411. *Alkenylation by Use of Lithium Alkenyls. Part II. The Condensation of* iso*Butenyl-lithium with Acraldehyde and Crotonaldehyde, and the Oxotropic Rearrangement of the Resulting Carbinols.* (*Studies in Molecular Rearrangement. Part IV.*)

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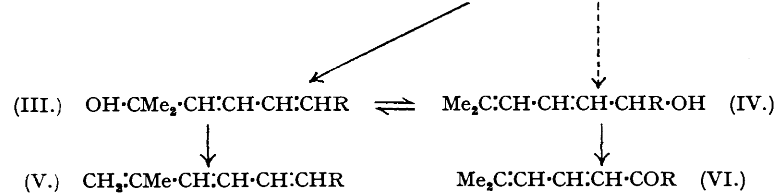
*iso*Butenyl-lithium (see Part I, preceding paper) condenses normally with acraldehyde and crotonaldehyde to give the expected substituted divinylcarbinols (I*a* and I*b*), the constitutions of which are proved by catalytic hydrogenation. The *iso*butenyl group in propenyl*iso*butenylcarbinol (I*b*) is surprisingly resistant to hydrogenation with a platinic oxide catalyst.

On treatment with very dilute mineral acids, the divinylcarbinols undergo irreversible oxotropic rearrangement to give exclusively the substituted tertiary butadienylcarbinols (III). Under more strongly acid conditions, the latter undergo further reversible rearrangement to the primary or secondary isomers (IV), as well as partial dehydration to the substituted hexatrienes (V).

In Part I (preceding paper) condensation of *iso*butenyl-lithium with benzaldehyde and acetophenone has been described. These reactions showed that the alk-1-enyl-lithium derivative behaves normally towards carbonyl compounds, but the synthesis of arylalkenylcarbinols by this route is of limited preparative value as these are also accessible through the arylmagnesium derivatives. The present work provides some examples of the use of *iso*butenyl-lithium for the synthesis of otherwise relatively inaccessible dialkenylcarbinols.

*iso*Butenyl-lithium reacted in the expected manner with acraldehyde and crotonaldehyde to give the substituted divinylcarbinols, vinyl- (I*a*) and propenyl-*iso*butenylcarbinol (I*b*) in 40% yields. Only a few simple carbinols of this type have previously been described, though some of the lower homologues, including divinylcarbinol itself, have been prepared by semi-hydrogenation of the corresponding ethynylcarbinols (Lespieau and Lombard, *Bull. Soc. chim.*, 1935, **2**, 372; Heilbron, Jones, McCombie, and Weedon, *J.*, 1945, 84, 88). A higher homologue, methyldi*iso*butenylcarbinol, has also been obtained by the condensation of phorone and methylmagnesium iodide (Fellenberg, *Ber.*, 1904, **37**, 3578).

The structures of (I*a*) and (I*b*) were proved by their transparency in the 2300-A. region and by catalytic hydrogenation to ethyl- and propyl-*iso*butylcarbinol, respectively. The carbinol (I*a*) readily absorbed two moles of hydrogen, when dry methanol was used as solvent and platinic oxide as catalyst. With (I*b*), the uptake of hydrogen practically ceased after one mole had been absorbed. The semi-hydrogenated product furnished acetone, but no propaldehyde on ozonisation, and is therefore propyl*iso*butenylcarbinol (II; R = Me). Further hydrogenation of the latter, over a palladium–calcium carbonate catalyst, resulted in the smooth uptake of a second mole of hydrogen to give propyl*iso*butylcarbinol. In view of the ready and complete hydrogenation of (I*a*) over platinum oxide, the resistance of the *iso*butenyl group in (I*b*) to hydrogenation in these conditions is rather surprising: the introduction of the additional methyl substituent in (I*b*) would not be expected to have any pronounced effect on the accommodation of the *iso*butenyl group on the catalyst. A somewhat similar observation has recently been reported, however, by Zafiriadis (*Compt. rend.*, 1948, **226**, 731) who found that ethyl cinnamylidenemethyl ketone is considerably more resistant to catalytic hydrogenation than cinnamylideneacetone.



