22. *Studies in the Polyene Series. Part XIX. The Semihydrogenation of Ethynylcarbinols derived from αβ-Unsaturated Aldehydes, and the Anionotropic Rearrangements of the Resulting Vinylcarbinols.**

By I. M. HEILBRON, E. R. H. JONES, J. T. McCOMBIE, and B. C. L. WEEDON.

Partial hydrogenation of the acetylenic linkage of propenylethynylcarbinol (I) and of two related ethynylcarbinols proceeds smoothly with a 0·3% palladium–calcium carbonate catalyst. The resulting vinylcarbinols are much more readily isomerised by acids than the parent ethynylcarbinols; for instance, whereas vinylethynylcarbinol is unaffected by 25% sulphuric acid, divinylcarbinol is isomerised merely by shaking with 1% acid at room temperature. The butadienylcarbinols (VI, VII, and VIII) resulting from these rearrangements exhibit ultra-violet absorption characteristic of conjugated dienes, and although they add readily to maleic anhydride they give rise to lactonic acids (*e.g.*, X), containing a highly stable lactone ring.

The electron-repelling properties of the methyl group appear to be of paramount importance in determining the nature of the isomerisation product of propenylvinylcarbinol, which is shown to be the secondary alcohol, hexa-3 : 5-dien-2-ol (VI), since it yields methylbutylcarbinol on complete hydrogenation. The rearrangement of divinylcarbinol is unambiguous, and that of *iso*propenylvinylcarbinol probably leads to 2-methylpenta-2 : 4-dien-1-ol (VIII).

THE partial reduction of acetylenic linkages has been extensively investigated, particularly during the past twenty years, and Campbell and Campbell (*Chem. Reviews*, 1942, **31**, 77) have surveyed the catalytic, chemical, and electrochemical methods which have all been employed. In general, catalytic hydrogenation is the most convenient and effective method, and palladium catalysts (usually in the colloidal state) are the most selective, but with an iron catalyst of the Raney type (Paul and Hilly, *Bull. Soc. chim.*, 1939, **6**, 218; Thompson and Wyatt, *J. Amer. Chem. Soc.*, 1940, **62**, 2555, and later papers) hydrogenation is reported to cease at the olefin stage. Although the ethylenic compounds often hydrogenate as rapidly as or even more rapidly than the original acetylenic compounds and no appreciable discontinuity in the rate of uptake of hydrogen can therefore be discerned, it is nevertheless possible to obtain excellent yields of the required semihydrogenation products by interrupting the reaction at the appropriate stage. It has been suggested (Farkas, *Trans. Faraday Soc.*, 1939, **35**, 909) that selective adsorption of the acetylenic compound on the catalyst is responsible for the stepwise reduction.

The partial reduction of propenylethynylcarbinol (I) to propenylvinylcarbinol (II) in aqueous suspension by use of Bourguel's colloidal palladium catalyst was originally reported by Lespieau and Lombard (*Bull. Soc. chim.*, 1935, **2**, 372), who noted an acceleration in the rate of hydrogenation after one mol. of hydrogen had been absorbed and a diminution in rate after 2 mols. had been taken up. We have observed a similar behaviour with both palladium–norit and palladium–calcium carbonate catalysts but, as has usually been the experience of other workers with numerous acetylenic compounds, with a platinic oxide catalyst no discontinuity in the rate of hydrogenation is discernible. With propenylethynylcarbinol (I) the rate of hydrogenation is so rapid that it is most convenient to employ a palladium–calcium carbonate catalyst containing only 0·3% of palladium. The hydrogenation can readily be interrupted so that reduction proceeds exclusively at the acetylenic linkage,

(I.) $CH_3\cdot CH{:}CH\cdot CH(OH)\cdot C{\vdots}CH$ $\qquad$ $CH_3\cdot CH{:}CH\cdot CH(OH)\cdot CH{:}CH_2$ (II.)

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* Patent application pending.

giving propenylvinylcarbinol (II) in 90% yield, its homogeneity being proved by fractionation through a column of high efficiency, whereafter no appreciable variation in refractive index is observed. The carbinol contains one active hydrogen atom (Zerewitinoff), it gives no trace of a silver salt with ammoniacal silver nitrate, and it is readily characterised as the *α-naphthylurethane*, m. p. 93·5—94·5°.

