68. *Studies in the Polyene Series. Part X. Condensation of 3-Methylpent-2-en-4-yne (1 : 2-Dimethylvinylacetylene) with Butaldehyde, Crotonaldehyde, and Citral. Anionotropic Rearrangements with Vinylacetylenecarbinols derived from αβ-Unsaturated Aldehydes.*

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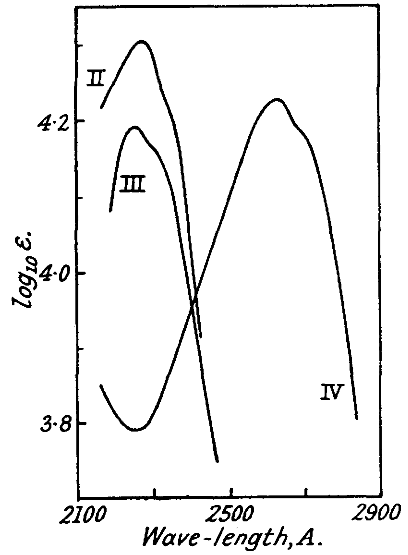
3-Methylpent-2-en-4-yne condenses normally with the above aldehydes by the Grignard method, and the sodium in liquid ammonia process is shown to be applicable in the one case in which it is employed. 7-*Methylnonan*-4-*ol* is obtained by hydrogenation of both the butaldehyde and the crotonaldehyde product, and the latter smoothly undergoes the expected anionotropic conversion into the isomeric *divinylacetylenecarbinol* (IV) on treatment with dilute acid. The carbinol (VI) from citral is extremely labile, undergoing simultaneous rearrangement and dehydration, even on distillation at 10^{-4} mm.

ETHYNYLCARBINOLS from αβ-unsaturated aldehydes have been prepared by condensation with sodium acetylide in liquid ammonia (Jones and McCombie, J., 1942, 733), and their rearrangement in the presence of acidic reagents has been investigated (*idem*, this vol., p. 261). In Part IX (previous paper) the condensation of 1-hexyne with crotonaldehyde and isomerisation of the acetylenic carbinol with sulphuric acid was described, so a study of the reaction of conjugated vinylacetylenes with αβ-unsaturated aldehydes represents a logical continuation of this programme, directed ultimately towards the synthesis of polyene alcohols related to vitamin A. Many condensations between conjugated vinylacetylenes containing a free ethynyl group and carbonyl compounds are recorded in the literature, but there are few examples of reactions of vinylacetylene and its homologues with unsaturated aldehydes. Carothers and Jacobson (*J. Amer. Chem. Soc.*, 1933, **55**, 1097) reported that condensation between vinylacetylene and crotonaldehyde gave rise to resinous products and Nazarov and Elizarova (*Chem. Abstracts*, 1942, **36**, 742) claimed that, although the condensation of vinylacetylenemagnesium bromide and furfuraldehyde gave the desired carbinol, it darkened rapidly during isolation and exploded on attempted distillation.

It is generally agreed that the most satisfactory method of condensing conjugated vinylacetylenes with aldehydes and ketones is by means of their Grignard compounds, although other condensing agents (*e.g.*, sodamide, potassium hydroxide, and potassium *tert.*-amyloxide) have been employed (Carothers *et al.*, *J.*

Amer. Chem. Soc., 1933, **55**, 1094, 1097; F.P., 753,465; U.S.P. 1,963,934—5; Nazarov *et al.*, *Chem. Abstracts*, 1939, **33**, 5682; 1941, **35**, 4733, 5092; 1942, **36**, 1296; Thompson, Milas, and Rovno, *J. Amer. Chem. Soc.*, 1941, **63**, 752). As far as we are aware, no syntheses of vinylacetylene-carbinols have been made from the sodium derivatives of the hydrocarbons in liquid ammonia solution.

FIG. 1.



