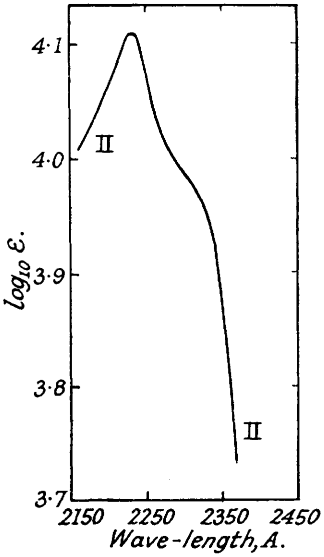
66. *Studies in the Polyene Series. Part VIII. A New Anionotropic Rearrangement. Isomerisation of Ethynylcarbinols from αβ-Unsaturated Aldehydes.**

By E. R. H. JONES and J. T. MCCOMBIE.

A new anionotropic rearrangement, typified by the conversion of propenylethynylcarbinol (I) into *hex*-3-*en*-5-*yn*-2-*ol* (II) in the presence of acid reagents, is reported, and a detailed account given of the isomerisation of (I) under varied experimental conditions. Several other examples are provided, and the constitutions of the rearranged carbinols are rigidly proved. The conjugated vinylacetylene group present in the latter is found to exhibit characteristic light absorption of high intensity in the ultra-violet. The effect of certain substituents on the mobility of the anionotropic system is indicated, but no final conclusions can be drawn from the semi-quantitative data so far available.

IN connection with the programme outlined in Part V (Heilbron, Johnson, Jones, and Spinks, J., 1942, 727) for the synthesis of vitamin A and analogues, a systematic examination of the properties of propenylethynylcarbinol and other ethynylcarbinols from αβ-unsaturated aldehydes (Jones and McCombie, J., 1942, 733) has been undertaken. When shaken for some hours at room temperature with, *e.g.*, 5% sulphuric acid, propenylethynylcarbinol (I) is isomerised almost quantitatively into *hex*-3-*en*-5-*yn*-2-*ol* (II) (*phenylurethane*, β-*naphthylurethane*). The constitution (II) for the latter was suggested by its much higher refractive index than that of (I), its ultra-violet absorption (see Table I and figure), and the fact that it contains two active hydrogen atoms (Zerewitinoff). Final proof was obtained by catalytic hydrogenation to methylbutylcarbinol, oxidised to methyl butyl ketone. When propenylethynylcarbinol was first prepared by Lespieau and Lombard (*Bull. Soc. chim.*, 1935, **2**, 369) by the Grignard method, it was suggested that hex-3-en-5-yn-2-ol was probably formed on decomposition of the Grignard complex with acids, since on complete hydrogenation of the product obtained in this manner they isolated a carbinol which seemed to be methylbutylcarbinol, although no proof of this identity was furnished.

On similar treatment of *iso*butenylethynylcarbinol (III) with acids, 2-*methylhex*-3-*en*-5-*yn*-2-*ol* (IV) (*phenylurethane*) is produced, absorption spectra data (Table I) and hydrogenation to dimethylbutylcarbinol (*phenylurethane*) providing proof of its constitution. 4-Methylhex-4-en-1-yn-3-ol (V) is isomerised to 3-*methylhex*-3-*en*-5-*yn*-2-*ol* (VI) (α-*naphthylurethane*) which yields 3-methylhexan-2-ol, oxidised to 3-methylhexan-2-one, on hydrogenation. 4-Ethyloct-4-en-1-yn-3-ol (VII) similarly gives 5-*ethyloct*-5-*en*-7-*yn*-4-*ol* (VIII) (α-*naphthylurethane*). These isomerised carbinols are obtained in good yields as colourless liquids which can be kept for months at 0° without undergoing appreciable decomposition or resinification.



