## Alkenylation with Lithium Alkenyls. Part IX.* Synthesis of Dimethylbutadienecarboxylic Acids.

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2-Hydroxy-2 : 4-dimethylpent-3-en-1-al has been prepared in high yield from *iso*butenyl-lithium and pyruvaldehyde diethyl acetal and has been converted into 2 : 4-dimethylpenta-2 : 4-dienoic acid by a variety of routes. The transformations involved, and the spectral properties of the products, are discussed.

THE aim of the work described in this paper was the synthesis of a buta-1 : 3-diene-2-carboxylic acid. Except for one cyclic derivative which has been described recently (Part VIII, Braude and Evans), diene acids of this type appear to be almost unknown, although the occurrence of such structures has been postulated in certain natural products, particularly α-longinecic and ridellic acids (Adams, Govindachari, Looker, and Edwards, *J. Amer. Chem. Soc.*, 1952, **74**, 700; Adams and Van Duuren, *ibid.*, 1953, **75**, 4638). The preparation of simple analogues and an examination of their chemical and physical properties would therefore be of interest.

A previous attempt to obtain an open-chain 1 : 3-diene-2-carboxylic acid directly from a lithium alkadienyl intermediate was unsuccessful (Part VIII, *loc. cit.*), but an alternative approach, involving the use of a more stable lithium alkenyl, appeared to be that outlined in (I) ⟶ (VI). This sequence of reactions has been carried out, but the desired product, 4 : 4-dimethylbuta-1 : 3-diene-2-carboxylic acid (VI), proved to be highly unstable and to undergo prototropic rearrangement with great ease to the isomeric 1 : 3-dimethyl-buta-1 : 3-diene-1-carboxylic acid (2 : 4-dimethylpenta-2 : 4-dienoic acid) (X).

The preparation of *iso*butenyl bromide and its conversion into *iso*but-1-enyl-lithium (I) (Braude and Timmons, Part I, *J.*, 1950, 2000; Braude and Coles, Part III, *J.*, 1950, 2012) has been simplified and considerably improved. Reaction of *tert.*-butyl alcohol with bromine gave 1 : 2-dibromo*iso*butane directly, without isolation of *iso*butene [cf. Pansevich-Kolyada and Prilezhaev, *J. Gen. Chem. (U.S.S.R.)*, 1951, **21**, 517; *Chem. Abs.*, 1951, **45**, 8442; Andrews and Keefer, *J. Amer. Chem. Soc.*, 1953, **75**, 3557]. Dehydrobromination is best effected by potassium hydroxide in ethylene glycol; after careful refractionation, the *iso*butenyl bromide obtained in this way attacks lithium in ether exothermally after an induction period of only a few minutes, in contrast to the rather sluggish reaction observed previously (Parts I and III, *loc. cit.*; Braude and Timmons, *J.*, 1953, 3131). This is undoubtedly due to the fact that the present procedure gives the bromide in an even higher state of purity, and further illustrates the effect, previously noted, of minute traces of impurities on the metallation reaction. In a recent series of papers, Normant (*Compt. rend.*,

1954, **239**, 1510, 1811; 1955, **240**, 314, 440, 631, 1111) has reported that vinyl halides can be converted into Grignard reagents in high yields in tetrahydrofuran, though few details are disclosed. In our hands, *iso*butenyl bromide failed to react with magnesium under such conditions, in agreement with previous experience (Part I, *loc. cit.*). Addition of *iso*butenyl-lithium to pyruvaldehyde diethyl acetal (II) afforded the hydroxy-acetal (III; R = Et); the yield (64%) was considerably higher than those achieved earlier with this lithium alkenyl and the extent of the Wurtz side-reaction giving tetramethylbutadiene was considerably reduced. Rather lower yields of the hydroxy-acetal (III; R = Me) were obtained from pyruvaldehyde dimethyl acetal.
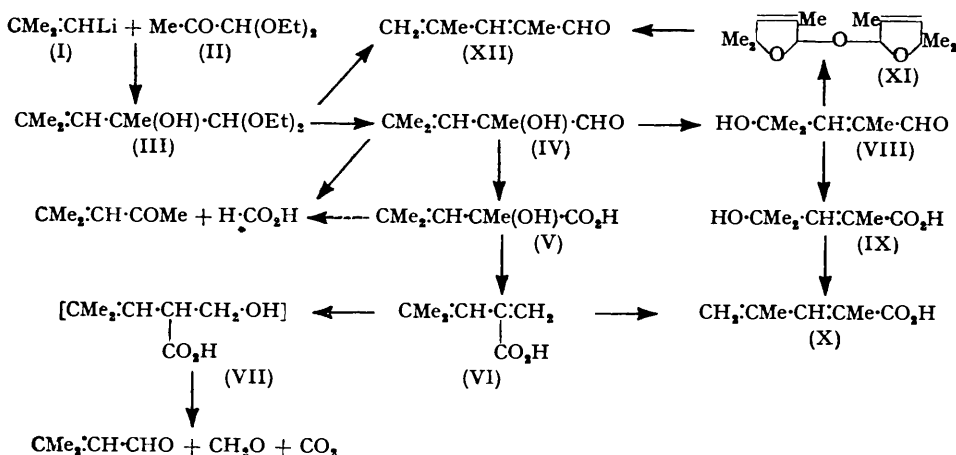