(*a*) R = H. (*b*) R = Me.

Propenyl*iso*butenylcarbinol also proved surprisingly resistant to oxidation by the Oppenauer method, no significant yield of the expected ketone being obtained on prolonged treatment with acetone and aluminium *tert.*-butoxide in boiling benzene. When *p*-benzoquinone, a more powerful hydrogen acceptor, is used, oxidation does occur, but the quinol produced immediately acts as acidic catalyst causing rearrangement of the carbinol, and the product isolated is mainly 6-methylhepta-3 : 5-dien-2-one, derived from the isomeric carbinol (IV*b*) (see below).

The acid-catalysed oxotropic rearrangement of divinylcarbinols was first described by Heilbron, Jones, McCombie, and Weedon (*loc. cit.*) who showed that divinylcarbinol itself is converted into penta-2 : 4-dien-1-ol on treatment with dilute acids, and that vinylpropenylcarbinol (VII) is similarly converted into hexa-3 : 5-dien-2-ol (VIII). The rearrangement of vinylpropenylcarbinol could theoretically proceed in two directions, with migration of the hydroxyl group to either the unsubstituted or the methyl-substituted γ-carbon atom, but none of the alternative rearrangement product, sorbyl alcohol (IX), was obtained and the exclusive formation of (VIII) was ascribed to the superior electron-donating properties of the propenyl compared with the vinyl group.

$$\begin{tikzcd}
 & \text{CHMe}{:}\text{CH}{\cdot}\text{CH(OH)}{\cdot}\text{CH}{:}\text{CH}_2 \ \text{(VII.)} \arrow[dl] \arrow[dr, dashed] & \\
\text{(VIII.)}\ \text{OH}{\cdot}\text{CHMe}{\cdot}\text{CH}{:}\text{CH}{\cdot}\text{CH}{:}\text{CH}_2 \arrow[rr, phantom, "\rightleftharpoons"] & & \text{CHMe}{:}\text{CH}{\cdot}\text{CH}{:}\text{CH}{\cdot}\text{CH}_2{\cdot}\text{OH}\ \text{(IX.)}
\end{tikzcd}$$

Since the ease of rearrangement of vinylpropenylcarbinol is much greater than that of divinylcarbinol (Braude and Jones, *J.*, 1946, 128), a rapidly increasing order of mobility was to be expected for the oxotropic systems represented by (I*a*) and (I*b*). Treatment of the two carbinols with 0·001M-sulphuric acid in aqueous acetone at room temperature for 4 hours and for 10 minutes, respectively, results in quantitative isomerisation to the conjugated tertiary carbinols, dimethylbutadienylcarbinol (2-methylhexa-3 : 5-dien-2-ol) (III*a*) and dimethylpentadienylcarbinol (2-methylhepta-3 : 5-dien-2-ol) (III*b*), which exhibit ultra-violet light absorption properties typical of mono- and di-alkylated conjugated dienes (see Table) and were characterised by their maleic anhydride adducts. The adducts contain one free carboxyl group as shown by alkalimetric titration and are therefore lactonic acids analogous to those obtained from lower homologues (Heilbron *et al.*, *loc. cit.*). The lability of (I*a*) and, even more so, of (I*b*) is so great that unless careful precautions are taken to eliminate all traces of acids during their preparation, partly or largely rearranged products are obtained. The carbinol (III*a*) has previously been prepared from two different acetylenic precursors by Nazarov and Fisher (*Bull. Acad. Sci. U.R.S.S., Cl. Sci. Chim.*, 1945, 631; 1948, 311), and the physical constants obtained in the present work are in good agreement with those previously recorded. The structure of (III*b*) was proved by catalytic hydrogenation in the presence of platinic oxide to give dimethyl-*n*-amylcarbinol, identified by the 3 : 5-dinitrobenzoate.

