50. *Studies in the Polyene Series. Part XIV. Anionotropic Rearrangements of the Carbinols obtained from Condensation of Crotonaldehyde with both Vinyl- and 2-Methylvinyl-acetylene.*

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Condensations of crotonaldehyde with both vinylacetylene and 2-methylvinylacetylene by either the Grignard or the sodium in liquid ammonia method are described. The propenylcarbinols undergo the expected anionotropic rearrangements (I $\longrightarrow$ II) on shaking with 5% sulphuric acid.

In Part X (Heilbron, Johnson, Jones, and Raphael, J., **1943**, 265) the preparation of 7-methylnona-2 : 7-dien-5-yn-4-ol (I; $R_1 = R_2 = Me$) from crotonaldehyde and 1 : 2-dimethylvinylacetylene, and its anionotropic rearrangement to 7-methylnona-3 : 7-dien-5-yn-2-ol (II; $R_1 = R_2 = Me$) in the presence of acids, were described. In spite of the statement by Carothers and Jacobson (*J. Amer. Chem. Soc.*, 1933, **55**, 1097) that unsaturated aldehydes and ketones are usually resinified completely by the sodio-derivative of vinylacetylene, attempts to condense crotonaldehyde with vinylacetylene itself appeared to offer promise of success. The conditions employed by the above authors, *viz.*, addition of sodamide to a solution of the aldehyde and vinylacetylene in dry ether, were such as to admit of extensive self-condensation of the crotonaldehyde, a reaction which can be suppressed almost entirely when this aldehyde is condensed with sodium acetylide in liquid ammonia (Jones and McCombie, J., **1942**, 733). Also, there seems little reason why normal condensation should not occur by the Grignard method, and in a patent (Carothers and Berchet, U.S.P., 1,963,935) enumerating numerous reactions with vinylacetylenylmagnesium halides, crotonaldehyde is mentioned amongst many other aldehydes and ketones, but no details of either the condensation or the product obtained are given.

By the interaction of vinylacetylenylmagnesium bromide and crotonaldehyde, *octa*-2 : 7-*dien*-5-*yn*-4-*ol* (I; $R_1 = R_2 = H$) (α-*naphthylurethane*) was isolated in 35% yield, and a slightly lower yield was obtained by employing sodio-vinylacetylene in liquid ammonia. Similarly, from 2-methylvinylacetylene 7-*methylocta*-2 : 7-*dien*-5-*yn*-4-*ol* (I; $R_1 = Me$; $R_2 = H$) (α-*naphthylurethane*) was produced in 50 and 42% yields by the Grignard and the liquid ammonia method, respectively. On shaking with 5% sulphuric acid the carbinols were smoothly isomerised * into *octa*-3 : 7-*dien*-5-*yn*-2-*ol* (II; $R_1 = R_2 = H$) and 7-*methylocta*-3 : 7-*dien*-5-*yn*-2-*ol* (II; $R_1 = Me$; $R_2 = H$) (α-*naphthylurethane*) respectively, the constitution of the former being proved by hydrogenation and subsequent oxidation of the crude saturated carbinol to methyl hexyl ketone. Hydrogenation of the methylvinylacetylene product (II; $R_1 = Me$; $R_2 = H$) gave 7-*methyloctan*-2-*ol* (α-*naphthylurethane*), oxidised to 7-*methyloctan*-2-*one* (*semicarbazone*).

$$CH_3\cdot CH{:}CH\cdot CH(OH)\cdot C{\vdots}C\cdot CR_1{:}CHR_2 \quad (I.)$$
$$CH_3\cdot CH(OH)\cdot CH{:}CH\cdot C{\vdots}C\cdot CR_1{:}CHR_2 \quad (II.)$$

	$\lambda_{max.}$, A.	$\varepsilon_{max.}$	$\lambda_{infl.}$, A.	$\varepsilon_{infl.}$
7-Methylnona-2 : 7-dien-5-yn-4-ol (I; $R_1 = R_2 = Me$) *	2250	15,500	2290	15,000
Octa-2 : 7-dien-5-yn-4-ol (I; $R_1 = R_2 = H$)	2240	15,000	2330	11,000
7-Methylocta-2 : 7-dien-5-yn-4-ol (I; $R_1 = Me$; $R_2 = H$)	2250	14,500	2300	12,000
7-Methylnona-3 : 7-dien-5-yn-2-ol (II; $R_1 = R_2 = Me$) *	2635	16,500	2690	15,500
Octa-3 : 7-dien-5-yn-2-ol (II; $R_1 = R_2 = H$)	2585	17,000	2450	13,500
			2700	15,500
7-Methylocta-3 : 7-dien-5-yn-2-ol (II; $R_1 = Me$; $R_2 = H$)	2585	17,000	2680	13,500

* Heilbron, Johnson, Jones, and Raphael, *loc. cit.*

The absorption spectra of the conjugated vinylacetylenyl- and divinylacetylenyl-carbinols (table; alcoholic solutions) described in this paper are closely analogous, in both location and intensity of the maxima and inflexions, to those previously recorded (Parts VIII—XI, J., **1943**, 261—270).