Preliminary experiments showed that the hydroxy-acetals (III) and their hydrolysis products were very much more sensitive to acid treatment than the corresponding ketal prepared from diacetyl monoketal (Braude and Timmons, 1953, *loc. cit.*). By treatment with 2% aqueous tartaric acid at room temperature under carefully controlled conditions (cf. Lunt and Sondheimer, *J.*, 1950, 3361), the hydroxy-aldehyde (IV) was, however, obtained in excellent yield (93%). It exhibited ultraviolet-light absorption characteristic of an α-hydroxy-aldehyde group ($\lambda_{max.}$ 2830 Å, ε 65), but failed to give a semicarbazone, and no 2 : 4-dinitrophenylhydrazone was formed in pyridine solution, in contrast to the behaviour of the corresponding methyl ketone (Braude and Timmons, 1953, *loc. cit.*). Treatment with Brady's reagent gave the derivative of the isomeric aldehyde (VIII) (see below).

Oxidation of the hydroxy-aldehyde (IV) with silver oxide (cf. Kuhn and Trischmann, *Annalen*, 1951, **573**, 58) furnished the hydroxy-acid (V), together with mesityl oxide and ββ-dimethylacraldehyde, isolated and identified as the 2 : 4-dinitrophenylhydrazones, as well as formic acid. The hydroxy-acid (V) itself is very unstable and could not be obtained pure, but was converted into the methyl ester with diazomethane. The mesityl oxide and formic acid are probably derived from the hydroxy-aldehyde (IV) by reverse aldol reaction and subsequent oxidation of the formaldehyde; this would be analogous to the ready decomposition of mandelaldehyde, Ph·CH(OH)·CHO, into benzaldehyde and formaldehyde (Rinkes, *Rec. Trav. chim.*, 1920, **39**, 709; Marshall and Walker, *J.*, 1952, 467) and of diphenylglycollaldehyde, $Ph_2C(OH)\cdot CHO$, into benzophenone and formaldehyde (Danilow, *Ber.*, 1927, **60**, 2390; 1929, **62**, 2653; cf. McElvain, Mirviss, and Stevens, *J. Amer. Chem. Soc.*, 1951, **73**, 3807). Alternatively, mesityl oxide may be formed by direct fission of the hydroxy-acid (V), similarly to the decomposition of mandelic acid, Ph·CH(OH)·CO₂H, into benzaldehyde and formic acid (Biedermann, *Ber.*, 1886, **19**, 638).

The dimethylacraldehyde, on the other hand, presumably arises through dehydration of the hydroxy-acid (V) to the desired diene acid (VI), followed by hydration of the vinyl grouping in the latter and reversed aldol reaction and decarboxylation of the resulting

isomeric hydroxy-acid (VII). An attempt to prepare the ethyl ester of the acid (V) directly by the action of *iso*butenyl-lithium upon ethyl pyruvate gave a mixture of products which could not be separated satisfactorily.

The methyl ester of the hydroxy-acid (V) proved remarkably resistant to dehydration. Mainly unchanged ester was recovered after heating with potassium hydrogen sulphate or iodine, but dehydration could be effected by naphthalene-2-sulphonic acid at 130—140°. The ultraviolet-light absorption ($\lambda_{max.}$ 2560 Å, $\varepsilon$ 11,000) of the product was not incompatible with that expected for the methyl ester of the desired diene acid (VI). However, ozonolysis afforded only a trace of acetone, together with formaldehyde, indicating that rearrangement to the ester of the isomeric diene acid (X) had taken place.

Attempts to dehydrate the methyl ester of (V) under conditions which might be less conducive to isomerisation were unsuccessful; thus treatment with thionyl chloride in pyridine or with phosphoric oxide and triethylamine in benzene (cf. McElvain and Clarke, *J. Amer. Chem. Soc.*, 1947, **69**, 2657) gave mixtures containing unchanged starting material and the methyl ester of (X). Other, more regulated routes to the acid (X) are described below. The formation of the diene-acid (X) from the hydroxy-acid (V) could theoretically proceed along either of two paths, anionotropic rearrangement to the conjugated hydroxy-acid (IX) followed by dehydration, or dehydration to the diene acid (VI), followed by prototropic rearrangement. Acid conditions would normally favour anionotropic rearrangement, but the anionotropic mobility of the acid (V) would, by analogy with 2-hydroxypent-3-enoic acid (Fittig, *Annalen*, 1898, **299**, 37; Braude, *Quart. Rev.*, 1950, **4**, 404), be expected to be low. This makes the path (V) —→ (IX) —→ (X) less likely, and confirmation was obtained by examining the effect of acid treatment on (V) spectro-metrically; the absorption maximum at 2170 Å characteristic of (IX) could not be detected under conditions under which (X) is produced. On the other hand, ethylenic acids and esters are well known to possess high prototropic mobility (Linstead and Noble, *J.*, 1934, 614, and earlier papers) and, although protropy is usually catalysed by bases, acid-catalysed prototropy has been observed to occur in preference to anionotropy in other systems containing strongly electron-attracting substituents (Braude, *loc. cit.*). Thus, the path (V) —→ (VI) —→ (X) is the more probable one. The apparently ready conversion of (VI) into (X) is not unexpected; although the extent of hyperconjugation in the two isomeric diene-acids will not be very different, the isomer (VI) will be the less stable in virtue of its " cross "-conjugated system, as compared with the " straight "-conjugated system in (X). Thus, the present results suggest that a 1 : 3-diene-2-carboxylic acid system is unlikely to survive unless isomerisation to a 1 : 3-diene-1-carboxylic acid system is structurally precluded.