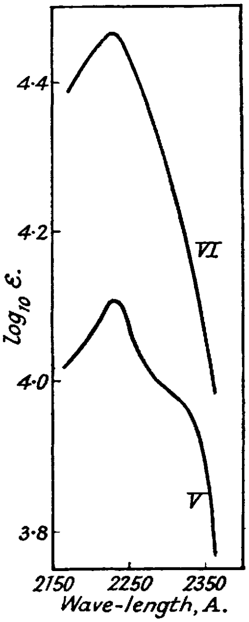
In a similar manner, divinylcarbinol (III) (*α-naphthylurethane*) can be prepared in 70% yield from vinylethynylcarbinol, and *iso*propenylethynylcarbinol gives iso*propenylvinylcarbinol* (IV) (*α-naphthylurethane*) in 80% yield. As would be expected, none of the carbinols (II, III, and IV) exhibits any light absorption of appreciable intensity in the 2200—4000 A. range.

(III.) $CH_2{:}CH{\cdot}CH(OH){\cdot}CH{:}CH_2$ $CH_2{:}CMe{\cdot}CH(OH){\cdot}CH{:}CH_2$ (IV.)

The anionotropic rearrangement of acetylenylcarbinols and glycols derived from αβ-unsaturated carbonyl compounds, first observed (Jones and McCombie, J., 1943, 261) with propenylethynylcarbinol (I) which gives (V), has been extensively investigated (J., 1943—1945; Parts VIII—XVIII inclusive), and an examination of the behaviour of the vinylcarbinols (*e.g.*, II, III, and IV) represents a logical continuation of this study. When propenylvinylcarbinol (II) is shaken at room temperature for two hours with 1% sulphuric acid an 80% yield of *hexa*-3 : 5-*dien*-2-*ol* (*methyl*-1-*butadienylcarbinol*) (VI) is obtained. The yield diminishes with increasing concentrations of acid; *e.g.*, 2·5% acid for 4½ hours gives only a 60% yield, and with 5% acid at 90° for 20 minutes the product is a pale yellow viscous liquid which fails to distil up to 140°/4 mm. The striking difference in the ease of rearrangement of (I) and (II) [(I) is only isomerised to the extent of 5% with 2·5% acid during one hour at 20°] must clearly be related to the relative electronic properties of the acetylenic and the ethylenic bonds. Comparison of the strengths of corresponding pairs of carboxylic acids (Dippy, *Chem. Reviews*, 1939, **25**, 180), *viz.*, $CH_3{\cdot}CH{:}CH{\cdot}CO_2H$, $10^5K = 2{\cdot}03$, $CH_3{\cdot}C{\vdots}C{\cdot}CO_2H$, $10^5K = 222{\cdot}8$, clearly demonstrates the greater ability of the ethylenic bond to release electrons, which must be the main factor responsible for the superior mobility of the system present in propenylvinylcarbinol. Such electron release will clearly facilitate the formation of the oxonium ion which has been postulated (Braude and Jones, J., 1944, 436) as the principal intermediate in the isomerisation of propenylethynylcarbinol.

(V.) $CH_3{\cdot}CH(OH){\cdot}CH{:}CH{\cdot}C{\vdots}CH$ $CH_3{\cdot}CH(OH){\cdot}CH{:}CH{\cdot}CH{:}CH_2$ (VI.)

The rearrangement product contains one active hydrogen atom (Zerewitinoff), it gives an *α-naphthylurethane* and a crystalline adduct (see below) with maleic anhydride, and its ultra-violet absorption (Fig. and Table) is characteristic of the conjugated diene system. This light absorption is about twice as intense as that of the related vinylethynylcarbinol (V), and although the locations of the maxima are identical, the inflexion, typical of the conjugated enyne chromophore, is absent from the spectrum of (VI) (see Fig.).



	$\lambda_{max.}$, A.	$\varepsilon_{max.}$		$\lambda_{max.}$, A.	$\varepsilon_{max.}$
Hexa-3 : 5-dien-2-ol (VI)	2230	28,000	Piperylene[1]	2235	23,000
Penta-2 : 4-dien-1-ol (VII)	2230	25,000	$\Delta^{2:4}$-Hexadiene[1]	2270	22,500
2-Methylpenta-2 : 4-dien-1-ol (VIII)	2285	25,500	Hex-3-en-5-yn-2-ol[2] (V)	2230 *2300	13,500 9,500

* Inflexion.

[1] Booker, Evans, and Gillam, J., 1940, 1453.

