204. *Researches on Acetylenic Compounds. Part VI. Carbinols derived from Methyl β-Chlorovinyl Ketone and their Conversion into Unsaturated Aldehydes.*

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Methyl β-chlorovinyl ketone reacts with sodium acetylide in liquid ammonia giving a 45% yield of the carbinol (II) and with the Grignard complexes from 1-hexyne and vinylacetylene to give similar carbinols (IV; R = *n*-Bu and CH:CH$_2$ respectively) in about 90% yields. On treatment with dilute acids all three carbinols undergo anionotropic rearrangement followed by elimination of hydrogen chloride, yielding conjugated acetylenic–ethylenic aldehydes of type (III). Rearrangement-halogenation occurs with concentrated hydrochloric acid and leads to 1 : 1-dichloro-compounds such as (VI). Light-absorption data for the latter and for the aldehydes, their semicarbazones, and their 2 : 4-dinitrophenylhydrazones are recorded.

The carbinol obtained by reaction of the chlorovinyl ketone with methylmagnesium bromide is similarly converted into β-methylcrotonaldehyde in about 30% yield. This may well develop into a useful general method of synthesising otherwise difficultly accessible αβ-ethylenic aldehydes.

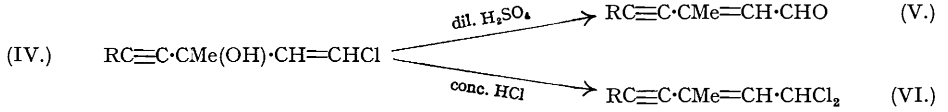
The isomerisation of acetylenic carbinols and glycols, derived from αβ-ethylenic aldehydes and ketones, in the presence of acids, to conjugated ethylenic–acetylenic carbinols and glycols, *e.g.*,

$$\mathrm{HC{\equiv}C{\cdot}CH(OH){\cdot}CH{=}CH{\cdot}CH_3 \longrightarrow HC{\equiv}C{\cdot}CH{=}CH{\cdot}CH(OH){\cdot}CH_3}$$

has been extensively investigated in these laboratories (see *J.*, 1943, 261—270; 1944, 134—147, 436; 1945, 77—94). It seemed probable that the carbinols obtained by condensation of acetylenic compounds with β-chlorovinyl ketones would, on treatment with acids, be converted into conjugated acetylenic–ethylenic aldehydes, following elimination of hydrogen chloride from the unstable intermediates.

$$\underset{\text{(I.)}}{\mathrm{Me{\cdot}CO{\cdot}CH{=}CHCl}} \xrightarrow{\mathrm{C_2H_2}} \underset{\text{(II.)}}{\mathrm{HC{\equiv}C{\cdot}CMe(OH){\cdot}CH{=}CHCl}} \xrightarrow{\text{acids}} \mathrm{[HC{\equiv}C{\cdot}CMe{=}CH{\cdot}CH(OH)Cl]} \longrightarrow \underset{\text{(III.)}}{\mathrm{HC{\equiv}C{\cdot}CMe{=}CH{\cdot}CHO}}$$

Methyl β-chlorovinyl ketone (I) was chosen for this study because of its ready availability by condensation of acetyl and vinyl chlorides in the presence of aluminium chloride. It suffers from the disadvantage, however, of being rather unstable, and has to be used immediately after preparation. By interaction with an equimolecular quantity of 1-hexynylmagnesium bromide in ethereal solution 1-*chloro*-3-*methylnon*-1-*en*-4-*yn*-3-*ol* (IV; R = *n*-Bu) was obtained in 45% yield, but, when the proportion of Grignard reagent was doubled and the reaction carried out in boiling ethereal solution, the yield of the desired carbinol was increased to 95%. Employing an identical procedure vinylacetylene gave an 85% yield of the corresponding *carbinol* (IV; R = CH=CH$_2$).



