67. *Studies in the Polyene Series. Part IX. The Condensation Product of 1-Hexyne with Crotonaldehyde and its Anionotropic Rearrangement.*

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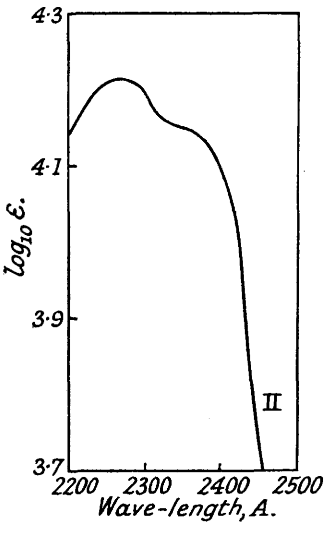
Dec-2-en-5-yn-4-ol (I) is prepared from crotonaldehyde and 1-hexyne in 30% and 80% yields by the sodium in liquid ammonia and the Grignard method, respectively. It undergoes anionotropic rearrangement on treatment with 25% sulphuric acid to *dec-3-en-5-yn-2-ol* (II), which exhibits the expected high-intensity absorption in the ultra-violet, its constitution being proved by hydrogenation to methyloctylcarbinol.



It has already been shown (Jones and McCombie, J., 1942, 733) that condensation between sodium acetylide and αβ-unsaturated aldehydes can readily be effected in liquid ammonia solution. We now find that monoalkyl acetylenes behave similarly, reaction between the sodio-compound of 1-hexyne and crotonaldehyde furnishing *dec-2-en-5-yn-4-ol* (I) (*α-naphthylurethane*) in 30% yield; the constitution of (I) was proved by hydrogenation to propylhexylcarbinol (3 : 5-*dinitrobenzoate*) and by oxidation of the latter to propyl hexyl ketone. The comparatively poor yield obtained in the above condensation is due to the reduction of 1-hexyne by sodium in liquid ammonia, an effective reducing agent for the semihydrogenation of acetylenic linkages (Campbell and Eby, *J. Amer. Chem. Soc.*, 1941, **63**, 216), although great care was taken to ensure that only the smallest excess of sodium was ever present in the ammonia solution. This was rendered difficult, however, by the extremely slow reaction of the metal with 1-hexyne, much slower than its reaction with either acetylene or vinylacetylene. The Grignard method, although unsatisfactory with acetylene itself, is more convenient with substituted acetylenes and, as was to be expected, from hexynylmagnesium bromide and crotonaldehyde, dec-2-en-5-yn-4-ol is obtained in excellent yield.

In view of the facile anionotropic rearrangement observed with propenylethynylcarbinol and similar compounds on shaking with dilute mineral acids (Part VIII, preceding paper), it was of interest to investigate the behaviour of (I) under these conditions. The substituted acetylenic group appears to have a powerful retarding influence on the ease of isomerisation, for whereas propenylethynylcarbinol is completely isomerised into hex-3-en-5-yn-2-ol on shaking with 5% sulphuric acid for 12 hours, dec-2-en-5-yn-4-ol remains unchanged even when shaken with 10% acid for 24 hours; with 25% sulphuric acid, however, it is isomerised almost quantitatively into

$$CH_3{\cdot}CH{:}CH{\cdot}CH(OH){\cdot}C{\vdots}C{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3 \quad \text{(I.)}$$
$$CH_3{\cdot}CH(OH){\cdot}CH{:}CH{\cdot}C{\vdots}C{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3 \quad \text{(II.)}$$

dec-3-en-5-yn-2-ol (II) (*α-naphthylurethane*). Since these experiments were not carried out in a homogeneous medium, the comparisons made above have no absolute significance, as the expected difference in water solubility between propenylethynylcarbinol and (I) may be sufficient to account for the apparent differences in ease of mobility. However, the behaviour of vinylacetylenecarbinols of similar molecular weight to (I) would appear to indicate that the solubility factor is not of great significance (see following paper); kinetic experiments in homogeneous media are in progress, and should provide an accurate picture of the effect of ethynyl substitution on the mobility of the hydroxyl group in propenylethynyl systems.

The carbinol (II) exhibits intense light absorption in the ultra-violet (see figure), exactly analogous in both location and intensity to that observed with the conjugated vinylacetylene carbinols (Part VIII). It is noteworthy that complete substitution in the acetylenic group has little or no effect on either the location or the intensity of the maximum absorption, and the characteristic inflexion already noted is again apparent. The constitution of (II) is proved by its hydrogenation to methyloctylcarbinol (3 : 5-*dinitrobenzoate*), and oxidation of the latter to methyl octyl ketone.

Experimental.

(Absorption spectra were determined in alcoholic solutions.)