The hydroxy-aldehyde (IV), like the hydroxy-acid (V), represents a potential aniono-tropic system, though of a little studied type. The only example analogous to (IV) is the corresponding methyl ketone whose aniontropic mobility was found to be exceptionally low owing to the strong electron-attracting properties of the acetyl group (Braude and Timmons, 1953, *loc. cit.*). With aqueous acids as catalysts, the aldehyde (IV) undergoes rearrangement very much more readily, being converted into the conjugated isomer (VIII) by 2% tartaric acid at room temperature, whereas 2% sulphuric acid at 80° was employed for the ketone. Since a formyl group would be expected, and has in other cases been found, to be *more* electron-attracting than an acetyl group (cf. Burkhardt, Horrex, and Jenkins, *J.*, 1936, 1654), the anionotropic mobility of the aldehyde (IV) would be expected to be *smaller* than that of the corresponding methyl ketone. It is possible that the reverse relation indicated by the preparative experiments under heterogeneous conditions is only apparent and due to the greater water-solubility of the aldehyde; further discussion of this point is therefore deferred until kinetic data for homogeneous media have been determined.

The hydroxy-aldehyde (VIII) showed light absorption typical of the conjugated enal system ($\lambda_{max.}$ 2270 Å). It was characterised by a crystalline 3 : 5-dinitrobenzoate and gave the 2 : 4-dinitrophenylhydrazone of its methyl ether on treatment with methanolic Brady's reagent; the same derivative is obtained from the aldehyde (IV) under these conditions. When either the hydroxy-aldehyde (IV) or the starting acetal (III) was subjected to more

strongly acid conditions, *e.g.*, dilute sulphuric acid, the yields of the rearranged hydroxy-aldehyde (VIII) were much reduced and cyclisation and etherification to give the self-ether of 5-hydroxy-2 : 2 : 4-trimethyl-2 : 5-dihydrofuran (XI) occurred. Analogous changes have been observed with other $\gamma$-hydroxy-$\alpha\beta$-ethylenic aldehydes and ketones (Braude and Timmons, 1953, *loc. cit.*). On treatment with 85% phosphoric acid, the ether underwent fission and dehydration to the diene aldehyde (XII) ($\lambda_{max.}$ 2650 Å), characterised by a 2 : 4-dinitrophenylhydrazone ($\lambda_{max.}$ 3950 Å). This diene aldehyde was also obtained by direct pyrolysis of the acetal (III) over aluminium phosphate at 310°. Attempted dehydration of the acetal under milder conditions, *e.g.*, with potassium hydrogen sulphate alumina at 100°, resulted in difficultly separable mixtures of dehydration, hydrolysis, and rearrangement products.

Oxidation of the rearranged hydroxy-aldehyde (VIII) with silver oxide furnished the rearranged hydroxy-acid (IX), which was isolated as the methyl ester after treatment with diazomethane. Dehydration of the ester with naphthalene-2-sulphonic acid gave methyl 2 : 4-dimethylpenta-2 : 4-dienoate, identical in physical properties with that obtained
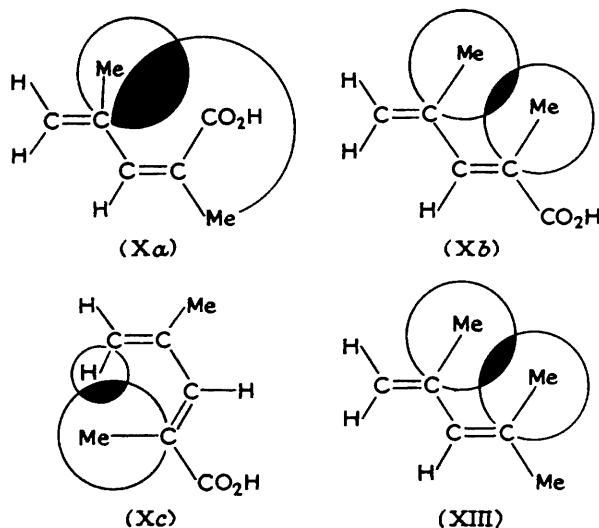


