20°. Isolation of the product by means of ether yielded the *carbinol* (10·5 g.) as a colourless mobile liquid, b. p. 84°/2 mm., 28° (bath temp.)/10^{-4} mm., $n_D^{19^\circ}$ 1·4786 (Found: C, 79·65; H, 11·0. $C_{11}H_{18}O$ requires C, 79·45; H, 10·9%). *Active hydrogen* (Zerewitinoff): The carbinol (94 mg.) gave 13·5 c.c. of methane at 23°/769 mm. (1·0 active hydrogen atom per mol.). The *α-naphthylurethane* separated from light petroleum (b. p. 40—60°) in needles, m. p. 71° (Found: N, 4·2. $C_{22}H_{25}O_2N$ requires N, 4·2%).

4-*Methyldecan*-2-*ol*.—A solution of 4-methyldec-3-en-5-yn-2-ol (5·4 g.) in ethyl acetate (100 c.c.) was shaken with platinic oxide (100 mg.) and hydrogen until absorption ceased. The catalyst was filtered off and the solvent removed through a column, leaving a residue of 4-*methyldecan*-2-*ol* (3·8 g.), b. p. 104°/12 mm., $n_D^{19^\circ}$ 1·4332 (Found: C, 76·45; H, 13·8. $C_{11}H_{24}O$ requires C, 76·65; H, 14·05%). *Active hydrogen* (Zerewitinoff): The carbinol (105 mg.) gave 15·6 c.c. of methane at 28°/755 mm. (1·05 active hydrogen atoms per mol.). The *α-naphthylurethane* separated from methyl alcohol as needles, m. p. 63° (Found: N, 4·2. $C_{22}H_{31}O_2N$ requires N, 4·1%).

4-*Methyldecan*-2-*one*.—Oxidation of the above carbinol with chromic–sulphuric acid mixture gave the ketone, b. p. 95—96°/12 mm., $n_D^{21^\circ}$ 1·4294. The semicarbazone separated from light petroleum (b. p. 40—60°) in plates, m. p. 69° (Found: C, 63·55; H, 11·0. Calc. for $C_{12}H_{25}ON_3$: C, 63·4; H, 11·1%). (Bouveault and Locquin, *Bull. Soc. chim.*, 1904, **31**, 1158, give b. p. 115°/25 mm. for the ketone and m. p. 66° for the semicarbazone.)

3-*Methylnon*-2-*en*-4-*yn*-1-*ol* (II; $R_1 = R_2 = H$).—A mixture of 3-methylnon-1-en-4-yn-3-ol (5·5 g.) and sulphuric acid (1000 c.c.; 0·5% w/v) was shaken at 20° under nitrogen for 4 hours. Isolation with ether gave 3-*methylnon*-2-*en*-4-*yn*-1-*ol* (4·9 g.) as a colourless mobile liquid, b. p. 75·5—76°/3·5 mm.; $n_D^{17^\circ}$ 1·4858 (Found: C, 79·1; H, 10·45. $C_{10}H_{16}O$ requires C, 78·9; H, 10·6%). *Active hydrogen* (Zerewitinoff): The carbinol (90 mg.) evolved 15·1 c.c. of methane at 20°/766 mm. (1·05 active hydrogen atoms per mol.). The *α-naphthylurethane*, obtained after allowing the carbinol to react with α-naphthyl *iso*cyanate for only 6 hours at 20°, separated from methyl alcohol in needles, m. p. 69—70° (Found: N, 4·45. $C_{21}H_{23}O_2N$ requires N, 4·35%).

3-*Methylnonan*-1-*ol*.—A solution of the preceding carbinol (5·1 g.) in ethyl acetate (30 c.c.) together with platinic oxide

(100 mg.) was shaken with hydrogen until absorption was complete. Removal of the catalyst by filtration, followed by distillation of the solvent through a column, left a residue of 3-methylnonan-1-ol (5·0 g.), b. p. 121—121·5°/24 mm., $n_D^{19^\circ}$ 1·4372 (Levene and Taylor, *J. Biol. Chem.*, 1922, **54**, 351, and Levene and Marker, *ibid.*, 1931, **91**, 77, give b. p. 122°/24 mm., $n_D^{25^\circ}$ 1·4348). The α-*naphthylurethane* separated from alcohol in needles, m. p. 49° (Found : N, 4·45. $C_{21}H_{29}O_2N$ requires N, 4·3%).

2-n-*Hexylbutyric Acid.*—(a) A portion of a solution of methyl hexyl ketone (17 g.) and ethyl bromoacetate (22·5 g.) in dry benzene (300 c.c.) was added to zinc needles (9 g.), and the mixture heated under reflux with stirring. When reaction commenced, the remainder of the solution was dropped in during 2 hours, and refluxing and stirring were continued for 2 hours longer. The hydroxy-ester was isolated in the normal manner, and on heating it to 100—150°/760 mm., smooth dehydration occurred after which the unsaturated ester distilled at 237—238°. Redistillation gave ethyl 2-methyl-2-*n*-hexylacrylate (16·6 g.; 62% yield), b. p. 126—126·5°/18 mm., $n_D^{18^\circ}$ 1·4460 (Bouveault and Blanc, *Bull. Soc. chim.*, 1904, **31**, 1208, give b. p. 119—120°/14 mm.).