[2] Jones and McCombie, *loc. cit.*

The rearrangement of (II) might conceivably give rise either to the primary carbinol, sorbyl alcohol, or to the secondary dienol (VI), both of which would be expected to show the properties referred to above. The constants quoted for sorbyl alcohol in the literature (m. p. 30·5—31·5°, b. p. 76—77°/12 mm.; Reichstein, Ammann, and Trivelli, *Helv. Chim. Acta*, 1932, **15**, 261), however, are quite different from those of the actual isomerisation product, and the formulation of the latter as (VI), which is strongly supported by the exact location of the absorption maximum, referred to again later, is conclusively proved by its complete hydrogenation to methylbutylcarbinol. The greater electron-repelling tendency of the methyl group as compared with that of the hydrogen atom must be the controlling factor in determining the direction of isomerisation in this case : $CH_3{\rightarrow}CH{:}CH{\cdot}CH(OH){\cdot}CH{:}CH{-}H$.

Theoretically, the partial reduction of conjugated vinylacetylenes can proceed in three ways. 1 : 2-Addition, *i.e.*, semihydrogenation of the acetylenic linkage, leading to a conjugated diene; 1 : 4-addition, giving an allene; and 3 : 4-addition, resulting in the formation of a simple acetylene. Although many cases of successful 1 : 2-addition are reported in the literature, these are usually supported only by evidence of a qualitative nature and the quantitative selectivity of any particular catalyst cannot readily be assessed. Palladium catalysts, however, would appear to be the most efficacious, and consequently the partial reduction of hex-3-en-5-yn-2-ol (V) was examined by employing a palladium–calcium carbonate catalyst. The hydrogenation was stopped at the appropriate stage, and by careful fractionation a 40% yield of hexa-3 : 5-dien-2-ol (VI) was obtained. The light absorption and other properties of this product were identical with those of the carbinol obtained by the alternative route. There is a little doubt that 1 : 2-hydrogenation occurs mainly if not almost exclusively in this case, since the dienol actually formed more than 60% of the distillable product; much undistillable material was obtained, probably formed from the somewhat sensitive dienol during the protracted fractionation.

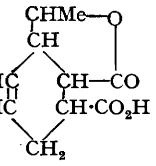
In contrast to the behaviour of vinylethynylcarbinol, which is unaffected by treatment with 25% sulphuric acid (Jones and McCombie, *loc. cit.*), divinylcarbinol (III) is isomerised to *penta*-2 : 4-*dien*-1-*ol* (VII) (α-*naphthylurethane*) in 20% yield by shaking with 1% sulphuric acid for 24 hours. The rearrangement in this case is accompanied by the formation of much low b. p. material which may be of the methyldihydrofuran or the dihydropyran type. Unfortunately, the relative inaccessibility of vinylethynylcarbinol and hence of divinylcarbinol, precluded the possibility of more detailed investigations of the isomerisation conditions and of these by-products. The butadienylcarbinol (VII) gives *n*-amyl alcohol on complete hydrogenation, it exhibits high-intensity light absorption (Table), and readily forms an adduct (see below) with maleic anhydride.

(VII.) $CH_2(OH)\cdot CH{:}CH\cdot CH{:}CH_2$ $CH_2(OH)\cdot CMe{:}CH\cdot CH{:}CH_2$ (VIII.) $CH_2{:}CMe\cdot CH{:}CH\cdot CH_2\cdot OH$ (IX.)

*iso*Propenylethynylcarbinol, like the closely related vinylethynylcarbinol, is not isomerised even on shaking for 24 hours with 25% sulphuric acid, but this is again by no means true of its semihydrogenation product. The isomerisation of *iso*propenylvinylcarbinol (IV) could conceivably proceed in either of two directions, giving the primary carbinols (VIII) or (IX). The product obtained in 45% yield on shaking (IV) with 2% sulphuric acid for 24 hours appears to consist essentially of 2-*methylpenta*-2 : 4-*dien*-1-*ol* (VIII), since 2-methylpentan-1-ol is produced on complete hydrogenation. The carbinol absorbs strongly in the ultra-violet (Table), and in spite of a notable tendency to polymerise, it gives an α-*naphthylurethane* and a maleic anhydride *adduct* (see below).