On treatment with more concentrated mineral acids, *e.g.*, when shaken with 0·1M-aqueous hydrochloric acid, (I*a*) is converted into an approximately equimolar mixture of the tertiary isomer (III*a*) and the primary isomer, 5-methylhexa-2 : 4-dien-1-ol (IV*a*), which could be separated by fractional distillation. The primary isomer (IV*a*) can readily be distinguished from (III*a*) by its longer wave-length absorption maximum, which has the location expected for a trialkylated conjugated diene (see Table), and like 1 : 1 : 4-trimethylbutadiene (Bacon and Farmer, *J.*, 1937, 1065, erroneously quoted by Norton, *Chem. Reviews*, 1942, **31**, 369; Henne and Turk, *J. Amer. Chem. Soc.*, 1942, **64**, 826) fails to give a crystalline maleic anhydride adduct. An approximately equimolar mixture of (III*a*) and (IV*a*) is also obtained by the acid treatment of (III*a*). Quantitative kinetic measurements (which will be reported in detail in a separate communication) show that the rearrangement (III*a*) → (IV*a*) is slower by a factor of *ca.* 10^3 than the rearrangement (I*a*) → (III*a*), and that (IV*a*) is not formed *directly* from (I*a*) to any measurable extent even under the more strongly acid conditions. The rearrangement (III*a*) → (IV*a*) represents a five-carbon oxotropic change and is reversible, (IV*a*) being isomerised similarly. Isomerisation in homogeneous solution is accompanied by some dehydration of (III*a*) to 2-methylhexa-1 : 3 : 5-triene (VI*a*).

The isomerisation of (III*a*) and (IV*a*) has previously been reported by Nazarov and Fisher (*locc. cit.*) who, however, employed somewhat different conditions and were only able to effect *ca.* 20% conversion, without establishing equilibria. The same workers have also recently described (*loc. cit.*, 1948) the partial interconversion of the lower homologues, methylbutadienylcarbinol (VIII) and sorbyl alcohol (IX).

The higher homologue (III*b*) similarly undergoes further isomerisation to an approximately equimolar mixture of (III*b*) and the secondary conjugated isomer, 6-methylhepta-3 : 5-dien-2-ol (IV*b*), but in this case a complete separation of the two isomers by fractionation could not be readily effected. The isomers (III*b*) and (IV*b*) again differ in the location of their ultra-violet absorption maxima (see Table), and (IV*b*) does not furnish a maleic anhydride adduct. As in the case of (III*a*), the further rearrangement of (III*b*) in homogeneous solution is accompanied by some dehydration; a sample of the resulting 2-methylhepta-1 : 3 : 5-triene (V*b*), which exhibited the expected light-absorption properties (see Table), was also obtained by the combined rearrangement and dehydration of (I*b*) with potassium hydrogen sulphate, but sufficient material was not available for complete purification.

The structure of (IV*b*) was proved by oxidation of the equilibrium mixture of (III*b*) and (IV*b*) with *p*-benzoquinone and aluminium *tert.*-butoxide in boiling benzene. The tertiary carbinol (III*b*) is unaffected by the Oppenauer reagent, whereas (IV*b*) is oxidised to 6-methylhepta-3 : 5-dien-2-one (VI*b*). The quinol produced in the reaction acts as acidic catalyst, converting more (III*b*) into (IV*b*) as the oxidation proceeds. The dienone has previously been obtained by Kuhn and Hoffer (*Ber.*, 1932, **65**, *B*, 651) by the condensation of acetone and β-methylcrotonaldehyde. Since the latter is not very readily accessible, the dienone was more conveniently prepared from β-methylcrotonic acid by reduction with lithium aluminium hydride to 2-methylcrotyl alcohol, followed by simultaneous oxidation and condensation with acetone in the presence of aluminium *tert.*-butoxide (cf. Heilbron *et al. J.*, 1938, 175; 1949, 2031). The dienone was identified as semicarbazone and 2 : 4-dinitrophenylhydrazone.

Ultra-violet light absorption properties of substituted butadienes and butadienylcarbinols in ethanol.