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

$$(III.)\ CMe_2{:}CH{\cdot}CH(OH){\cdot}C{\vdots}CH \longrightarrow CMe_2(OH){\cdot}CH{:}CH{\cdot}C{\vdots}CH\ (IV.)$$

$$(V.)\ CH_3{\cdot}CH{:}CMe{\cdot}CH(OH){\cdot}C{\vdots}CH \longrightarrow CH_3{\cdot}CH(OH){\cdot}CMe{:}CH{\cdot}C{\vdots}CH\ (VI.)$$

$$(VII.)\ CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH{:}CEt{\cdot}CH(OH){\cdot}C{\vdots}CH \longrightarrow CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH(OH){\cdot}CEt{:}CH{\cdot}C{\vdots}CH\ (VIII.)$$

Hex-3-en-5-yn-2-ol (II) exhibits intense ultra-violet absorption with a maximum at 2230 A. and a marked inflexion at 2300 A. (see Fig.). The light-absorbing properties of the carbinols (IV), (VI), and (VIII) are strictly analogous both in location and in intensity of the absorption maxima (Table I) and it might well be suggested on the basis of this evidence that the conjugated vinylacetylene system resembles a conjugated diene system in light-absorption properties. The intensities of the light absorption of these vinylacetylenes are, however, markedly lower than those of typical dienes (Booker, Evans, and Gillam, *loc. cit.*) and the presence of a characteristic inflexion at about 2300 A. in the spectra of the carbinols listed in Table I renders the analogy between

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* A patent application is pending involving the subject matter of this and the two following papers.

TABLE I.

	$\lambda_{max.}$, A.	$\epsilon_{max.}$	$\lambda_{infl.}$, A.	$\epsilon_{infl.}$
Hex-3-en-5-yn-2-ol (II)	2230	13,500	2300	9,500
2-Methylhex-3-en-5-yn-2-ol (IV)	2230	10,000	2310	8,500
3-Methylhex-3-en-5-yn-2-ol (VI)	2240	13,000	2310	11,000
5-Ethyloct-5-en-7-yn-4-ol (VIII)	2270	12,500	2330	11,000
1 : 2-Dimethylvinylacetylene	2195	9,000	2260	7,000
Piperylene *	2235	23,000	—	—
$\Delta^{2:4}$-Hexadiene *	2270	22,500	—	—

* Booker, Evans, and Gillam, J., 1940, 1453.

the two chromophores rather incomplete. These inconsistencies, coupled with the fact that we find that 2 : 7-dimethylocta-3 : 5-diyn-2 : 7-diol (Zal'kind and Aïzikovitch, *J. Gen. Chem. Russia*, **1937**, **7**, 227) fails to show any high-intensity light absorption, suggest that in many respects ethylenic and acetylenic bonds are fundamentally different in their light-absorption behaviour. The acetylenic bond appears to be somewhat akin to the carbonyl bond, which, as is well known, when conjugated to an ethylenic linkage, gives rise to a maximum in the region 2200—2500 A., and, in compounds such as $R{\cdot}CO{\cdot}CO{\cdot}R$, where the carbonyl groups cannot enolise, fails to produce any high-intensity absorption in the ultra-violet. Such an analogy would demand that αβ-acetylenic ketones should fail to absorb strongly in the ultra-violet, an implication which will be tested at the earliest opportunity. On the other hand, as far as can be ascertained from the literature, isolated carbonyl and acetylenic groups do not exhibit similar absorption properties, and when the latter are present in a conjugated system such as $>C{:}CH{\cdot}C{\vdots}C{\cdot}CH{:}C<$ the conjugation is not "crossed" as it would be by a carbonyl group similarly situated (see Parts X and XI). Further information about the rôle of acetylenic linkages in light absorption is gradually being accumulated as a result of work in this field.

Since the unisomerised ethynylcarbinols are optically transparent, measurements of ultra-violet absorption intensity can be utilised to determine the extent of isomerisation in any particular case. By employing this method, a detailed study of the kinetics of these rearrangements has been begun, but we here refer only to some experiments of a semiquantitative nature from which certain obvious conclusions can be drawn. The results recorded in Table II were obtained by treating small portions of propenylethynylcarbinol under the conditions described, isolating the product by means of ether, and determining the absorption spectrum of the residue obtained on evaporation. From the intensities observed at 2230 A. the proportion of rearranged carbinol in the product could be determined approximately.

TABLE II.