$$\text{(IV.)}\quad \mathrm{RC{\equiv}C{\cdot}CMe(OH){\cdot}CH{=}CHCl} \begin{cases} \xrightarrow{\text{dil. } \mathrm{H_2SO_4}} \mathrm{RC{\equiv}C{\cdot}CMe{=}CH{\cdot}CHO} & \text{(V.)} \\ \xrightarrow{\text{conc. } \mathrm{HCl}} \mathrm{RC{\equiv}C{\cdot}CMe{=}CH{\cdot}CHCl_2} & \text{(VI.)} \end{cases}$$

From previous experience of condensations of αβ-unsaturated ketones with sodium acetylide in liquid ammonia (Cymerman, Heilbron, and Jones, *J.*, 1945, 90) it was to be expected that the yield of carbinol from methyl β-chlorovinyl ketone would be very dependent upon the proportions of reactants employed. In the case of methyl vinyl ketone the yield was found to increase with increasing proportions of acetylide, reaching 40% when 4·5 moles of sodium acetylide were used. Equimolecular proportions of the acetylide and the chlorovinyl ketone gave a 20% yield of the *carbinol* (II); an acetylide : ketone ratio of 2 : 1 gave a 45% yield, but this was reduced to about 10% when the proportion was further increased to 3 : 1. The optimum conditions, which have yet to be determined, are obviously quite critical.

All three carbinols described above were converted into aldehydes in good yields on treatment with dilute acids, but rather different conditions were necessary in the three cases on account of the different solubilities of the carbinols. With the simplest carbinol (II), a 70% yield of the *aldehyde* (III) was obtained simply by treatment with dilute sulphuric acid at 20°. The vinyl acetylenic carbinol (IV; R = CH=CH$_2$) gave the *aldehyde* (V; R = CH=CH$_2$) in 60% yield in dilute sulphuric acid–dioxan, but the *aldehyde* (V; R = *n*-Bu) could only be obtained in reasonable yield by using trimethylcetylammonium bromide to emulsify the carbinol in a dilute sulphuric acid–dioxan medium.

The light-absorption data for alcoholic solutions of these aldehydes and of their *semicarbazones* and 2 : 4-*dinitrophenylhydrazones* are detailed in Table I. In general they are in agreement with expectations, except that in the case of the dinitrophenylhydrazone of the aldehyde (V; R = CH=CH$_2$), no bathochromic effect corresponding to the presence of the additional conjugated ethenoid linkage is apparent, although such an effect is observed with both the aldehyde itself and its semicarbazone.

When acetylenylcarbinols derived from αβ-unsaturated carbonyl compounds are treated with concentrated hydrochloric acid, rearrangement-halogenation is readily effected (Heilbron, Jones, Lacey, McCombie, and Raphael, *J.*, 1945, 77):

$$\mathrm{CH_3{\cdot}CH{=}CH{\cdot}CH(OH){\cdot}C{\equiv}CH \longrightarrow CH_3{\cdot}CHCl{\cdot}CH{=}CH{\cdot}C{\equiv}CH}$$

TABLE I.

			2 : 4-Dinitrophenylhydrazone.		Semicarbazone.	
	$\lambda_{max.}$, A.	$\epsilon_{max.}$	$\lambda_{max.}$, A.	$\epsilon_{max.}$	$\lambda_{max.}$, A.	$\epsilon_{max.}$
$HC{\equiv}C{\cdot}CMe{=}CH{\cdot}CHO$	2615	12,500	2600 3850	15,500 33,500	2920	32,500
n-$BuC{\equiv}C{\cdot}CMe{=}CH{\cdot}CHO$	2700 2760	14,000 14,000	2640 † 3050 3900	17,500 10,000 32,000	2950 3060 *	35,000 31,000
$CH_2{=}CH{\cdot}C{\equiv}C{\cdot}CMe{=}CH{\cdot}CHO$	2200 2820 2920 3000	9,000 12,000 12,000 11,500	2670 † 3080 3900	18,000 10,000 40,000	3080	27,500
$HC{\equiv}C{\cdot}CH{=}CH{\cdot}CO{\cdot}Me$ [1]	2550	11,500	3780 †	30,000		

[1] Bowden, Heilbron, Jones, and Weedon, this vol., p. 39. * Inflexion. † In chloroform.