EXPERIMENTAL.

Octa-2 : 7-*dien*-5-*yn*-4-*ol* (I; $R_1 = R_2 = H$).—(*a*) A solution of vinylacetylene [23 g. (crude), made according to Schmitz and Schumacher, *Z. Electrochem.*, 1939, **45**, 503] in ether (120 c.c.) was added during one hour to a stirred ethereal solution of ethylmagnesium bromide (from 7 g. of magnesium) contained in a three-necked flask fitted with a double-surface condenser containing solid carbon dioxide. The mixture was kept at 20° for 2 hours after completion of the addition, and was then treated dropwise with a solution of crotonaldehyde (19 g.) in ether (20 c.c.). It was stirred for a further 4 hours and then set aside over-night. The Grignard complex was decomposed with ice and ammonium chloride (50 g.), and the product isolated by means of ether. This gave *octa*-2 : 7-*dien*-5-*yn*-4-*ol* (12 g.) as a practically colourless liquid, which darkens on standing, b. p. 72—73°/3·5 mm., $n_D^{19°}$ 1·5076 (Found: C, 78·7; H, 8·5. $C_8H_{10}O$ requires C, 78·65; H, 8·25%). *Active hydrogen* (Zerewitinoff): The carbinol (118 mg.) evolved 24 c.c. of methane at 19°/762 mm., corresponding to 1·05 active hydrogen atoms per mol. The *a-naphthylurethane* separated from light petroleum (b. p. 60—80°) or aqueous acetone in needles, m. p. 95—96° (Found: C, 78·65; H 6·2. $C_{19}H_{17}O_2N$ requires C, 78·3; H, 5·9%).

(*b*) Sodium (13·5 g.) and a solution of vinylacetylene (43 g.: crude) in ether (200 c.c.) were gradually added to stirred liquid ammonia (1500 c.c.) in such a manner that the solution became colourless before each fresh addition of sodium was made. The operation took approximately 2 hours, after which the solution was treated with crotonaldehyde (42 g.) in ether (50 c.c.) during 45 minutes. The mixture was stirred for a further 2½ hours, ammonium chloride (33 g.) added, and

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* Patent protection pending.

the ammonia allowed to evaporate off overnight in a stream of nitrogen. Isolation by means of ether gave octa-2 : 7-dien-5-yn-4-ol (24 g.), b. p. 77—79°/4·5 mm., $n_{\mathrm{D}}^{19^\circ}$ 1·5063.

Octa-3 : 7-*dien*-5-*yn*-2-*ol* (II ; $R_1 = R_2 = H$).—A mixture of the above carbinol (8·5 g.) and sulphuric acid (50 c.c. ; 5% w/v) was shaken under nitrogen at 20° for 24 hours. The upper layer was separated with ether and gave *octa*-3 : 7-*dien*-5-*yn*-2-*ol* (6 g.) as an almost colourless oil, b. p. about 78°/4 mm., $n_{\mathrm{D}}^{17^\circ}$ 1·5388 (Found : C, 78·5; H, 8·1. $C_8H_{10}O$ requires C, 78·65; H, 8·25%). Much dinaphthylurea was formed on treating the carbinol with α-naphthyl *iso*cyanate at 20°, and no crystalline α-naphthylurethane could be obtained.

Methyl Hexyl Ketone.—A solution of octa-3 : 7-dien-5-yn-2-ol (3·4 g.) in ethyl acetate (35 c.c.) was shaken with hydrogen in presence of platinic oxide (100 mg.) until absorption was complete. The carbinol obtained after removal of catalyst and solvent was oxidised with chromic acid in sulphuric acid, giving methyl hexyl ketone, b. p. 56—59°/11 mm., $n_{\mathrm{D}}^{20^\circ}$ 1·4163 (Brühl, *Annalen*, 1880, **203**, 29, gives b. p. 173°/753 mm., $n_{\mathrm{D}}^{20^\circ}$ 1·4161). The semicarbazone had m. p. 122—123° (Bouveault and Locquin, *Bull. Soc. chim.*, 1904, **31**, 1157, give m. p. 122°) and gave no depression on admixture with an authentic specimen.