from the hydroxy-acid (V) but giving only formaldehyde on ozonolysis. Alkaline hydrolysis of both samples of ester yielded the free acid as a high-boiling liquid, which gave a crystalline benzylamine salt having an unusual composition in that it contained the acid and amine in the proportion 2 : 1. The ultraviolet and infrared absorption properties of 2 : 4-dimethyl-penta-2 : 4-dienoic acid and its methyl ester ($\lambda_{max.}$ 2560 Å, $\varepsilon$ 12,500 in ethanol) resemble those of sorbic acid and methyl sorbate ($\lambda_{max.}$ 2580 Å, $\varepsilon$ 27,000) as far as the location of the maxima are concerned, but the intensity of the triple chromophore band near 2650 Å is reduced to less than half. This is undoubtedly to be ascribed to the hindrance to uni-planarity in either of the two possible geometrical configurations (X*a*) and (X*b*). Configuration (X*b*), which is the more probable, could adopt either the hindered *s-trans*-conformation shown or the less hindered *s-cis*-conformation (X*c*).* In (X*b*), $\varepsilon$ will be reduced relatively to sorbic acid in which the analogous conformation is unhindered, owing to non-planarity of the conjugated system, while in (X*c*) $\varepsilon$ will be reduced owing to the decreased effective length of the chromophore (cf. Braude and Waight, " Progress in Stereochemistry," Ed. W. Klyne, Butterworths, London, 1954). The extent of steric overlap in (X*b*) is identical with that in the *s-trans*-conformation of 1 : 1 : 3-tri-methylbutadiene (XIII) and it is interesting that the reduction in $\varepsilon$ in the hindered diene

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* We use the term " configuration " in connexion with geometrical isomerism about conventional double bonds, and the term " conformation " in connexion with rotational isomerism about conventional single bonds in acyclic systems.

($\epsilon/\epsilon_0 = 8500/23,000 = 0.37$) is quite similar to that in the hindered diene acid ($\epsilon/\epsilon_0 = 12,500/27,000 = 0.46$). The mean interplanar angles $\theta$ between the two ethylenic groups in the ground states, calculated from the equation $\cos^2 \theta = \epsilon/\epsilon_0$ (cf. Braude, Sondheimer, and Forbes, *Nature*, 1954, **173**, 117), are 52° and 47°, respectively.

## EXPERIMENTAL

M. p.s were taken on a Kofler block and are corrected. Analytical data were determined by Mr. F. H. Oliver and the staff of the micro-analytical laboratory of this Department. Ultra-violet spectra were determined by Mrs. A. I. Boston using Hilger-Spekker and Unicam instruments. Infrared spectra were determined by R. L. Erskine using a Grubb-Parsons double beam instrument. Microhydrogenations were carried out with platinic oxide in acetic acid.

*isoButenyl Bromide.*—Bromine (2150 g.) was added dropwise to *tert.*-butyl alcohol (1 kg.), heated under reflux on a steam-bath. After an induction period of a few minutes, the bromine was rapidly decolorised and the rate of addition was adjusted to keep the exothermic reaction under control. After cooling, the top layer (consisting mostly of unchanged alcohol and water) was separated and discarded and the lower layer was washed with water, dried (CaCl$_2$), and distilled once through an 8″ Dufton column, giving 1 : 2-dibromo*iso*butane (2000 g.), b. p. 38—42°/10 mm., $n_D^{23}$ 1·5035—1·5075, which was sufficiently pure for the next stage.

The dibromide (1500 g.) was added dropwise to a stirred mixture of potassium hydroxide (500 g.) in ethylene glycol (1300 ml.) in a 3-necked copper flask which was immersed in an oil-bath at 125—130°. *iso*Butenyl bromide (490 g., 36% based on *tert.*-butyl alcohol) distilled and was collected, washed with 5% potassium hydroxide (100 ml.) and water (3 × 250 ml.), dried (CaCl$_2$), and fractionated from a small piece of sodium through an 8″ Dufton column. It was re-distilled from sodium immediately before use and had b. p. 92°/760 mm., $n_D^{24}$ 1·4615 (Braude and Timmons, *J.*, 1950, 2000, give $n_D^{21}$ 1·4603; Braude and Coles, *J.*, 1950, 2012, give $n_D^{22}$ 1·4610).

*Pyruvaldehyde Diethyl Acetal* (1 : 1-*Diethoxyacetone*).—Commercial pyruvaldehyde (300 ml.; 30% aqueous solution), ethanol (550 ml.), benzene (550 ml.), and concentrated sulphuric acid were heated under partial reflux for 24 hr., water (330 ml.) being removed azeotropically. The residue was neutralised with solid potassium hydroxide and fractionated, giving the acetal (80 g.) as a very pale yellow liquid, b. p. 52°/11 mm., 47°/7 mm., $n_D^{24}$ 1·4045, $\lambda_{max.}$ 2880 Å, $\epsilon$ 36 in hexane (Found : C, 56·4; H, 9·5. Calc. for C$_7$H$_{14}$O$_3$ : C, 57·5; H, 9·65%) (Wohl and Lange, *Ber.*, 1908, **41**, 3612, give b. p. 54°/14 mm.; Dakin and Dudley, *J.*, 1914, **105**, 2453, give b. p. 58°/24 mm.).