	$\lambda_{max.}$, A.	$\varepsilon_{max.}$	Substitution.
$CH_2{=}CH{\cdot}CH{=}CHMe$	2235	23,000[1]	Mono
$CH_2{=}CH{\cdot}CH{=}CH{\cdot}CH_2{\cdot}OH$	2230	25,000[2]	,,
$CH_2{=}CH{\cdot}CH{=}CH{\cdot}CHMe{\cdot}OH$	2230	28,000[2]	,,
$CH_2{=}CH{\cdot}CH{=}CH{\cdot}CMe_2{\cdot}OH$ (III*a*)	2235	26,000	,,
$CHMe{=}CH{\cdot}CH{=}CHMe$	2270	22,500[1]	Di
$CHMe{=}CH{\cdot}CH{=}CH{\cdot}CMe_2{\cdot}OH$ (III*b*)	2270	26,600	,,
$Me_2C{=}CH{\cdot}CH{=}CH{\cdot}CH_2{\cdot}OH$ (IV*a*)	2360	18,700	Tri
$Me_2C{=}CH{\cdot}CH{=}CH{\cdot}CHMe{\cdot}OH$ (IV*b*)	2360	22,300	,,

[1] Booker, Evans, and Gillam, *J.*, 1940, 1453.
[2] Heilbron, Jones, McCombie, and Weedon, *J.*, 1945, 84.

The work described above shows that unsymmetrically substituted divinylcarbinols initially undergo irreversible rearrangement, the hydroxyl group migrating exclusively to the more highly substituted γ-carbon atom, and that the resulting butadienylcarbinols then undergo a further, much slower, reversible rearrangement to the primary or secondary isomers. The fact that the equilibrium mixtures formed in the latter rearrangements contain approximately equal proportions of the tertiary and primary or secondary isomers shows that, although the mobility of the five-carbon oxotropy is much smaller than that of the preceding three-carbon oxotropy, the stabilities of the two possible final products are very similar. It might, therefore, at first sight, appear somewhat surprising that the initial rearrangement should proceed exclusively in one direction. Our interpretation of these phenomena is, briefly, as follows (a more detailed discussion will be presented later in conjunction with kinetic data). The direction of the initial rearrangement will be determined by the relative ease of electron-withdrawal from the two γ-carbon atoms, because the rate-determining step involves the detachment of a water molecule at the α-carbon atom and the simultaneous migration of the double-bond electron pair from the βγ- to the αβ-position (Braude and Jones, *loc. cit.*; Braude, *J.*, 1948, 794). Methyl substituents facilitate electron-withdrawal from the carbon atom to which they are attached, and will therefore influence the relative rates of two possible rearrangements of the same carbinol in the same way as they influence the relative rates of the same rearrangement in two different carbinols. A γ-methyl substituent generally increases the rate of rearrangement by a factor of over 100; hence (III) might be expected to be formed from (I) at least 100 times faster than (IV), and, under conditions which cause the rearrangement into (III) to proceed at a measurable rate, the amount of (IV) formed will be undetectably small. The position of the equilibrium in the subsequent five-carbon oxotropy will similarly be governed by the relative rates of the opposing reactions, (III) $\longrightarrow$ (IV), and (IV) $\longrightarrow$ (III). Now, (III) and (IV) differ only in the disposition of methyl substituents on the α- and ε-carbon atoms. Quantitative data on the relative effects of α- and ε-methyl substituents are not at present available, but they may be expected to be of the same order. Therefore, the forward and backward rates of the reaction (III) $\rightleftharpoons$ (IV) will be similar, and the equilibrium will be evenly balanced. Analogous considerations will, of course, apply to the rearrangements of the lower homologue (VII) $\longrightarrow$ (VIII) $\rightleftharpoons$ (IX).

The equilibria can also be discussed from a slightly different point of view, in terms of energetic considerations (cf. Braude and Stern, *J.*, 1947, 1096; Catchpole, Hughes, and Ingold, *J.*, 1948, 16). The difference in energy levels of the unconjugated and conjugated isomers will be comparatively large (*ca.* 7 kcals./g.-mol.), corresponding to the resonance energy of the butadiene system formed in the three-carbon oxotropic rearrangement, which is therefore, for practical purposes irreversible. The difference in energy levels of the two conjugated isomers, on the other hand, will be comparatively small, corresponding only to the change in hyperconjugation energy (*ca.* 2 kcals./g.-mol.) arising from the different number of alkyl substituents directly attached to the conjugated system, and the five-carbon rearrangement is, therefore, reversible.