Acid reagent.	Conditions.*	Isomerisation, % (approx.).	Acid reagent.	Conditions.*	Isomerisation, % (approx.).
H_2SO_4, 10% w/v	S, 2 hrs., 20°	40	HNO_3, 1%	R, 0·5 hr., 100°	100
,, 5%	S, 12 hrs., 20°	100	H_3PO_4, 5%	S, 12 hrs., 20°	30
,, 5%	S, 2 hrs., 20°	20	,, 25%	S, 70 hrs., 20°	100
,, 2·5%	S, 48 hrs., 20°	100	H_3BO_3, 25%	R, 0·5 hr., 100°	90
,, 2·5%	S, 1 hr., 20°	5	$KHSO_4$, 10%	S, 12 hrs., 20°	60
,, 2·5%	R, 0·5 hr., 100°	100	,, 10%	S, 70 hrs., 20°	100
,, 1%	R, 0·5 hr., 100°	100	$H{\cdot}CO_2H$, 25%	S, 12 hrs., 20°	30
,, 1%	S.d.	100	HOAc, 25%	S, 12 hrs., 20°	7
,, 0·1%	R, 0·5 hr., 100°	100	,, 25%	S, 70 hrs., 20°	30
,, 0·01%	R, 0·5 hr., 100°	40	Tartaric acid, 25%	R, 0·5 hr., 100°	100
,, 0·01%	R, 1 hr., 100°	60	Ac_2O	H, 4 hrs., 110°	0
,, 0·01%	R, 2 hrs., 100°	90		R, 4·5 hrs. in presence of anhydrous NaOAc	50
HCl, 5%	S, 12 hrs., 20°	100			

* S = Shaking, R = refluxing, S.d. = steam distillation, H = heating.

The above results demonstrate that the rate of anionotropic rearrangement of propenylethynylcarbinol is considerably accelerated by increase of temperature and also by increase in the concentration of the acid. Phenylpropenylcarbinol is smoothly isomerised in dilute acetic acid (0·5%) at the ordinary temperature (Kenyon, Partridge, and Phillips, J., **1937**, 207), from which it is obvious that the mobility of the propenylethynyl system is of a comparatively low order. Dissociation-constant measurements reveal that the ethynyl group attracts electrons more strongly than the phenyl group (Ingold, *Chem. Reviews*, **1934**, **15**, 239). The greater mobility of the phenylpropenyl, as compared with the propenylethynyl system is consistent with this fact, the ethynyl group being less able, because of its greater electron-attracting properties, to stabilise the positive charge on the adjacent carbon atom after the separation of the anion. However, in view of the dual influence of the phenyl group in promoting both prototropic and anionotropic changes, and other considerations, an interpretation solely in terms of the inductive effects of the groups involved must be considered insufficient. It can only be said that the phenyl group exhibits a greater resilience towards both positive and negative charges, or that it contains a more mobile electronic system, than the ethynyl group.

Burton and Ingold (J., **1928**, 904) and Burton (J., **1928**, 1650), who first made a systematic study of anionotropic rearrangements, mentioned that the ease of isomerisation in such systems would be expected to increase with increasing strength of the acid HX, where X is the migrating anion, *i.e.*, Br > OAc > OH. It is noteworthy in this connection that the propenylethynyl system is stable in the presence of acetic anhydride at 110° and is isomerised only partly on heating under reflux with the same reagent, whereas Burton (J., 1929, 455) observed the complete conversion of phenylpropenylcarbinol into styrylmethylcarbinyl acetate in boiling acetic anhydride. The generalisation mentioned above is fully borne out by the observation that compounds such as propenylethynylcarbinyl chloride are so readily isomerised that their isolation is well nigh impossible (unpublished work).

In spite of treatment with 25% sulphuric acid, even at elevated temperatures, numerous attempts to isomerise vinylethynylcarbinol were unsuccessful, the starting material being recovered essentially unchanged; similarly, styrylethynylcarbinol was unaffected by shaking its ethereal solution with 10% sulphuric acid for 48 hours. The observed lack of mobility of the hydroxyl group in vinylethynylcarbinol is closely paralleled by the similar observations made by Burton and Ingold (*loc. cit.*) with phenylvinylcarbinol, the enhanced mobility in the propenylcarbinols being attributable to the greater inductive effect of the methyl group than of the hydrogen atom. This is even more readily apparent in the ease of isomerisation of *iso*butenylethynylcarbinol (see Experimental), where the still greater inductive effect of the *gem*-dimethyl group is involved. No study of the mobility of the system present in phenyl*iso*butenylcarbinol has apparently been made; this should be of interest, as this carbinol should be even more labile than the phenylpropenyl type. The presence of methyl and ethyl substituents on the carbon atom adjacent to the hydroxyl group does not appear to have any marked effect on the ease of rearrangement of 4-methylhex-4-en-1-yn-3-ol (V) and 4-ethyloct-4-en-1-yn-3-ol (VII).