The corresponding dimethyl acetal, b. p. 40°/10 mm., $n_D^{24}$ 1·4480, was prepared similarly, but in lower yield and admixed with unchanged aldehyde.

1 : 1-*Diethoxy*-2 : 4-*dimethylpent-3-en-2-ol* (III).—*iso*Butenyl bromide (81 g.) in ether (200 ml.) was added dropwise to a stirred suspension of finely cut lithium (8·3 g.) in ether (800 ml.), under nitrogen. Reaction set in after *ca.* 5 min., and the ether refluxed without external heating. Metallation was complete after 4 hr. Pyruvaldehyde diethyl acetal (45 g.) in ether (100 ml.) was then added and stirring was continued overnight. After cooling to 0°, saturated aqueous ammonium chloride (500 ml.) was added and the ethereal layer was separated, washed with water, dried (Na$_2$SO$_4$), and fractionated, giving (i) tetramethylbutadiene (6 g.), b. p. 28°/10 mm., $n_D^{22}$ 1·4662, and (ii) 1 : 1-*diethoxy*-2 : 4-*dimethylpent-3-en-2-ol* (40 g., 64% based on acetal), b. p. 46°/0·2 mm., $n_D^{22}$ 1·4411 (Found : C, 65·4; H, 11·0. C$_{11}$H$_{22}$O$_3$ requires C, 65·3, H, 11·0%). It showed no light absorption with $\epsilon > 100$ in the 2000—4000 Å range.

The corresponding dimethyl acetal analogous to (III) was obtained under similar conditions in only 10% yield and impure.

No reaction occurred between *iso*butenyl bromide (13·5 g.) and magnesium (2·4 g.) in tetra-hydrofuran (200 ml.) even after addition of iodine (20 mg.) and ethyl bromide (0·5 g.) and re-fluxing for 24 hr. (cf. Normant, *Compt. rend.*, 1954, **239**, 1510; 1955, **240**, 316, 440); practically all the metal was recovered unchanged.

2-*Hydroxy*-2 : 4-*dimethylpent-3-en-1-al* (IV) *and* 4-*Hydroxy*-2 : 4-*dimethylpent-2-en-1-al* (VIII).—(*a*) A mixture of the foregoing ethyl acetal (10 g.) and 2% aqueous tartaric acid (200 ml.) was shaken for 14 hr. at 20°. The product was isolated with ether and fractionated, giving 2-*hydroxy*-2 : 4-*dimethylpent-3-en-1-al* (6 g., 93%), b. p. 80°/11 mm., $n_D^{21}$ 1·4515, $\lambda_{max.}$ 2830 Å, $\epsilon$ 65 in hexane (Found : C, 65·8; H, 9·3. C$_7$H$_{12}$O$_2$ requires C, 65·6; H, 9·4%). The 3 : 5-*dinitrobenzoate*, prepared in pyridine–light petroleum, crystallised from light petroleum (b. p. 40—60°) (CO$_2$-methanol bath) as plates, m. p. 104°, $\lambda_{max.}$ 2280 ($\epsilon$ 23,000) and 2540 Å

(ε 8000) in EtOH (Found : C, 52·5; H, 4·6; N, 8·6. $C_{14}H_{14}O_7N_2$ requires C, 52·2; H, 4·4; N, 8·7%). The aldehyde did not form a semicarbazone under the usual conditions, or a 2 : 4-dinitrophenylhydrazone in boiling pyridine. On treatment with 2 : 4-dinitrophenylhydrazine in methanolic sulphuric acid, the derivative of 4-methoxy-2 : 4-dimethylpent-2-en-1-al (m. p. 160°, undepressed on admixture with the sample described below) was obtained.

(*b*) A mixture of the acetal (10 g.) and 2% aqueous tartaric acid (200 ml.) was shaken for 20 hr. at 20°. Isolation of the products as above and fractionation gave (i) 2-hydroxy-2 : 4-dimethylpent-3-en-1-al (4 g., 62%), b. p. 72°/8 mm., $n_D^{23}$ 1·4502, $\lambda_{max.}$ 2830 Å (ε 65) in hexane (3 : 5-dinitrobenzoate, m. p. 103°, undepressed on admixture with the specimen described above), and (ii) *4-hydroxy-2 : 4-dimethylpent-2-en-1-al* (2 g., 31%), b. p. 102°/10 mm., 61°/0·5 mm., $n_D^{25}$ 1·4651, $\lambda_{max.}$ 2270 Å, ε 9000 in hexane (Found : C, 66·2; H, 9·5. $C_7H_{12}O_2$ requires C, 65·6; H, 9·4%). On treatment with 2 : 4-dinitrophenylhydrazine in methanol–sulphuric acid, the aldehyde gave *4-methoxy-2 : 4-dimethylpent-2-en-1-al 2 : 4-dinitrophenylhydrazone* which crystallised from methanol–ethyl acetate in orange needles, m. p. 161°, $\lambda_{max.}$ 3860 Å, ε 28,000 in $CHCl_3$ (Found : C, 52·0; H, 5·7; N, 17·5. $C_{14}H_{18}O_5N_4$ requires C, 52·2; H, 5·6; N, 17·4%).