The above-mentioned carbinols prepared from methyl β-chlorovinyl ketone behave similarly, the dichloro-compounds (VI) (listed in Table II, where their light-absorption properties are recorded) being produced in yields ranging from 55—85%.

TABLE II.

	$\lambda_{max.}$, A.	$\epsilon_{max.}$		$\lambda_{max.}$, A.	$\epsilon_{max.}$
$HC{\equiv}C{\cdot}CMe{=}CH{\cdot}CHCl_2$	2290	13,000	$HC{\equiv}C{\cdot}CH{=}CH{\cdot}CH_2Cl$ [1]	2280	10,500
n-$BuC{\equiv}C{\cdot}CMe{=}CH{\cdot}CHCl_2$	2370	15,000	$CH_2{=}CH{\cdot}C{\equiv}C{\cdot}CH{=}CH{\cdot}CHCl{\cdot}CH_3$ [1]	2200	6,000
$CH_2{=}CH{\cdot}C{\equiv}C{\cdot}CMe{=}CH{\cdot}CHCl_2$	2610	14,500		2620	17,000
	2760 *	11,500		2750 *	13,500

[1] Heilbron, Jones, Lacey, McCombie, and Raphael, *loc. cit.* * Inflexion.

With anionotropic systems of the type

$$\text{(VII.)}\qquad RCH(OH){\cdot}CH{=}CH_2 \rightleftharpoons RCH{=}CH{\cdot}CH_2{\cdot}OH \qquad \text{(VIII.)}$$

the conversion of (VII) into (VIII) in the presence of acids is usually quantitative when R = aryl, acetylenyl, or vinyl (see *inter alia*, Burton and Ingold, *J.*, 1928, 904; Burton, *J.*, 1928, 1650; Jones and McCombie, *J.*, 1943, 261; Heilbron, Jones, McCombie, and Weedon, *J.*, 1945, 84), but when R = alkyl, the mobility of the system is markedly diminished (Baudrenghien, *Bull. Soc. chim. Belg.*, 1922, **31**, 160; Burton, *J.*, 1929, 455; 1930, 248) and in the simplest cases the systems only become actively tautomeric when the hydroxyl group is replaced by a halogen atom, etc. (Young and Lane, *J. Amer. Chem. Soc.*, 1937, **59**, 2051; 1938, **60**, 847; Baudrenghien, *loc. cit.*). The mobility of such systems is considerably enhanced, however, if a *gem*-dialkyl group is present, as in dimethylvinylcarbinol (Locquin and Wouseng, *Compt. rend.*, 1922, **174**, 1711; **175**, 100; Sung, *Ann. Chim.*, 1924, **1**, 386) and it seemed possible, as an extension of the work already described in this paper, that in the presence of acids, simple chlorovinylcarbinols (*e.g.*, IX) might be converted into αβ-ethylenic aldehydes, *e.g.* (XI),

$$\underset{\text{(IX.)}}{Me_2C(OH){\cdot}CH{=}CHCl} \rightleftharpoons \underset{\text{(X.)}}{Me_2C{=}CH{\cdot}CH(OH)Cl} \longrightarrow \underset{\text{(XI.)}}{Me_2C{=}CH{\cdot}CHO}$$

the equilibrium (IX $\rightleftharpoons$ X) being disturbed by the elimination of hydrogen chloride from the isomeric chloro-carbinols (*e.g.*, X). Such a conversion has now been realised. The *carbinol* (IX), obtained by reaction of methyl β-chlorovinyl ketone with methylmagnesium bromide, yields β-methylcrotonaldehyde (XI) on treatment with 10% sulphuric acid at room temperature. We intend to study this reaction in more detail as opportunity permits, since, although only a 30% yield of aldehyde was obtained in the single experiment so far carried out, the method promises to be of such wide applicability that a detailed study of reaction conditions appears desirable.

EXPERIMENTAL.

(Absorption spectra were determined in alcoholic solutions.)