The discovery of this isomerisation of unsaturated ethynylcarbinols is of considerable interest for the synthesis of polyenes related to vitamin-A, particularly in view of the recent success of Thomson and Shaw (*J. Amer. Chem. Soc.*, 1942, **64**, 363) in the selective hydrogenation of vinylacetylenes to conjugated butadienes by employing a Raney-type iron catalyst. The many implications of these rearrangements are being examined in these laboratories.

EXPERIMENTAL.

(M. p.'s are uncorrected. Absorption spectra were determined in alcoholic solutions. All distillations were carried out in a nitrogen atmosphere. Except where stated otherwise, light petroleum refers to that fraction of b. p. 40—60°.)

Hex-3-en-5-yn-2-ol (II).—(*a*) A mixture of propenylethynylcarbinol (220 g.) and sulphuric acid (2000 c.c.; 5% w/v) was shaken vigorously under nitrogen for 14 hours at 22°. The product was isolated by thorough extraction with ether, after saturation with salt, and the ethereal extract was washed with saturated sodium bicarbonate solution, dried, and evaporated. Two distillations of the residue yielded *hex-3-en-5-yn-2-ol* (192 g.) as a colourless oil, b. p. 103—106°/100 mm., 69—70°/18 mm., $n_D^{22^\circ}$ 1·4791 (Found: C, 75·1; H, 8·5. C_6H_8O requires C, 75·0; H, 8·4%). On standing, the carbinol develops a brown colour and slight resinification occurs; this is appreciably retarded in the presence of a trace of quinol. *Active hydrogen* (Zerewitinoff): The carbinol (105 mg.) evolved 50·0 c.c. of methane at 758 mm. and 22°, after being heated to 90°, equivalent to 2·0 active hydrogen atoms per molecule. The *phenylurethane* separated from either aqueous alcohol or light petroleum (b. p. 60—80°) in plates, m. p. 83—84° (Found: C, 72·9; H, 6·2. $C_{13}H_{13}O_2N$ requires C, 72·6; H, 6·0%). The *β-naphthylurethane* crystallised from the latter solvent in leaflets, m. p. 77—78° (Found: C, 76·8; H, 5·9. $C_{17}H_{15}O_2N$ requires C, 77·0; H, 5·7%).

Acetyl derivative. Hex-3-en-5-yn-2-ol (5 g.) was heated with acetic anhydride (10 g.) at 110° for 4 hours in nitrogen. Isolated in the usual manner, the *acetyl* derivative distilled as a colourless oil (6 g.) which darkened on standing; b. p. 101—103°/70 mm., $n_D^{18·5^\circ}$ 1·4576 (Found: C, 69·35; H, 7·3. $C_8H_{10}O_2$ requires C, 69·6; H, 7·25%). *Light absorption*: Maximum, 2240 A.; log ε = 4·06.

(*b*) A mixture of propenylethynylcarbinol (20 g.) and sulphuric acid (20 c.c.; 0·1% w/v) was refluxed for 30 mins. in an atmosphere of nitrogen. Isolation of the product as described under (*a*) gave hex-3-en-5-yn-2-ol (18·4 g.), b. p. 67—70°/18 mm., $n_D^{17^\circ}$ 1·4772.

Methylbutylcarbinol and Methyl Butyl Ketone.—A solution of hex-3-en-5-yn-2-ol (2 g.) in methyl alcohol (20 c.c.) was shaken with palladium–norit (0·5 g.; 10%) in hydrogen until absorption was complete. The catalyst was filtered off, and the solvent removed through a column; the residual methylbutylcarbinol had b. p. 135—137° (Sutter, *Helv. Chim. Acta*, 1938, **21**, 1269, gives b. p. 135—137°). A synthetic specimen of this alcohol, made by reaction between methylmagnesium iodide and *n*-valeraldehyde, had b. p. 135—137°. The carbinol was oxidised with chromic anhydride in a mixture of dilute acetic and sulphuric acids to methyl butyl ketone; semicarbazone, m. p. 121—122° (Kyner, *J. pr. Chem.*, 1901, **64**, 115, gives m. p. 122°), and 2 : 4-dinitrophenylhydrazone, m. p. 106—107° (Allen, *J. Amer. Chem. Soc.*, 1930, **52**, 2957, gives m. p. 106°). Neither derivative depressed the m. p. of an authentic specimen.