The proportions of the two aldehydes formed are very sensitive to the conditions. The results of other experiments with aqueous tartaric acid are summarised in the Table; they indicate that the hydrolysis of the acetal to the aldehyde (IV) is faster than the subsequent

| Acid concn. (% w/v) ......... | 1 | 2 | 2 | 2 | 2 | 2 | 5 | 6 |
|---|---|---|---|---|---|---|---|---|
| Time (hr.) .......................... | 35 | 14 | 15·5 | 17 | 20 | 30 | 20 | 48 |
| Aldehyde (IV), yield (%) ... | 66 | 93 | 79 | 62 | 62 | 47 | 62 | 45 |
| Aldehyde (VIII), yield (%) | 12 | <5 | 16 | 31 | 31 | 35 | 31 | 34 |

rearrangement of the latter to the aldehyde (VIII). In each case, the acetal was shaken with 10—20 ml. of acid at room temperature (20—22°).

(*c*) The acetal (10 g.) and 2% (v/v) sulphuric acid (100 ml.) were shaken together for 24 hr. at 20°. Isolation of the product as above and fractionation gave impure aldehyde (IV) (2·1 g., 34%), b. p. 78—84°/30 mm., $n_D^{24}$ 1·4542, and the aldehyde (VIII) (4·2 g., 68%), b. p. 80—82°/20 mm., $n_D^{24}$ 1·4592.

A similar experiment with 2% (v/v) sulphuric acid for 8 hr. gave 32% of aldehyde (IV) and 16% of aldehyde (VIII), while with 0·2% (v/v) acid for 24 hr. 25% of each aldehyde was obtained.

*2 : 4-Dimethylpenta-2 : 4-dien-1-al* (XII).—(*a*) 1 : 1-Diethoxy-2 : 4-dimethylpent-3-en-2-ol (5 g.) and 4% (v/v) sulphuric acid (200 ml.) were kept at 65° for 26 hr. The products were isolated by extraction with ether and fractionated, giving a mixture of low-boiling materials and then *di-(3 : 5 : 5-trimethyl-2 : 5-dihydro-2-furyl) ether* (?) (XI) (1·6 g.), b. p. 74°/10⁻² mm., $n_D^{24}$ 1·4778 (Found : C, 70·3; H, 9·35; *M*, in camphor 233. $C_{14}H_{22}O_3$ requires C, 70·55; H, 9·3%; *M*, 238), which gave no precipitate with Brady's reagent in the cold. The ether (XI) was steam-distilled with 85% phosphoric acid (4 ml.), and the distillate (150 ml.) treated with Brady's reagent. The oily derivative formed was extracted with benzene, chromatographed on alumina in benzene–chloroform, and crystallised from ethyl acetate-methanol, giving plates (30 mg.), m. p. 199°, undepressed on admixture with the sample described below.

(*b*) The acetal (III) (4 g.) was passed during 1 hr. through a tube packed with porous tile impregnated with aluminium phosphate at 300—310°/10 mm. (cf. Heilbron, Jones, and Richardson, *J.*, 1949, 287; Leese and Raphael, *J.*, 1950, 2725). The products were collected in a trap at 0° and extracted with ether. The ether extract, which gave a deep colour with Schiff's reagent, was dried ($Na_2SO_4$) and fractionated, and fractions (2·9 g.) with b. p. 65—75°/10 mm., $n_D^{24}$ 1·4482—1·4488, $\lambda_{max.}$ 2650 Å ($E_{1\ cm.}^{1\%}$ 250—300) were treated with Brady's reagent, giving *2 : 4-dimethylpenta-2 : 4-dien-1-al 2 : 4-dinitrophenylhydrazone* which after chromatography on alumina in benzene–chloroform crystallised from ethyl acetate–methanol in red plates, m. p. 199°, $\lambda_{max.}$ 3950 Å (ε 32,000 in $CHCl_3$) (Found : N, 19·2. $C_{13}H_{14}O_4N_4$ requires N, 19·3%).

(*c*) The acetal (III) (1·0 g.) was treated with a mixture (0·3 g.) of potassium hydrogen sulphate and alumina for 30 min. at 100°/11 mm. Distillation gave a mixture, b. p. 68—78°/11 mm., $n_D^{23}$ 1·450—1·454, which could not be separated and was treated with Brady's reagent. The resulting red oil was chromatographed, giving : (i) 4-methoxy-2 : 4-dimethylpenta-2 : 4-dien-1-al 2 : 4-dinitrophenylhydrazone, which crystallised from methanol in orange needles, m. p. 161—162°, undepressed on admixture with the sample described above; and (ii) a *2 : 4-dinitrophenyl-hydrazone* which crystallised from methanol–ethyl acetate in red needles, m. p. 171°, $\lambda_{max.}$ 3900 Å (ε 25,000 in $CHCl_3$) (Found : C, 53·5; H, 4·8; N, 19·0. $C_{13}H_{14}O_4N_4$ requires C, 53·8;

H, 4·9; N, 19·3%). The latter may be either a stereoisomer of the derivative, m. p. 199°, described above, or possibly the derivative of 4-formyl-2-methylpenta-2 : 4-diene.