EXPERIMENTAL.

(M. p.s were determined on a Kofler block and are corrected.)

*Vinyl*iso*butenylcarbinol* (5-*Methylhexa*-1 : 4-*dien*-3-*ol*) (I*a*).—Acraldehyde (25 g.) in ether (75 ml.) was added dropwise to a stirred, ethereal solution of *iso*butenyl-lithium (from Li, 7 g.) at 10° (see Part I, preceding paper). After a further ½ hour's stirring at room temperature, saturated ammonium chloride solution (200 ml.) was added, and the ethereal layer was separated and dried (Na_2SO_4–K_2CO_3). The ether was removed by distillation through a column, and the residue fractionated from a trace of potassium carbonate to give *vinyl*iso*butenylcarbinol* (18 g., 36%) as a colourless liquid, b. p. 57°/8 mm., n_D^{18} 1·4614 (Found : C, 74·9; H, 10·9. $C_7H_{12}O$ requires C, 75·0; H, 10·8%). Light absorption in ethanol : $\varepsilon < 500$ in the range 2200—4000 A.

Hydrogenation of the carbinol (1·6 g.) in methanol (20 ml.) in the presence of platinic oxide and a little potassium carbonate resulted in the uptake of 2 moles of hydrogen to give ethyl*iso*butylcarbinol (1·2 g.), b. p. 100—102°/140 mm., n_D^{24} 1·4170, which was oxidised with potassium dichromate in sulphuric acid to ethyl *iso*butyl ketone, identified by the semicarbazone, m. p. 149—153° (Nazarov, *Bull. Acad. Sci. U.R.S.S.*, 1940, 545, gives m. p. 148—149°), and by the 2 : 4-dinitrophenylhydrazone, m. p. 74—76° (Allen, *J. Amer. Chem. Soc.*, 1930, **52**, 2955, gives m. p. 75°), both undepressed on admixture with authentic samples.

Dimethylbutadienylcarbinol (2-*Methylhexa*-3 : 5-*dien*-2-*ol*) (III*a*).—A solution of vinyl*iso*butenylcarbinol (9 g.) in 60% aqueous acetone (200 ml.) containing sulphuric acid (0·001M.) was set aside for 4 hours at room temperature. The solution was made just alkaline with aqueous 2N-sodium hydroxide and most of the acetone was distilled off through a column. The residue was diluted with water (50 ml.) and extracted with ether. Fractionation of the ethereal extract afforded 2-methylhexa-3 : 5-dien-2-ol (7 g.), b. p. 92—93°/85 mm., n_D^{20} 1·4758 (Found : C, 74·9; H, 11·0. Calc. for $C_7H_{12}O$: C, 75·0; H, 10·8%) (Nazarov and Fisher, *Bull. Acad. Sci. U.R.S.S., Cl. sci. chim.*, 1945, 631; 1948, 311, give b. p. 44—45°/10 mm., n_D^{20} 1·4710, 1·4760). Light absorption in ethanol : see Table.

A solution of the carbinol (1 g.) and maleic anhydride (1 g.) in benzene (10 ml.) was set aside for 3 days at room temperature. The lactonic *acid* (0·7 g.) which separated crystallised from water in needles and sublimed in plates, m. p. 204—207° (Found : C, 62·8; H, 6·8; equiv. by titration with 0·01M-KOH, 212. $C_{10}H_{13}O_2\cdot CO_2H$ requires C, 62·9; H, 6·7%; equiv., 210).