As a necessary preliminary to the employment of crotonaldehyde in these reactions, the Grignard condensation between butaldehyde and 3-methylpent-2-en-4-yne (I) was examined. This furnished a 60% yield of 7-*methylnon*-7-*en*-5-*yn*-4-*ol* (II) (3 : 5-*dinitrobenzoate* and β-*naphthylurethane*) which on hydrogenation gave 7-*methylnonan*-4-*ol* (3 : 5-*dinitrobenzoate*), oxidised to 7-*methylnonan*-4-*one* (*phenylsemicarbazone*). The carbinol (II) exhibited light absorption (Fig. 1 and table) similar to that

(I.) $\mathrm{HC{\vdots}C{\cdot}CMe{:}CHMe}$
(II.) $\mathrm{CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH(OH){\cdot}C{\vdots}C{\cdot}CMe{:}CHMe}$
(III.) $\mathrm{CH_3{\cdot}CH{:}CH{\cdot}CH(OH){\cdot}C{\vdots}C{\cdot}CMe{:}CHMe}$
(IV.) $\mathrm{CH_3{\cdot}CH(OH){\cdot}CH{:}CH{\cdot}C{\vdots}C{\cdot}CMe{:}CHMe}$
(V.) $\mathrm{CH_3{\cdot}CH{:}CH{\cdot}CH(OH){\cdot}C{\vdots}C{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3}$

previously recorded (Jones and McCombie, this vol., p. 261) for compounds containing the conjugated vinylacetylene chromophore. With crotonaldehyde and dimethylvinylacetylene, 7-*methylnona*-2 : 7-*dien*-5-*yn*-4-*ol* (III) (α-*naphthylurethane*) was obtained by either the Grignard (80% yield) or the sodium in liquid ammonia (65%) method. The anticipated absorption spectrum (Fig. 1 and table) was observed, and complete hydrogenation of (III) gave 7-methylnonan-4-ol, identical with that given by the butaldehyde product (II).

	$\lambda_{\text{max.}}$, A.	$\varepsilon_{\text{max.}}$	$\lambda_{\text{infl.}}$, A.	$\varepsilon_{\text{infl.}}$
3-Methylpent-2-en-4-yne (I)	2195	9,000	2260	7,000
7-Methylnon-7-en-5-yn-4-ol (II) (Fig. 1)	2280	20,500	2320	18,000
7-Methylnona-2 : 7-dien-5-yn-4-ol (III) (Fig. 1)	2250	15,500	2290	15,000
Hex-3-en-5-yn-2-ol (Part VIII)	2230	13,000	2300	9,500
Dec-3-en-5-yn-2-ol (Part IX)	2260	16,000	2350	15,000
7-Methylnona-3 : 7-dien-5-yn-2-ol (IV) (Fig. 1)	2640	16,500	2690	15,500
Octatrienol	2760 2645 2560	46,500 53,000 42,500	— — —	— — —

On being shaken for 24 hours with 5% sulphuric acid, the carbinol (III) was converted in good yield into the isomeric 7-*methylnona*-3 : 7-*dien*-5-*yn*-2-*ol* (IV) (α-*naphthylurethane*). Hydrogenation of (IV) yielded 7-*methylnonan*-2-*ol* (3 : 5-*dinitrobenzoate*) which was oxidised to 7-*methylnonan*-2-*one* (*semicarbazone*, *phenylsemicarbazone*). The comparative ease of isomerisation of (III) is in striking contrast to that of the isomeric dec-2-en-5-yn-4-ol (V) (preceding paper) which required 25% acid for complete conversion.

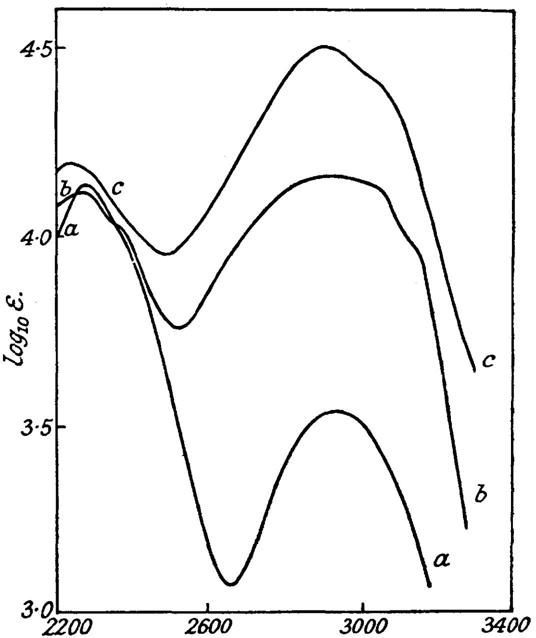
The absorption spectrum of (IV) (Fig. 1 and table) reveals that the *s*-divinylacetylene chromophore absorbs at corresponding wave-lengths to a conjugated triene, although an appreciable difference in intensity is observed, similar to the differences already noted with the conjugated vinylacetylenes (Part VIII).