1-*Chloro*-3-*methylpent*-1-*en*-4-*yn*-3-*ol* (II).—A solution of sodium acetylide (from sodium, 28 g.) in liquid ammonia (750 c.c.) was prepared *via* sodamide using sodium oxide (from sodium 0·8 g.) and hydrated ferric nitrate (0·24 g.) in the manner previously described (Heilbron, Jones, and Weedon, *J.*, 1945, 81). Freshly prepared methyl β-chlorovinyl ketone (62·5 g.; B.P. 466,891; U.S.P. 2,137,664) in ether (100 c.c.) was added during 1 hour, the mixture was stirred for a further 2½ hours, and then the reaction was terminated by the gradual addition of ammonium chloride (66 g.). The ammonia was allowed to evaporate overnight and the product isolated by filtration and careful washing of the residue with ether. The combined ethereal solutions were dried and evaporated and gave 1-*chloro*-3-*methylpent*-1-*en*-4-*yn*-3-*ol* (35 g.), b. p. 91°/50 mm., 75°/20 mm., 64°/12 mm., $n_D^{18^\circ}$ 1·4785 (Found: C, 54·95; H, 5·45. C_6H_7OCl requires C, 55·2; H, 5·4%).

1-*Chloro*-3-*methylnon*-1-*en*-4-*yn*-3-*ol* (IV; R = n-Bu).—1-Hexyne (55 g.) in ether (50 c.c.) was added over 1 hour to a stirred solution (700 c.c.) of ethylmagnesium bromide (from magnesium, 16·2 g.) and the mixture was refluxed for 3 hours. Freshly prepared methyl β-chlorovinyl ketone (42 g.) in ether (60 c.c.) was added with cooling (ice) during

2 hours and the stirring continued for 30 minutes at room temperature and finally for 1 hour under reflux. Decomposition with ammonium chloride (ice) followed by isolation by means of ether gave 1-*chloro*-3-*methylnon*-1-*en*-4-*yn*-3-*ol* (69·9 g.), b. p. 77—78·5°/0·3 mm., 59°/0·1 mm., $n_D^{17^\circ}$ 1·4818 (Found : C, 64·55; H, 8·15. $C_{10}H_{15}OCl$ requires C, 64·35; H, 8·1%).

1-*Chloro*-3-*methylhepta*-1 : 6-*dien*-4-*yn*-3-*ol* (IV; R = CH:CH$_2$).—A solution of vinylacetylene [52 g. (crude) made according to Schmitz and Schumacher, *Z. Electrochem.*, 1939, **45**, 503] in ether (150 c.c.) was added during 1 hour to a stirred ethereal solution (500 c.c.) of ethylmagnesium bromide (from magnesium 24 g.) contained in a three-necked flask fitted with a double surface condenser containing solid carbon dioxide. The mixture was refluxed for 2 hours, ecoold, and then treated dropwise with a solution of freshly prepared methyl β-chlorovinyl ketone (52 g.) in ether (100 c.c.) during 1 hour. Stirring was continued for 30 minutes at room temperature and finally, after dilution of the solution to 1 l. with ether, under reflux for 1 hour. Decomposition with ammonium chloride (110 g.) and ice followed by isolation by means of ether gave 1-*chloro*-3-*methylhepta*-1 : 6-*dien*-4-*yn*-3-*ol* (67 g.), b. p. 78°/1 mm., 60°/0·4 mm., 46°/0·1 mm., 37°/0·05 mm., $n_D^{17^\circ}$ 1·5168 (Found: C, 60·6, 60·0; H, 6·0, 5·8. C_8H_9OCl requires C, 61·35; H, 5·8%). Light absorption : Maxima, 2230, 2320 A.; ϵ = 14,500 and 12,500 respectively.