5-*Methylhexa*-2 : 4-*dien*-1-*ol* (IV*a*) *and* 2-*Methylhexa*-1 : 3 : 5-*triene* (V*a*).—(*a*) Vinyl*iso*butenylcarbinol (12 g.) was shaken for 17 hours with aqueous 0·1M-hydrochloric acid (15 ml.). The upper layer was separated and dried (Na_2SO_4–K_2CO_3). Fractionation from a trace of potassium carbonate afforded 2-methylhexa-3 : 5-dien-2-ol (5 g.), b. p. 56°/12 mm., n_D^{17} 1·4763, $\lambda_{max.}$ 2235 A., $\varepsilon = 26{,}000$, and 5-methylhexa-2 : 4-dien-1-ol (3 g.), b. p. 87°/12 mm., n_D^{17} 1·4996 (Found : C, 74·5; H, 10·8. Calc. for $C_7H_{12}O$: C, 75·0; H, 10·8%) (Nazarov and Fisher, *loc. cit.*, give b. p. 76—78°/8 mm., n_D^{20} 1·5060). Light absorption in ethanol : see Table.

(*b*) A solution of 2-methylhexa-3 : 5-dien-2-ol (6 g.) in 80% aqueous acetone (100 ml.) containing sulphuric acid (0·04M.) was allowed to stand for 5 days at room temperature. Isolation of the products as before afforded 2-methylhexa-3 : 5-dien-2-ol (2 g.), 5-methylhexa-2 : 4-dien-1-ol (2 g.), and impure 2-methylhexa-1 : 3 : 5-triene (1 g.), b. p. 48—52°/110 mm., n_D^{16} 1·5127. The triene, which rapidly polymerised, was also obtained by distilling 2-methylhexa-3 : 5-dien-2-ol from potassium hydrogen sulphate, and had light absorption in ethanol : Max. 2480, 2570, and 2670 A., $\varepsilon = 21{,}000$, 28,000, and 22,000, respectively.

*Propenyl*iso*butenylcarbinol* (2-*Methylhepta*-2 : 5-*dien*-4-*ol*) (I*b*).—Crotonaldehyde (30 g.) in ether (60 ml.) was added drop-wise to a stirred, ethereal solution of *iso*butenyl-lithium (from Li, 7 g.) at 10°. Stirring was continued at room temperature for 2 hours, and saturated aqueous ammonium chloride solution (200 ml.) was added. Isolation of the products in the usual manner afforded *propenyl*iso*butenylcarbinol* (26 g., 40%), b. p. 74°/6 mm., n_D^{21} 1·4666 (Found : C, 76·2; H, 11·1. $C_8H_{14}O$ requires C, 76·1; H, 11·2%). Light absorption in ethanol $\varepsilon < 1000$ in the range 2200—4000 A. Attempted oxidation of the carbinol by heating it with acetone and aluminium *tert.*-butoxide in benzene for 24 hours under reflux gave no significant amount of high-boiling ketonic material. Oxidation with *p*-benzoquinone is accompanied by rearrangement, giving 2-methylhepta-2 : 4-dien-6-one (see below).

*Propyl*iso*butenylcarbinol* (2-*Methylhept*-2-*en*-4-*ol*) (II*b*) *and Propyl*iso*butylcarbinol* (2-*Methylheptan*-4-*ol*).—Hydrogenation of propenyl*iso*butenylcarbinol (9 g.) in methanol (50 ml.) in the presence of platinic oxide and a trace of potassium carbonate resulted in the uptake of 1 mole of hydrogen (1760 ml. at 18°/768 mm.), to give *propyl*iso*butenylcarbinol* (8·5 g.), b. p. 73—75°/12 mm., n_D^{24} 1·4444 (Found : C, 75·0; H, 12·8. $C_8H_{16}O$ requires C, 74·9; H, 12·7%). The 3 : 5-*dinitrobenzoate* separated from pentane in colourless needles, m. p. 46—48° (Found : N, 9·0. $C_{14}H_{18}O_6N_2$ requires N, 9·0%). Ozonisation of the carbinol (1·8 g.) in acetic acid solution afforded acetone, isolated as the 2 : 4-dinitrophenylhydrazone (1·9 g.), m. p. 127—128°, undepressed on admixture with an authentic specimen but depressed to 105—112° on admixture with the propaldehyde derivative.