A solution of the above ester (7·6 g.) in methyl alcohol (75 c.c.) was hydrogenated in the presence of platinic oxide (100 mg.), giving ethyl 2-*n*-hexylbutyrate (7·5 g.), b. p. 123·5°/24 mm., $n_D^{18^\circ}$ 1·4268 (Levene *et al.*, *J. Biol. Chem.*, 1931, **91**, 77; 1922, **54**, 351, give b. p. 115°/13 mm., 135°/36 mm., $n_D^{25^\circ}$ 1·4232). The ester was hydrolysed by refluxing with 25% alcoholic potassium hydroxide, yielding 2-*n*-hexylbutyric acid, b. p. 98—99°/2 mm., $n_D^{21^\circ}$ 1·4352 (Chargaff and Abel, *Biochem. J.*, 1934, **28**, 1901, give b. p. 115—120°/3 mm.). The p-*toluidide*, prepared by heating the acid under reflux with *p*-toluidine, formed needles from alcohol, m. p. 76—77° (Found : C, 78·35; H, 10·45; N, 5·7. $C_{17}H_{27}ON$ requires C, 78·1; H, 10·4; N, 5·35%).

(b) Oxidation of 3-methylnonan-1-ol with chromic acid also gave 2-*n*-hexylbutyric acid, b. p. 162°/22 mm., $n_D^{17^\circ}$ 1·4372 (Levene *et al.*, *loc. cit.*, give b. p. 147—148°/12 mm., 133°/8 mm., $n_D^{25^\circ}$ 1·4339). The *p*-toluidide, prepared as above, had m. p. 76—77°, undepressed on admixture with the synthetic specimen.

(c) A mixture of 4-methyldecan-2-one (850 mg.) and sodium hypobromite solution (100 c.c.; 12%) was shaken at 20° for 43 hours. From the alkaline solution on acidification there were obtained 600 mg. of 2-*n*-hexylbutyric acid, b. p. 116—118°/3 mm., $n_D^{16^\circ}$ 1·4384. The *p*-toluidide had m. p. 75—76°, undepressed on admixture with a synthetic specimen.

2 : 4-*Dimethyldec*-3-*en*-5-*yn*-2-*ol* (II; $R_1 = R_2 =$ Me).—A mixture of 2 : 4-dimethyldec-2-en-5-yn-4-ol (2·4 g.) and sulphuric acid (500 c.c.; 0·5% w/v) was shaken vigorously for 5 hours at 20°, and isolation by means of ether yielded the *carbinol* (2·1 g.) as a colourless mobile liquid, b. p. 35° (bath temp.)/10^{-4} mm., $n_D^{18^\circ}$ 1·4774 (Found : C, 79·9; H, 11·4. $C_{12}H_{20}O$ requires C, 79·9; H, 11·2%). *Active hydrogen* (Zerewitinoff) : The carbinol (103 mg.) gave 12·9 c.c. of methane at 21°/767 mm. (0·95 active hydrogen atom per mol.).

2 : 4-*Dimethyldeca*-2 : 7-*dien*-5-*yn*-4 : 9-*diol* (VIII).—Condensation between hex-3-en-5-yn-2-ol (6 g.) and mesityl oxide (6·1 g.) was effected in the usual manner, yielding the *glycol* (3·2 g.) as a pale yellow liquid, b. p. 60° (bath temp.)/10^{-4} mm., $n_D^{19^\circ}$ 1·4962 (Found : C, 74·2; H, 9·6. $C_{12}H_{18}O_2$ requires C, 74·2; H, 9·35%). *Active hydrogen* (Zerewitinoff) : The glycol (91 mg.) evolved 22·9 c.c. of methane at 18°/758 mm. (2·0 active hydrogen atoms per mol.). *Light absorption :* Maximum, 2330 A.; $\varepsilon = 12{,}650$. Inflexion, 2630 A., $\varepsilon = 4400$.

7-*Methyltrideca*-5 : 8-*diyn*-7-*ol* (X).—Oct-3-yn-2-one (3·5 g.) was condensed with 1-hexyne (2·7 g.) by the Grignard method, 0·7 g. of magnesium being used. The reaction mixture was refluxed for 2½ hours, and the product then isolated in the usual manner. Distillation gave two fractions, (*a*) recovered ketone, b. p. 79—81°/20·5 mm. (1 g.) and (*b*) 7-methyltrideca-5 : 8-diyn-7-ol (1·9 g.), b. p. 149—149·5°/20·5 mm., which on redistillation had b. p. 100°/3 mm., $n_D^{21^\circ}$ 1·4667 (Kroeger and Nieuwland, *loc. cit.*, give $n_D^{24^\circ}$ 1·4660) (Found : C, 81·5. H, 10·55. Calc. for $C_{14}H_{22}O$: C, 81·5; H, 10·75%). *Active hydrogen* (Zerewitinoff): The carbinol (102 mg.) evolved 12·8 c.c. of methane at 18°/772 mm. (1·15 active hydrogen atoms per mol.).

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