3-*Methylpent*-2-*en*-4-*yn*-1-*al* (III).—A solution of 1-chloro-3-methylpent-1-en-4-yn-3-ol (5 g.) in dilute sulphuric acid (400 c.c.; 10% w/v) containing a trace of quinol was kept at room temperature for 42 hours. It was then saturated with ammonium sulphate and extracted thoroughly with ether. Evaporation of the ethereal solution and distillation of the residue gave 3-*methylpent*-2-*en*-4-*yn*-1-*al* (2·6 g.) as a pale yellow, lachrymatory liquid that undergoes partial polymerisation even in the presence of quinol, both on distillation and on keeping. B. p. 71—73°/50 mm., 53—54°/20 mm., $n_D^{23^\circ}$ 1·4993 (Found: C, 76·7, 76·35; H, 6·65, 6·6. C_6H_6O requires C, 76·6; H, 6·4%). The 2 : 4-*dinitrophenylhydrazone* formed small red needles from alcohol, m. p. 144—145° (Found : N, 20·7. $C_{12}H_{10}O_4N_4$ requires N, 20·45%). The *semicarbazone* crystallised in needles from aqueous alcohol, m. p. 180° (decomp.; bath preheated to 160°) (Found : N, 27·5. $C_7H_9ON_3$ requires N, 27·8%).

3-*Methylnon*-2-*en*-4-*yn*-1-*al* (V; R = *n*-Bu).—A mixture of 1-chloro-3-methylnon-1-en-4-yn-3-ol (20 g.), dilute sulphuric acid (1800 c.c.; 10% w/v), dioxan (900 c.c.), and trimethylcetylammonium bromide (1 g.) was stirred vigorously for 48 hours at 45—50° in nitrogen, and the product was then isolated by means of ether. Distillation gave 3-*methylnon*-2-*en*-4-*yn*-1-*al* (*ca.* 10 g.) as a very pale yellow liquid, b. p. 78—82°/1 mm., $n_D^{16^\circ}$ 1·4982 (Found : C, 79·75; H, 9·55. $C_{10}H_{14}O$ requires C, 79·95; H, 9·4%). The 2 : 4-*dinitrophenylhydrazone* formed red needles from methyl alcohol, m. p. 109·5—110° (Found : N, 17·3. $C_{16}H_{18}O_4N_4$ requires N, 16·95%). The *semicarbazone* crystallised in leaflets from aqueous alcohol, m. p. 143—144° (Found : N, 20·3. $C_{11}H_{17}ON_3$ requires N, 20·25%).

3-*Methylhepta*-2 : 6-*dien*-4-*yn*-1-*al* (V; R = CH:CH$_2$).—A solution of 1-chloro-3-methylhepta-1 : 6-dien-4-yn-3-ol (10·5 g.) in dioxan (450 c.c.) and dilute sulphuric acid (1 l.; 10% w/v) was kept at room temperature for 24 hours. Dilution with water to 2·5 l. and isolation by means of ether gave 3-*methylhepta*-2 : 6-*dien*-4-*yn*-1-*al* (4·2 g.) as a pale yellow mobile liquid, b. p. 51°/1 mm.; 46—48°/0·4 mm., $n_D^{19^\circ}$ 1·5582 (Found : C, 79·6; H, 6·95. C_8H_8O requires C, 80·0; H, 6·7%). The 2 : 4-*dinitrophenylhydrazone* crystallised as dark red needles from methyl alcohol, m. p. 148—149° (Found : N, 18·6. $C_{14}H_{12}O_4N_4$ requires N, 18·65%). The *semicarbazone* formed pale yellow needles from aqueous alcohol, m. p. 180—181° (Found : N, 23·9. $C_9H_{11}ON_3$ requires N, 23·7%).

1 : 1-*Dichloro*-3-*methylpent*-2-*en*-4-*yne* (VI; R = H).—1-Chloro-3-methylpent-1-en-4-yn-3-ol (5 g.) and concentrated hydrochloric acid (100 c.c.) were shaken together at room temperature in nitrogen for 45 minutes. After dilution with water to 200 c.c. the product was isolated by means of ether. Distillation gave 1 : 1-*dichloro*-3-*methylpent*-2-*en*-4-*yne* (3·8 g.), b. p. 72—73°/50 mm., 49—50°/18 mm., $n_D^{16^\circ}$ 1·4989 (Found : C, 48·7; H, 4·35. $C_6H_6Cl_2$ requires C, 48·35; H, 4·05%).