When citral is condensed with 3-methylpent-2-en-4-yne (I) by the Grignard method, the undistilled product consists mainly of the carbinol (VI) as shown by the fact that it contains 0·9 active hydrogen atom and also by its absorption spectrum [Fig. 2(*a*)], which, with its maximum at 2250 A., is

$\mathrm{Me_2C{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CMe{:}CH{\cdot}CH(OH){\cdot}C{\vdots}C{\cdot}CMe{:}CHMe}$ (VI.)
$\mathrm{Me_2C{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}C(OH)Me{\cdot}CH{:}CH{\cdot}C{\vdots}C{\cdot}CMe{:}CHMe}$ (VII.)
$\mathrm{Me_2C{:}CH{\cdot}CH_2{\cdot}CH{:}CMe{\cdot}CH{:}CH{\cdot}C{\vdots}C{\cdot}CMe{:}CHMe}$ (VIII.)

similar to those of the carbinols (II) and (III). On attempting to purify (VI) by distillation at 10^{-4} mm., considerable rearrangement occurs [Fig. 2(*b*)], accompanied by dehydration, affording the hydrocarbon (VIII)—the intermediate tertiary carbinol (VII), which would be expected to

FIG. 2.



absorb at about 2650 A. by analogy with (IV), evidently undergoes instantaneous dehydration. The conversion of (VI) into (VIII) could not be made complete, however, distillation of (VI) at 10^{-2} mm., followed by persistent chromatographic purification, yielding a product [light absorption, Fig. 2(*c*)] which still contained a few units % of carbinol. Complete hydrogenation of this material, followed by distillation from sodium, gave a saturated hydrocarbon, presumably 2 : 6 : 11-*trimethyl*-n-*tridecane*.

EXPERIMENTAL.

7-*Methylnon*-7-*en*-5-*yn*-4-*ol* (II).—3-Methylpent-2-en-4-yne (31 g.; Thompson, Burr, and Shaw, *J. Amer. Chem. Soc.*, 1941, **63**, 188) in ether (70 c.c.) was gradually added to a solution of ethylmagnesium bromide (from 9·2 g. of magnesium) in ether (100 c.c.) during an hour, after which the reaction mixture was refluxed for 2 hours. It was then cooled, treated dropwise with butaldehyde (27·4 g.) in ether (100 c.c.), set aside overnight, and the Grignard complex decomposed with ammonium chloride solution (ice). Isolated from the ethereal phase in the usual way, 7-*methylnon*-7-*en*-5-*yn*-4-*ol* (37 g.) was obtained as a colourless mobile liquid, b. p. 106°/15 mm., $n_{\mathrm{D}}^{18^\circ}$ 1·4800 (Found : C, 79·3; H, 10·8. $C_{10}H_{16}O$ requires C, 78·9; H, 10·6%). *Active hydrogen* (Zerewitinoff) : The carbinol (250 mg.) evolved 41·4 c.c. of methane at 20°/773 mm., equivalent to 1·0 active hydrogen atom. The 3 : 5-*dinitrobenzoate* formed needles from alcohol, m. p. 53° (Found : C, 59·1; H, 5·2; N, 8·3. $C_{17}H_{18}O_6N_2$ requires C, 58·95; H, 5·2; N, 8·1%). The *β-naphthylurethane* crystallised from aqueous alcohol in plates, m. p. 46° (Found : C, 78·5; H, 7·4. $C_{21}H_{23}O_2N$ requires C, 78·5; H, 7·2%).

7-*Methylnonan*-4-*ol*.—A solution of the above carbinol (4·3 g.) in methyl alcohol (200 c.c.) was shaken with hydrogen in the presence of platinic oxide (0·1 g.) until absorption was complete. The catalyst and solvent were removed, yielding 7-*methylnonan*-4-*ol* as a pleasant-smelling oil, b. p. 94°/12 mm., $n_{\mathrm{D}}^{22^\circ}$ 1·4317 (Found : C, 76·1; H, 13·4. $C_{10}H_{22}O$ requires C, 76·0; H, 13·9%). The 3 : 5-*dinitrobenzoate* crystallised from aqueous alcohol in needles, m. p. 60° (Found : C, 58·0; H, 6·8; N, 8·0. $C_{17}H_{24}O_6N_2$ requires C, 57·95; H, 6·85; N, 7·95%).