Hydrogenation of propenyl*iso*butenylcarbinol (1·8 g.) in methanol (30 ml.) in the presence of a 5% palladium–calcium carbonate catalyst (0·5 g.) resulted in the uptake of 1 mole of hydrogen to give propyl*iso*butylcarbinol (1 g.), b. p. 113—114°/130 mm., n_D^{23} 1·4198. An authentic specimen of the latter was prepared from *iso*valeraldehyde and *n*-propylmagnesium bromide (Muset, *Chem. Zentr.*, 1907, I, 1313, gives b. p. 160°, n_D 1·4203). Both samples gave the same 3 : 5-*dinitrobenzoate,* which crystallised from pentane in plates, m. p. 66—68° (Found : C, 54·2; H, 6·4; N, 9·0. $C_{14}H_{20}O_6N_2$ requires C, 53·8; H, 6·4; N, 9·0%).

Dimethylpentadienylcarbinol (2-*Methylhepta*-3 : 5-*dien*-2-*ol*) (III*b*).—A solution of propenyl*iso*butenylcarbinol (9 g.) in 80% aqueous acetone (200 ml.) containing sulphuric acid (0·001M.) was kept at room temperature for 10 minutes. Isolation of the product in the usual manner afforded 2-*methylhepta*-3 : 5-*dien*-2-*ol* (7 g.), b. p. 68—69°/9 mm., n_D^{17} 1·4850 (Found : C, 76·1; H, 10·8. $C_8H_{14}O$ requires C, 76·1; H, 11·2%). Light absorption in ethanol : see Table. The isomerisation could also be effected with a variety of other weakly acidic reagents, *e.g.*, dilute solutions of acetic acid, potassium dihydrogen phosphate, or quinol. No rearrangement, on the other hand, was observed on treatment with M-potassium *tert.*-butoxide in *tert.*-butanol for 24 hours at 78°.

A solution of the carbinol (1 g.) and maleic anhydride (1 g.) in benzene (3 ml.) was kept at room temperature for 6 days. The lactonic *acid* (0·7 g.) which separated crystallised from aqueous methanol as needles, m. p. 204—206° (Found : C, 64·8; H, 7·4%; equiv. by titration with 0·01M-KOH, 226. $C_{12}H_{16}O_4$ requires C, 64·3; H, 7·2%; equiv., 224).

Hydrogenation of the carbinol (2 g.) in methanol in the presence of platinic oxide resulted in the uptake of 2 moles of hydrogen to give dimethyl-*n*-amylcarbinol (1·5 g.), b. p. 74°/18 mm., n_D^{19} 1·4248. An authentic specimen of the latter, prepared from *n*-amylmagnesium bromide and acetone, had b. p. 106°/109 mm., n_D^{19} 1·4199 (Muset, *loc. cit.*, gives b. p. 162°/760 mm., n_D 1·4303). Both samples with 3 : 5-dinitrobenzoyl chloride in pyridine gave the same 3 : 5-*dinitrobenzoate,* which crystallised from pentane in needles, m. p. 47—48° (Found : C, 54·2; H, 6·5; N, 8·8. $C_{14}H_{20}O_6N_2$ requires C, 53·8; H, 6·5; N, 9·0%). Light absorption in ethanol : Max. 2260 A., ε = 27,600. The 3 : 5-dinitrobenzoate was also prepared by treating the carbinol in pyridine with 3 : 5-*dinitrobenzoyl bromide.* This bromide was obtained on treating the acid with phosphorus pentabromide and extracting the crude product with pentane in a Soxhlet apparatus. It crystallised from pentane in needles, m. p. 61—62° (Found : C, 31·2; H, 1·0; N, 10·4; Br, 29·1. $C_7H_3O_5N_2Br$ requires C, 30·6; H, 1·10; N, 10·2; Br, 29·0%).