Dec-2-en-5-yn-4-ol (I).—(*a*) 1-Hexyne (60 g.) and sodium (16·7 g.) were added to liquid ammonia (1500 c.c.) in such a manner that the blue colour persisted for the shortest possible time. When the addition was complete, the mixture was treated dropwise with crotonaldehyde (50 g.) in ether (100 c.c.), and stirring and cooling were continued for a further

2 hours, after which ammonium chloride (40 g.) was added and the ammonia was allowed to evaporate off overnight. The product was isolated by means of ether, and two distillations gave *dec*-2-*en*-5-*yn*-4-*ol* (33 g.) as a colourless liquid, b. p. 90°/1 mm., $n_{\mathrm{D}}^{21^\circ}$ 1·4681 (Found : C, 78·3; H, 10·6. $C_{10}H_{16}O$ requires C, 78·9; H, 10·6%). *Active hydrogen* (Zerewitinoff) : the carbinol (178 mg.) gave 26·3 c.c. of methane at 22·5°/775 mm., corresponding to 1·05 active hydrogen atoms per molecule. It exhibits no absorption of appreciable intensity in the range 2200—4000 A. The *a-naphthylurethane*, prepared in the usual manner, crystallised from light petroleum (b. p. 40—60°) in needles, m. p. 69° (Found : N, 4·1. $C_{21}H_{23}O_2N$ requires N, 4·35%).

(*b*) After a solution of 1-hexyne (12 g.) in ether (20 c.c.) had been added dropwise to an ethereal solution of ethylmagnesium bromide (from 3 g. of magnesium), the mixture was refluxed for 3 hours, cooled, treated during 1½ hours with a solution of crotonaldehyde (8·9 g.) in ether (20 c.c.), and set aside overnight. The Grignard complex was decomposed with ammonium nitrate (30 g.) in water (50 c.c.), and from the ethereal solution were isolated 15 g. of dec-2-en-5-yn-4-ol, b. p. 83—85°/1 mm., $n_{\mathrm{D}}^{18^\circ}$ 1·4700.

Propylhexylcarbinol and Propyl Hexyl Ketone.—A solution of dec-2-en-5-yn-4-ol (9·2 g.) in methyl alcohol (150 c.c.) was shaken with hydrogen in the presence of palladium–norit (100 mg.; 10%) until absorption was complete. The catalyst was filtered off, but although the solvent was distilled slowly through a column, considerable volatilisation of the product occurred (we have since found that methyl and ethyl acetates are ideal solvents for this type of hydrogenation). Distillation of the residual oil gave propylhexylcarbinol (2·5 g.), b. p. 71°/1 mm., $n_{\mathrm{D}}^{21^\circ}$ 1·4312 (Karrer, Shibata, Wettstein, and Jacubowicz, *Helv. Chim. Acta*, 1930, **13**, 1300, give b. p. 206—207°/724 mm.). The 3 : 5-*dinitrobenzoate* crystallised in needles, m. p. 24°, from light petroleum (b. p. 40—60°) (Found : N, 8·3. $C_{17}H_{24}O_6N_2$ requires N, 7·95%). Oxidation of the carbinol with chromic acid in the usual manner gave propyl hexyl ketone, b. p. 84°/3 mm., $n_{\mathrm{D}}^{21^\circ}$ 1·4240, which gave a semicarbazone, m. p. 56° (or as low as 51°, depending upon the rate of heating) (Karrer *et al.*, *loc. cit.*, give m. p. 51—52°).

Dec-3-*en*-5-*yn*-2-*ol* (II).—A mixture of dec-2-en-5-yn-4-ol (10 g.) and sulphuric acid (100 c.c.; 25% w/v) was shaken for 24 hours at 20° under nitrogen. Isolation by means of ether yielded *dec*-3-*en*-5-*yn*-2-*ol* (8 g.), b. p. 113—114°/3 mm., $n_{\mathrm{D}}^{22^\circ}$ 1·4833 (Found: C, 78·5; H, 10·4. $C_{10}H_{16}O$ requires C, 78·9; H, 10·6%). *Active hydrogen* (Zerewitinoff) : the carbinol (177 mg.) gave 26·5 c.c. of methane at 18°/765 mm., corresponding to 0·95 active hydrogen atom per molecule. *Light absorption* (see fig.) : Maximum, 2260 A., log ϵ = 4·21; inflexion, 2350 A.; log ε = 4·18. The *a-naphthylurethane* formed needles from light petroleum (b. p. 40—60°), m. p. 65° (Found : N, 4·45. $C_{21}H_{23}O_2N$ requires N, 4·35%).

Methyloctylcarbinol and Methyl Octyl Ketone.—A solution of dec-3-en-5-yn-2-ol (5 g.) in ether (150 c.c.) was shaken with hydrogen in the presence of palladium–norit (100 mg.; 10%) until absorption was complete. The catalyst was removed, and evaporation of the ether through a column gave methyloctylcarbinol (4·5 g.), b. p. 209°, $n_{\mathrm{D}}^{21^\circ}$ 1·4342 (Pickard and Kenyon, J., 1911, **99**, 58, give b. p. 210—211°). The 3 : 5-*dinitrobenzoate* separated from light petroleum (b. p. 40—60°) in clusters of needles, m. p. 44° (Found : N, 8·1. $C_{17}H_{24}O_6N_2$ requires N, 7·95%). Oxidation of the carbinol with chromic acid gave methyl octyl ketone, b. p. 86°/3 mm., $n_{\mathrm{D}}^{21^\circ}$ 1·4230 (Rupe and Willi, *Helv. Chim. Acta*, 1932, **15**, 845, give b. p. 92°/10 mm., $n_{\mathrm{D}}^{22^\circ}$ 1·4263). The semicarbazone formed plates from methyl alcohol, m. p. 124° (Rupe and Willi, *loc. cit.*, give m. p. 126°).

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