1 : 1-*Dichloro*-3-*methylnon*-2-*en*-4-*yne* (VI; R = *n*-Bu).—A mixture of 1-chloro-3-methylnon-1-en-4-yn-3-ol (15 g.) and concentrated hydrochloric acid (1 l.) was shaken at 20° in nitrogen for 2½ hours. Dilution with water to 2·5 l. and isolation of the product with ether gave 1 : 1-*dichloro*-3-*methylnon*-2-*en*-4-*yne* (14·3 g.) as a pale yellow oil, b. p. 84—86°/0·6 mm., 57—59°/0·15 mm., 50—51°/0·05 mm., $n_D^{20^\circ}$ 1·4990 (Found : C, 58·6; H, 7·0. $C_{10}H_{14}Cl_2$ requires C, 58·55; H, 6·9%).

1 : 1-*Dichloro*-3-*methylhepta*-2 : 6-*dien*-4-*yne* (VI; R = CH:CH$_2$).—1-Chloro-3-methylhepta-1 : 6-dien-4-yn-3-ol (10 g.) and concentrated hydrochloric acid (450 c.c.) were shaken at 20° in nitrogen for 3 hours. Dilution to 1200 c.c. with water and isolation of the product with ether gave 1 : 1-*dichloro*-3-*methylhepta*-2 : 6-*dien*-4-*yne* (6·3 g.) as a pale yellow oil, b. p. 75—76°/2·5 mm., 24°/0·05 mm., $n_D^{16^\circ}$ 1·5444 (Found : Cl, 39·4. $C_8H_8Cl_2$ requires Cl, 40·5%).

1-*Chloro*-3-*methylbut*-1-*en*-3-*ol* (IX).—Freshly prepared methyl β-chlorovinyl ketone (20 g.) in ether (40 c.c.) was added during 1 hour to methylmagnesium bromide (from magnesium 7 g.) in ether (500 c.c.) and, after 30 minutes' stirring at room temperature, the organometallic complex, which had separated out as a sticky, orange coloured solid, was decomposed with a solution of ammonium chloride (50 g.) in water. Isolation by means of ether and fractional distillation through a Dufton column (24 cm.) gave 1-*chloro*-3-*methylbut*-1-*en*-3-*ol* (11 g.), b. p. 55°/15 mm., $n_D^{18^\circ}$ 1·4590 (Found: C, 50·3, 49·75; H, 7·5, 7·95. C_5H_9OCl requires C, 49·8; H, 7·5%). A better yield would doubtless have been obtained by carrying out the Grignard condensation in benzene solution.

β-*Methylcrotonaldehyde* (XI).—A solution of the above 1-chloro-3-methylbut-1-en-3-ol (3 g.) in dilute sulphuric acid (250 c.c.; 10% w/v) was kept at room temperature in nitrogen for 3 days, during which time an oil separated. The crude product was isolated by means of ether and divided into two equal portions. The first was treated with semicarbazide acetate in aqueous alcoholic solution and gave the semicarbazone of β-methylcrotonaldehyde (0·45 g.; 25%) as needles from methyl alcohol, m. p. 219·5—220·5°, undepressed on admixture with an authentic specimen (m. p. 221—222°). Light absorption : Maxima, 2700 and 2780 A.; ϵ = 33,000 (Evans and Gillam, *J.*, 1943, 565, give maximum, 2730 A.; ϵ = 33,500). The second portion was treated with a methyl-alcoholic solution of 2 : 4-dinitrophenylhydrazine sulphate and gave the 2 : 4-dinitrophenylhydrazone of β-methylcrotonaldehyde (1·1 g.; 32%) as dark red needles from alcohol, m. p. 182—183° undepressed on admixture with an authentic specimen (m. p. 179°). Light absorption : Main maximum, 3800 A.; ϵ = 28,500 (Braude and Jones, *J.*, 1945, 498, give 3820 A.; ϵ = 24,000).

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