7-*Methylnonan*-4-*one*.—Oxidation of the above carbinol with chromic acid yielded 7-*methylnonan*-4-*one* as a pleasant-smelling oil, b. p. 86°/11 mm., $n_{\mathrm{D}}^{22^\circ}$ 1·4246 (Found : C, 76·7; H, 13·1. $C_{10}H_{20}O$ requires C, 76·85; H, 12·9%). The *phenylsemicarbazone* separated from aqueous methyl alcohol in needles, m. p. 65° (Found : N, 14·25. $C_{17}H_{27}ON_3$ requires N, 14·5%)

7-*Methylnona*-2 : 7-*dien*-5-*yn*-4-*ol* (III).—(*a*) 3-Methylpent-2-en-4-yne (40 g.) and sodium (13 g.) were added to liquid ammonia (1000 c.c.) at such a rate that no appreciable excess of sodium was ever present in solution. Crotonaldehyde (35 g.) in ether (50 c.c.) was then added, and stirring and cooling were continued for a further 2 hours; the mixture was then treated with ether (200 c.c.) and ammonium chloride (35 g.), and the ammonia allowed to evaporate off overnight in a slow stream of nitrogen. The reaction product was isolated by steam distillation and extraction with ether, yielding 7-*methylnona*-2 : 7-*dien*-5-*yn*-4-*ol* (49 g.) as a colourless liquid, b. p. 127°/16 mm., 85°/0·5 mm., $n_{\mathrm{D}}^{22^\circ}$ 1·4963 (Found : C, 79·8; H, 9·6. $C_{10}H_{14}O$ requires C, 80·0; H, 9·3%). *Active hydrogen* (Zerewitinoff) : The carbinol (114 mg.) gave 32·4 c.c. of methane at 21°/756 mm., corresponding to 1·0 active hydrogen atom per molecule. *Semimicrohydrogenation :* A mixture of the carbinol (132 mg.) and palladium–norit (50 mg.) in methyl alcohol absorbed 68·4 c.c. of hydrogen at 21°/748 mm., equivalent to $|\overline{\overline{4{\cdot}0}}$. The *a-naphthylurethane* crystallised from light petroleum (b. p. 60—80°) in small needles, m. p. 98° (Found : N, 4·45. $C_{21}H_{21}O_2N$ requires N, 4·4%).

(*b*) A solution of 3-methylpent-2-en-4-yne (20 g.) in dry ether (25 c.c.) was slowly added to an ethereal solution of ethylmagnesium bromide (from 6 g. of magnesium), and the mixture refluxed for 2 hours. The cooled solution was treated dropwise with crotonaldehyde (18 g.) in ether (25 c.c.) and set aside overnight. Decomposition of the Grignard complex with ammonium nitrate (60 g.) and water (100 c.c.) and isolation from the ethereal solution gave 7-methylnona-2 : 7-dien-5-yn-4-ol (31 g.), b. p. 86—88°/1 mm., $n_{\mathrm{D}}^{20^\circ}$ 1·4970.

7-*Methylnona*-3 : 7-*dien*-5-*yn*-2-*ol* (IV).—A mixture of 7-methylnona-2 : 7-dien-5-yn-4-ol (20 g.) and sulphuric acid (200 c.c.; 5% w/v) was shaken under nitrogen at 20° for 24 hours. Isolation of the product in the usual manner gave 7-*methylnona*-3 : 7-*dien*-5-*yn*-2-*ol* (17·5 g.), b. p. 122°/16 mm., 81—82°/1 mm., $n_{\mathrm{D}}^{21^\circ}$ 1·5210 (Found : C, 80·1; H, 9·5. $C_{10}H_{14}O$ requires C, 80·0; H, 9·3%). *Active hydrogen* (Zerewitinoff) : The carbinol (125 mg.) evolved 38·2 c.c. of methane at 23°/763 mm., corresponding to 0·95 active hydrogen atom per molecule. *Semimicrohydrogenation :* A mixture of the carbinol (151 mg.) and palladium–norit (50 mg.) in methyl alcohol absorbed 97·8 c.c. of hydrogen at 23°/755 mm., equivalent to $|\overline{\overline{3{\cdot}95}}$. The *a-naphthylurethane* crystallised from light petroleum (b. p. 40—60°) in needles, m. p. 82° (Found : N, 4·55. $C_{21}H_{21}O_2N$ requires N, 4·4%).