The marked differences in location of absorption maxima between (VIII) on the one hand, and (VI) and (VII) on the other (see Table), are in accord with observations on the effect of the degree of alkyl substitution on the absorption spectra of diene systems. According to the generalisations of Woodward (*J. Amer. Chem. Soc.*, 1942, **64**, 72), (VI) and (VII) and piperylene should, as monosubstituted butadienes, exhibit maxima at about 2220 A., whereas (VIII) and $\Delta^{2:4}$-hexadiene, being disubstituted butadienes, should show maximal absorption in the vicinity of 2270 A. The carbinol (IX) is also a disubstituted butadiene, and no differentiation between (VIII) and (IX) on the basis of the location of the absorption maximum is possible. Sorbyl alcohol, which originally had to be considered as a possible rearrangement product of (II), would be expected to absorb mainly at 2270 A., but von Euler, Karrer, Klussmann, and Morf (*Helv. Chim. Acta*, 1932, **15**, 502) do not quote the exact location of the absorption maximum.

When hexa-3 : 5-dien-2-ol (VI) reacts with maleic anhydride in benzene solution an adduct, m. p. 157—158°, is produced which is formulated as the γ-*lactone* of 3-α-*hydroxyethyl*-Δ^4-*cyclohexene*-1 : 2-*dicarboxylic acid* (X). Similarly constituted lactonic *acids* are obtained from carbinols (VII) and (VIII). The lactonic acid (X) fails to show any high-intensity absorption in the ultra-violet in the range 2200—4000 A., catalytic hydrogenation indicates the presence of one ethylenic linkage, on heating with *p*-toluidine it forms a *mono*-p-*toluidide*, and with diazomethane it gives a *monomethyl* ester. The lactone ring is extremely stable, as in phthalide and related compounds, and (X) is recovered unchanged after being heated at 50° with methyl sulphate and 35% potassium hydroxide. No analogous case of the immediate formation of lactonic acids by Diels–Alder addition reactions is mentioned in the review by Norton (*Chem. Reviews*, 1942, **31**, 319), but the anil of ethylhexenal is reported to react in its isomeric form ($CHEt{:}CH\cdot CEt{:}CH\cdot NHPh$) with maleic anhydride, giving a monobasic acid containing a five-membered lactam ring (Snyder, Hasbrouck, and Richardson, *J. Amer. Chem. Soc.*, 1939, **60**, 3558).



(X.)

EXPERIMENTAL.

(Absorption spectra were determined in alcoholic solutions.)

Propenylvinylcarbinol (II).—A solution of propenylethynylcarbinol (250 g., preceding paper) in ethyl acetate (400 c.c.) was shaken with hydrogen in the presence of palladium–calcium carbonate (20 g.; 0·3% Pd). Absorption of hydrogen was extremely rapid, and after 62 l. had been absorbed the catalyst was filtered off, and the solvent evaporated off through a column. Distillation of the residual oil through a column * containing a 50 × 1·5 cm. section packed with single-turn glass helices gave propenylvinylcarbinol (227 g.), b. p. 86—87°/100 mm., 71°/50 mm., 60—62°/28 mm., $n_D^{19^\circ}$ 1·4501 (Lespieau and Lombard, *loc. cit.*, give b. p. 140°, 52°/13 mm., $n_D^{24^\circ}$ 1·4482) (Found: C, 73·8; H, 10·25. Calc. for $C_6H_{10}O$: C, 73·4; H, 10·25%). *Active hydrogen* (Zerewitinoff): At 16°/772 mm. the carbinol (99·5 mg.) evolved 22·7 c.c. of methane, equivalent to 0·95 active hydrogen atom per mol. The α-*naphthylurethane* separated from light petroleum (b. p. 60—80°) in needles, m. p. 93·5—94·5° (Found: N, 5·35. $C_{17}H_{17}O_2N$ requires N, 5·25%).

Divinylcarbinol (III).—A solution of vinylethynylcarbinol (25 g.; Jones and McCombie, J., 1942, 733) in ether (100 c.c.) was hydrogenated, palladium–calcium carbonate (3 g.; 0·3% Pd) being used as catalyst. The experiment was interrupted after 9 l. of hydrogen had been absorbed and yielded divinylcarbinol (17·2 g.), a colourless liquid with a somewhat pungent odour, b. p. 64—66°/100 mm., $n_D^{17^\circ}$ 1·4400 (Lespieau and Lombard, *loc. cit.*, give b. p. 114·5—116°, $n_D^{19^\circ}$ 1·4452). The α-*naphthylurethane* separated from aqueous methyl alcohol as felted needles, m. p. 100—101° (Found: N, 5·45. $C_{16}H_{15}O_2N$ requires N, 5·55%).