6-*Methylhepta*-3 : 5-*dien*-2-*ol* (IV*b*) *and* 2-*Methylhepta*-1 : 3 : 5-*triene* (V*b*).—(*a*) Propenyl*iso*butenylcarbinol (10 g.) was shaken with aqueous 0·01M-hydrochloric acid for 12 hours at room temperature. Isolation of the products in the usual manner afforded a mixture (9 g.) of 2-methylhepta-3 : 5-dien-2-ol and 6-methylhepta-3 : 5-dien-2-ol. Ultra-violet light absorption data showed that the two isomers were present in approximately equal proportions ($\lambda_{max.}$ 2300 and 2360 A., ε = 22,500 and 22,500 respectively). Only partial separation was achieved on fractionation, the fraction containing the highest proportion of the secondary carbinol having b. p. 78—80°/9 mm., n_D^{18} 1·4975 (Found : C, 75·6; H, 10·6. Calc. for $C_8H_{14}O$: C, 76·1; H, 11·2%).

(*b*) A solution of 2-methylhepta-3 : 5-dien-2-ol (6 g.) in 80% aqueous acetone (100 ml.) containing sulphuric acid (0·001M.), kept at room temperature for 2 days, afforded a mixture (4 g.) of the carbinol and its secondary isomer in about equal proportions, and impure 2-methylhepta-1 : 3 : 5-triene (1 g.), b. p. 66—68°/100 mm., n_D^{16} 1·5246 (Found : C, 85·9, H, 11·8. Calc. for C_8H_{12} : C, 88·9; H, 11·2%). The triene was also obtained on distilling propenyl*iso*butenylcarbinol from potassium hydrogen sulphate. Light absorption in ethanol : Max. 2610 and 1710 A., ε = 41,000 and 31,000, respectively; inflection 2510 A., ε = 29,000.

6-*Methylhepta*-3 : 5-*dien*-2-*one* (VI*b*).—(*a*) Propenyl*iso*butenylcarbinol, or an equilibrium mixture of 2-methyl- and 6-methyl-hepta-3 : 5-dien-2-ol (see above) (5·0 g.), aluminium *tert.*-butoxide (10 g.), *p*-benzoquinone (5 g.), and benzene (50 ml.) were heated for 5 hours under reflux. The mixture was acidified with dilute sulphuric acid and extracted with ether. Fractionation of the ethereal extract afforded 6-methylhepta-3 : 5-dien-2-one, b. p. 83°/16 mm. (2 : 4-dinitrophenylhydrazone, m. p. 219—221°, undepressed on admixture with the authentic specimen described below).

(*b*) β-Methylcrotonic acid (5·5 g.) was reduced by treatment with lithium aluminium hydride (3·0 g.) in boiling ether (Nystrom and Brown, *J. Amer. Chem. Soc.*, 1947, **69**, 2548) to 2-methylcrotyl alcohol (3·8 g.), b. p. 84—86°/80 mm., n_D^{20} 1·4382 (Lennartz, *Ber.*, 1943, **78**, *B*, 841, gives b. p. 48°/11 mm., n_D^{17} 1·4420). The alcohol was heated with acetone (20 ml.), aluminium *tert.*-butoxide (8 g.), and benzene (50 ml.) for 30 hours under reflux, to give the dienone, b. p. 45°/0·3 mm., n_D^{20} 1·5278 (Kuhn and Hoffer, *Ber.*, 1932, **65**, *B*, 651, give b. p. 86—87°/15 mm., n_D^{19} 1·5292). Light absorption in ethanol: Max. 2860 A., ε = 18,000. The semicarbazone had m. p. 189—192° (Fischer and Löwenberg, *Annalen*, 1932, **494**, 263, give m. p. 192°). The 2 : 4-*dinitrophenylhydrazone* crystallised from benzene in bright red needles, m. p. 217—220° (Found : C, 55·6; H, 5·6; N, 18·6. $C_{14}H_{16}O_4N_4$ requires C, 55·3; H, 5·3; N, 18·4%). Light absorption in chloroform : Max. 2700, 3080, and 3990 A., ε = 20,000, 21,600, and 38,000 respectively; inflection 2800 A., ε = 13,500.

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