2-*Methylhex*-3-*en*-5-*yn*-2-*ol* (IV).—A mixture of *iso*butenylethynylcarbinol (10 g.) and sulphuric acid (25 c.c.; 5% w/v) was shaken under nitrogen for 3 hours at 20°. Isolation in the usual manner yielded 2-*methylhex*-3-*en*-5-*yn*-2-*ol* (7 g.), b. p. 91—93°/50 mm., $n_D^{24·5^\circ}$ 1·4711 (Found: C, 76·1; H, 9·3. $C_7H_{10}O$ requires C, 76·35; H, 9·1%). The *phenylurethane* separated from aqueous methyl alcohol in needles, m. p. 95—95·5° (Found: C, 73·6; H, 6·75. $C_{14}H_{15}O_2N$ requires C, 73·35; H, 6·55%).

Dimethylbutylcarbinol. 2-Methylhex-3-en-5-yn-2-ol (5 g.) in methyl alcohol (75 c.c.) was hydrogenated completely in the presence of palladium–norit (100 mg.; 10%) yielding dimethylbutylcarbinol, b. p. 85·5—88°/100 mm., $n_D^{24^\circ}$ 1·4180 (Whitmore and Woodburn, *J. Amer. Chem. Soc.*, 1933, **55**, 363, give b. p. 139—140°/735 mm., $n_D^{20^\circ}$ 1·4175). The *phenylurethane* formed needles from light petroleum, m. p. 44—45° (Found: N, 6·0. $C_{14}H_{21}O_2N$ requires N, 5·95%).

3-*Methylhex*-3-*en*-5-*yn*-2-*ol* (VI).—A mixture of 4-methylhex-4-en-1-yn-3-ol (10 g.) and sulphuric acid (100 c.c.; 5% w/v) was shaken under nitrogen at 20° for 21 hours. Isolation in the usual manner yielded 3-*methylhex*-3-*en*-5-*yn*-2-*ol* (6 g.), b. p. 78—81°/20 mm. (after two distillations), $n_D^{23^\circ}$ 1·4813 (Found: C, 76·15; H, 8·9. $C_7H_{10}O$ requires C, 76·35; H, 9·1%). The *α-naphthylurethane* separated in needles from light petroleum (b. p. 60—80°) or aqueous methyl alcohol; m. p. 93—94° (Found: N, 5·05. $C_{18}H_{17}O_2N$ requires N, 5·0%).

3-*Methylhexan*-2-*one*. 3-Methylhex-3-en-5-yn-2-ol (13·5 g.) in ethyl acetate (100 c.c.) was hydrogenated completely in the presence of platinic oxide (0·5 g.), yielding 3-methylhexan-2-ol (9 g.), b. p. 85—87°/65 mm., $n_D^{18^\circ}$ 1·4198. A portion of this was oxidised with chromic anhydride in dilute sulphuric acid to 3-methylhexan-2-one, b. p. 143—148°, $n_D^{20^\circ}$ 1·4035 (Powell, Murray, and Baldwin, *J. Amer. Chem. Soc.*, 1933, **55**, 1154, give b. p. 142—145°, $n_D^{24^\circ}$ 1·409). The semicarbazone had m. p. 112—113° (Hopff, *Ber.*, 1931, **64**, 2742, gives m. p. 114°).

5-*Ethyloct*-5-*en*-7-*yn*-4-*ol* (VIII).—A mixture of 4-ethyloct-4-en-1-yn-3-ol (30 g.) and sulphuric acid (120 c.c.; 10%

w/v) was shaken under nitrogen for 7 hours at 20°. Isolation in the usual manner yielded after two fractionations *5-ethyloct-5-en-7-yn-4-ol* (15 g.), b. p. 100—101·5°/14 mm., $n_D^{23^\circ}$ 1·4791 (Found: C, 78·4; H, 10·5. $C_{10}H_{16}O$ requires C, 78·95; H, 10·5%). The *α-naphthylurethane* crystallised in needles from light petroleum; m. p. 75—76° (Found: C, 78·5; H, 7·25. $C_{21}H_{23}O_2N$ requires C, 78·5; H, 7·15%).

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IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY, LONDON, S.W.7.

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