Unchanged acetal was recovered from a similar experiment with alumina alone.

*2-Hydroxy-2 : 4-dimethylpent-3-enoic Acid* (V).—A solution of the aldehyde (IV) (7 g.) and silver nitrate (20 g.) in water (60 ml.) and methanol (50 ml.) was treated dropwise with aqueous 15% potassium hydroxide (100 ml.), with stirring. Stirring was continued for 1 hr. after heat evolution had ceased, the mixture was then made alkaline to phenolphthalein and filtered, and the solution (A) extracted with ether. Evaporation of the ethereal extract (B) and treatment with Brady's reagent gave the 2 : 4-dinitrophenylhydrazone of ββ-dimethylacraldehyde (0·2 g.), which crystallised from ethyl acetate in red needles, m. p. and mixed m. p. 183°, $\lambda_{max.}$ 3860 Å (ε 28,000 in $CHCl_3$) (Found : C, 50·3; H, 4·7; N, 21·0. Calc. for $C_{11}H_{12}O_4N_4$ : C, 50·0; H, 4·6; N, 21·2%). The aqueous solution (A) was acidified with hydrochloric acid at 0° and extracted with ether (5 × 50 ml.). The ethereal solution was dried ($Na_2SO_4$) and treated with a slight excess of diazomethane in ether. The solvent was removed under reduced pressure and the residue was fractionated, giving (i) a mixture (0·6 g.), b. p. 112°/500 mm., of diacetone alcohol and mesityl oxide (2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 202°, $\lambda_{max.}$ 3860 Å, ε 24,000 in $CHCl_3$), and (ii) *methyl 2-hydroxy-2 : 4-dimethylpent-3-enoate* (1·1 g.), b. p. 76—78°/10 mm., 45°/0·3 mm., $n_D^{23}$ 1·4445 (Found : C, 61·1; H, 9·0. $C_8H_{14}O_3$ requires C, 60·7; H, 8·9%). The ester showed no absorption with ε > 100 between 2200 and 4000 Å in ethanol, or after being kept in alcoholic 0·1m-hydrogen chloride for 72 hr. When heated at 80° for 5 hr. the latter solution showed $\lambda_{max.}$ 2580 Å (ε 6500), indicating incomplete dehydration.

*4-Hydroxy-2 : 4-dimethylpent-2-enoic Acid* (IX).—4-Hydroxy-2 : 4-dimethylpent-2-en-1-al (7 g.) was oxidised with silver oxide, and the products were worked up as above, giving the *methyl ester* (2·5 g.), b. p. 63°/0·2 mm., $n_D^{21}$ 1·4627, $\lambda_{max.}$ 2170 Å (ε 8500 in EtOH) (Found : C, 61·0; H, 9·1. $C_8H_{14}O_3$ requires C, 60·7; H, 8·9%). No aldehydic or ketonic by-products were obtained in this case.

*2 : 4-Dimethylpenta-2 : 4-dienoic Acid* (X).—(a) The foregoing methyl ester (1 g.) was heated with naphthalene-2-sulphonic acid (20 mg.) for 10 min. at 130°/100 mm., and then distilled slowly at 10 mm. Redistillation from a trace of naphthalenesulphonic acid gave *methyl 2 : 4-dimethylpenta-2 : 4-dienoate* (0·7 g., 79%), b. p. 59°/8 mm., $n_D^{23}$ 1·4758 (Found : C, 68·4; H, 8·7. $C_8H_{12}O_2$ requires C, 68·5; H, 8·6%). Ultraviolet absorption : $\lambda_{max.}$ 2560 (ε 12,500 in EtOH), 2540 Å (ε 11,500 in hexane). Infrared max. (in 0·5% $CS_2$ solution, 0·05-cm. cell, apparent ε values in parentheses) : 1713 (610, C=O stretching), 1629 (95, C=C stretching), 1274, 1239 (390, 480, C—O stretching), 899, 753 (200, 130, C—H bending), and 1117 cm.$^{-1}$ (420; an unassigned band in this region has been observed in other αβ-ethylenic esters; cf. Bellamy, " The Infrared Spectra of Complex Molecules," Methuen, London, 1954). Methyl sorbate exhibits bands of comparable intensity at 1716, 1642, 1242, 1137, 889, and 796 cm.$^{-1}$. Ozonolysis of the ester (510 mg.) in acetic acid yielded only formaldehyde, isolated as the dimedone derivative (600 mg.), m. p. 189°.