7-*Methylocta*-2 : 7-*dien*-5-*yn*-4-*ol* (I ; $R_1 = Me$; $R_2 = H$).—(*a*) 2-Methylvinylacetylene (41 g. ; Thompson, Milas, and Rovno, *J. Amer. Chem. Soc.*, 1941, **63**, 752) was caused to react with sodium (12 g.) in liquid ammonia (750 c.c.) as previously described, and the solution of the sodio-derivative was treated with crotonaldehyde (43 g.) in ether (50 c.c.) and stirred for 3 hours. Isolation of the product in the usual manner gave 7-*methylocta*-2 : 7-*dien*-5-*yn*-4-*ol* (30 g.) as a pale yellow liquid, b. p. 62—68°/3 mm., $n_{\mathrm{D}}^{17^\circ}$ 1·5027 (Found : C, 79·4; H, 9·0. $C_9H_{12}O$ requires C, 79·35; H, 8·9%). *Active hydrogen* (Zerewitinoff) : The carbinol (95 mg.) gave 16·5 c.c. of methane at 19°/755 mm. (1·0 active hydrogen atom per mol.). The α-*naphthylurethane* crystallised from light petroleum (b. p. 60—80°) in needles, m. p. 99° (Found : C, 78·4; H, 6·2. $C_{20}H_{19}O_2N$ requires C, 78·65; H, 6·25%).

(*b*) A Grignard condensation between 2-methylvinylacetylene (67 g.) and crotonaldehyde (63 g.) effected as described above (ethylmagnesium bromide from magnesium, 22 g,) gave 7-methylocta 2 : 7-dien-5-yn-4-ol (58 g.), b. p. *ca.* 75°/3 mm., $n_{\mathrm{D}}^{17^\circ}$ 1·5015.

7-*Methylocta*-3 : 7-*dien*-5-*yn*-2-*ol* (II ; $R_1 = Me$; $R_2 = H$).—A mixture of 7-methylocta-2 : 7-dien-5-yn-4-ol (20 g.) and sulphuric acid (100 c.c. ; 5% w/v) was shaken at 20° for 24 hours in nitrogen. Isolation by means of ether gave the *carbinol* (II ; $R_1 = Me$; $R_2 = H$) (16·4 g.) as a very pale yellow liquid, b. p. 75—78°/2 mm., 27° (bath temp.)/10^{-4} mm., $n_{\mathrm{D}}^{17^\circ}$ 1·5265 (Found : C, 79·45; H, 8·9. $C_9H_{12}O$ requires C, 79·35; H, 8·9%). The α-*naphthylurethane* crystallised from light petroleum (b. p. 80—100°) in small needles, m. p. 89° (Found : C, 78·85; H, 6·35. $C_{20}H_{19}O_2N$ requires C, 78·65; H, 6·25%).

7-*Methyloctan*-2-*ol* and 7-*Methyloctan*-2-*one*.—A solution of 7-methylocta-3 : 7-dien-5-yn-2-ol (10 g.) in ethyl acetate (35 c.c.) was shaken with hydrogen in the presence of platinic oxide (200 mg.) until absorption was complete. The residue obtained after removal of catalyst and solvent was twice distilled, yielding 7-*methyloctan*-2-*ol* (6·3 g.), b. p. 57°/3 mm., $n_{\mathrm{D}}^{20^\circ}$ 1·4309 (Found : C, 74·25; H, 13·45. $C_9H_{20}O$ requires C, 74·9; H, 13·95%). The α-*naphthylurethane* separated from light petroleum (b. p. 40—60°) in needles, m. p. 75° (Found : C, 76·95; H, 8·6. $C_{20}H_{27}O_2N$ requires C, 76·65; H, 8·7%). Oxidation of the carbinol with chromic acid in sulphuric acid gave 7-*methyloctan*-2-*one*, b. p. 78°/17 mm., $n_{\mathrm{D}}^{15^\circ}$ 1·4228 (Found: C, 76·25; H, 12·85. $C_9H_{18}O$ requires C, 76·0; H, 12·75%). The *semicarbazone* crystallised from aqueous alcohol or benzene–light petroleum (b. p. 100—120°) in prismatic needles, m. p. 132—133° (Found : C, 60·65; H, 10·45; N, 21·3. $C_{10}H_{21}ON_3$ requires C, 60·25; H, 10·65; N, 21·1%).

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