7-*Methylnonan*-2-*ol*.—A solution of the above carbinol (10 g.) in acetic acid (100 c.c.) was shaken with hydrogen in the presence of platinic oxide (100 mg.) until absorption was complete. The filtered solution was neutralised with sodium hydroxide and thoroughly extracted with ether, from which was isolated 7-*methylnonan*-2-*ol*, an oil with a pleasant odour, b. p. 93°/4 mm., $n_{\mathrm{D}}^{18^\circ}$ 1·4330 (Found : C, 76·0, 77·9; H, 13·0, 14·0. $C_{10}H_{22}O$ requires C, 76·0; H, 13·9%). The 3 : 5-*dinitrobenzoate* crystallised from aqueous alcohol in needles, m. p. 65° (Found : N, 7·6. $C_{17}H_{24}O_6N_2$ requires N, 7·95%).

7-*Methylnonan*-2-*one*.—Oxidation of 7-methylnonan-2-ol with chromic acid gave 7-*methylnonan*-2-*one* as a pleasant-smelling liquid, b. p. 116°/6 mm., $n_{\mathrm{D}}^{22^\circ}$1·4257. For analysis the ketone was regenerated from the semicarbazone by steam-distillation with phthalic anhydride (Found : C, 76·2; H, 12·7. $C_{10}H_{20}O$ requires C, 76·85; H, 12·9%). The *semicarbazone* formed plates from aqueous methyl alcohol, m. p. 124° (Found : N, 19·3. $C_{11}H_{23}ON_3$ requires N, 19·7%). The *phenylsemicarbazone* crystallised from aqueous methyl alcohol in needles, m. p. 95·5° (Found : N, 14·1. $C_{17}H_{27}ON_3$ requires N, 14·5%).

Condensation of Citral with 3-*Methylpent*-2-*en*-4-*yne*.—A solution of 3-methylpent-2-en-4-yne (14·7 g.) in ether (50 c.c.) was treated with an ethereal solution of ethylmagnesium bromide (from 4·3 g. of magnesium), the mixture was refluxed for 2 hours, cooled, treated dropwise (1 hour) with a solution of citral (27·4 g.) in ether (100 c.c.), and set aside overnight. After 1 hour's refluxing, the Grignard complex was decomposed in the usual manner, and the ethereal solution yielded the carbinol (30·5 g.) as a dark oil, $n_{\mathrm{D}}^{26^\circ}$ 1·5040. *Active hydrogen* (Zerewitinoff) : The product (156 mg.) evolved 14·3 c.c. of methane at 24°/768 mm., equivalent to 0·9 active hydrogen atom per molecule. *Light absorption :* Maxima, 2250 and 2920 A.; $E^{1\%}_{1\,\mathrm{cm.}}$, 610 and 160, respectively. Distillation of a portion of the product at 70—80° (bath temp.)/10^{-4} mm. gave a pale yellow oil, $n_{\mathrm{D}}^{24^\circ}$ 1·5298, with maxima at 2250 and 2930 A.; $E^{1\%}_{1\,\mathrm{cm.}}$, 530 and 620, respectively. The main product underwent further dehydration on distillation at 10^{-2} mm., b. p. 114—116°, $n_{\mathrm{D}}^{22^\circ}$ 1·5349, and this was purified by chromatographic analysis on alumina from light petroleum (b. p. 40—60°), yielding the slightly impure hydrocarbon as a colourless oil, rapidly becoming yellow in air, $n_{\mathrm{D}}^{21^\circ}$ 1·5628 (Found : C, 87·5; H, 9·9. $C_{16}H_{22}$ requires C, 89·65; H, 10·35%). *Active hydrogen* (Zerewitinoff) : The product (142 mg.) evolved 1·3 c.c. of methane at 21°/762 mm. *Light absorption :* Maxima, 2250 and 2920 A.; $E^{1\%}_{1\,\mathrm{cm.}}$, 570 and 1320, respectively.

2 : 6 : 11-*Trimethyl*-n-*tridecane*.—A solution of the above slightly impure carbinol (5·1 g.) in methyl alcohol (250 c.c.) was shaken with hydrogen in the presence of platinic oxide (0·1 g.) until absorption was complete. After removal of

catalyst and solvent, the product was set aside over sodium for several days, and distillation from sodium then gave 2 : 6 : 11-*trimethyl*-n-*tridecane*, b. p. 152°/16 mm., $n_D^{20°}$ 1·4375 (Found: C, 85·0; H, 14·8. $C_{16}H_{34}$ requires C, 84·85; H, 15·15%).

The authors are indebted to the Rockefeller Foundation and to I.C.I. (Dyestuffs) Ltd. for financial assistance. They also wish to thank Mr. M. B. Green for assistance with the crotonaldehyde–dimethylvinylacetylene condensation.

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[*Received, March* 18*th*, 1943.]