The ester (450 mg.) was treated under reflux with 15% aqueous potassium hydroxide (10 ml.) for 2 hr. under nitrogen. The solution was extracted with ether to remove non-acidic products, acidified with hydrochloric acid, and then extracted again with ether. The ether extract was dried ($Na_2SO_4$) and evaporated, leaving a gum which could not be crystallised and was distilled, giving the *acid* (200 mg.), b. p. 45—55° (bath-temp.)/10$^{-4}$ mm., $n_D^{25}$ 1·4975, $\lambda_{max.}$ 2540 (ε 11,000 in EtOH), 2460 Å (ε 10,000 in ethanolic 0·1m-potassium hydroxide) (Found : C, 66·5; H, 8·3%; equiv., 134. $C_7H_{10}O_2$ requires C, 66·7; H, 8·0%; *M*, 126. Microhydrogenation no., found 66; requires 63).

The *benzylamine salt*, prepared in and crystallised from ethanol, formed needles, m. p. 110°, $\lambda_{max.}$ 2560 Å (ε 22,600 in EtOH) (Found : C, 69·9; H, 8·6; N, 3·9. $2C_7H_{10}O_2,C_7H_9N$ requires C, 70·2; H, 8·1; N, 3·9%).

(b) Methyl 2-hydroxy-2 : 4-dimethylpent-3-enoate (3 g.) was dehydrated with naphthalene-2-sulphonic acid as above, giving methyl 2 : 4-dimethyl-2 : 4-pentadienoate (probably admixed with a trace of methyl 4-methylpenta-1 : 3-diene-2-carboxylate) (1·8 g.), b. p. 97°/55 mm., 60°/8 mm., $n_D^{25}$ 1·4715, $\lambda_{max.}$ 2560 (ε 11,500 in EtOH) (Found : C, 68·0; H, 8·6%). The main bands in the infrared spectrum were identical with those reported under (a), but there was some additional low-intensity absorption in the 1400—1500 Å region. Ozonolysis of the ester (340 mg.) in acetic acid gave formaldehyde, as the dimedone derivative (430 mg.), m. p. 189°, and a trace of acetone, isolated as the 2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 122°. Alkaline hydrolysis of the ester (200 mg.) as above gave 2 : 4-dimethylpenta-2 : 4-dienoic acid (80 mg.), b. p. 45—50° (bath-temp.)/10$^{-4}$ mm., $n_D^{21}$ 1·5018, $\lambda_{max.}$ 2550 Å (ε 11,000 in EtOH)

(Found : C, 66·6; H, 8·3%). The benzylamine salt had m. p. 110°, undepressed on admixture with the specimen obtained as in (*a*).

(*c*) Methyl 2-hydroxy-2 : 4-dimethylpent-3-enoate (1 g.) was added to a mixture of phosphoric oxide (2 g.), triethylamine (2 ml.), and benzene (3 ml.) which was then refluxed for 30 min. (bath-temp. 100—110°) under nitrogen. After cooling, the liquid was decanted and the solid washed with ether (5 ml.). The liquid products and ether extract were combined and fractionated, giving methyl 2 : 4-dimethylpentadienoate, b. p. 83°/17 mm., $n_D^{22}$ 1·4705, $\lambda_{max.}$ 2570 (ε 9000 in EtOH).

*Reaction of* iso*Butenyl-lithium with Ethyl Pyruvate.*—*iso*Butenyl-lithium (from Li, 4·14 g., and *iso*butenyl bromide, 40·5 g.) in ether (800 ml.) was added to a stirred solution of ethyl pyruvate (11·6 g.) in ether (50 ml.) at 0° under nitrogen. Stirring was continued for 2 hr. at room temp. and saturated aqueous ammonium chloride (300 ml.) was then added. The ether layer was separated, dried ($Na_2SO_4$–$K_2CO_3$) and distilled, giving the following main fractions : (i) (4 g.) b. p. 30—35°/11 mm., $n_D^{22}$ 1·467, consisting mainly of tetramethylbutadiene; (ii) (3·5 g.) b. p. 38—40°/10$^{-3}$ mm., $n_D^{22}$ 1·462, $\lambda_{max.}$ 2280 ($E_{1\,cm.}^{1\%}$ 230) and 2560 Å ($E_{1\,cm.}^{1\%}$ 120 in EtOH) (Found : C, 72·85; H, 11·0. Calc. for $C_{12}H_{22}O_2$ : C, 72·7; H, 11·2%); (iii) (3·5 g.) b. p. 66—70° (bath-temp.)/10$^{-4}$ mm., $n_D^{20}$ 1·492, $\lambda_{max.}$ 2280 ($E_{1\,cm.}^{1\%}$ 200) and 2560 Å ($E_{1\,cm.}^{1\%}$ 140) (Found : C, 68·0; H, 9·2. Calc. for $C_{12}H_{20}O_3$ : C, 67·6; H, 9·4%); and (iv) higher-boiling products, similar in composition and light absorption to (iii). Fraction (iii) was refluxed with aqueous-methanolic potassium hydroxide for 2 hr. and the non-acidic products were isolated with ether, giving a colourless *compound* which after sublimation at 70°/10$^{-5}$ mm. had m. p. 88—90°, $\lambda_{max.}$ 2850 Å ($E_{1\,cm.}^{1\%}$ 80 in EtOH) (Found : C, 65·9; H, 9·1. $C_7H_{12}O_2$ requires C, 65·7; H, 9·3%), and was not further investigated.

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