iso*Propenylvinylcarbinol* (IV).—*iso*Propenylethynylcarbinol (20 g.; for preparation, see below) was hydrogenated in methyl acetate (100 c.c.) with palladium–calcium carbonate (2 g.; 0·3% Pd) as catalyst. The experiment was interrupted after 4·7 l. of hydrogen had been taken up, and fractionation of the product yielded iso*propenylvinylcarbinol* (16·5 g.), b. p. 66°/50 mm., $n_D^{16^\circ}$ 1·4530 (Found: C, 73·6; H, 10·1. $C_6H_{10}O$ requires C, 73·4; H, 10·25%). The α-*naphthylurethane* crystallised from light petroleum (b. p. 40—60°) in long, matted needles, m. p. 88—89° (Found: N, 5·4. $C_{17}H_{17}O_2N$ requires N, 5·25%).

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* This column has an efficiency of twelve theoretical plates when tested with a CCl_4–C_6H_6 mixture.

Hexa-3 : 5-*dien*-2-*ol* (VI).—(*a*) A mixture of propenylvinylcarbinol (210 g.) and sulphuric acid (550 c.c.; 1% w/v) together with a little quinol, was shaken under nitrogen at 20° for 2 hours. Isolation of the product by ethereal extraction followed by two distillations of the residual oil gave *hexa*-3 : 5-*dien*-2-*ol* (172 g.) as a colourless oil, b. p. 67—68°/26 mm,. $n_{\mathrm{D}}^{19^\circ}$ 1·4810 (Found: C, 73·75; H, 10·2. $C_6H_{10}O$ requires C, 73·4; H, 10·25%). Some resin was formed during the distillation. *Active hydrogen* (Zerewitinoff) : The carbinol (100 mg.) evolved 24·4 c.c. of methane at 12°/752 mm. (0·95 active hydrogen atom per mol.). The α-*naphthylurethane* crystallised from light petroleum (b. p. 60—80°) in clusters of leaflets, m. p. 86·5—87·5° (Found : N, 5·4. $C_{17}H_{17}O_2N$ requires N, 5·25%).

(*b*) Hex-3-en-5-yn-2-ol (150 g.; Jones and McCombie, J., 1943, 261) was hydrogenated in ethyl acetate (400 c.c.) by using a palladium–calcium carbonate catalyst (15 g.; 0·3% Pd), the experiment being interrupted when 34·5 l. of gas had been absorbed. The catalyst and solvent were eliminated and the residue was fractionated through a column containing a 50 × 1·5 cm. section packed with single-turn glass helices. The many fractions collected were readily divided into two main portions : (i) B. p. 65—73°/35 mm. (35 g.), $n_{\mathrm{D}}^{17^\circ}$ 1·4469—1·4740; (ii) hexa-3 : 5-dien-2-ol (61 g.), b. p. 73—75°/35 mm. $n_{\mathrm{D}}^{19^\circ}$ 1·4813. There was a cousiderable resinous residue. Portion (ii) showed light absorption identical with that of the material obtained under (*a*), and the same α-naphthylurethane was obtained.

Methylbutylcarbinol and Methyl Butyl Ketone.—Hexa-3 : 5-dien-2-ol (7 g.) in methyl acetate (85 g.) was hydrogenated completely by using platinic oxide (300 mg.) as catalyst. This procedure gave methylbutylcarbinol (6 g.), b. p. 135—139°, $n_{\mathrm{D}}^{15^\circ}$ 1·4130 (lit., b. p. 135—137°, $n_{\mathrm{D}}^{18^\circ}$ 1·4135), which was oxidised to methyl butyl ketone, the 2 : 4-dinitrophenylhydrazone of which had m. p. 108·5° (after chromatographic purification), undepressed on admixture with an authentic specimen (Allen, *J. Amer. Chem. Soc.*, 1930, **52**, 2957, gives m. p. 106°).

Penta-2 : 4-*dien*-1-*ol* (VII).—Divinylcarbinol (11·7 g.) was shaken with sulphuric acid (100 c.c.; 1% w/v) under nitrogen at 20° for 24 hours. Distillation of the product isolated with ether gave 3 fractions : (i) B. p. up to 75°/120 mm. (2·5 g.); (ii) b. p. 75—90°/120 mm. (1 g.), $n_{\mathrm{D}}^{19^\circ}$ 1·4443; (iii) b. p. 90—102°/120 mm. (3 g.), $n_{\mathrm{D}}^{19^\circ}$ 1·4823, and a pale yellow viscous residue. Redistillation of (iii) gave *penta*-2 : 4-*dien*-1-*ol* (2·5 g.) as a colourless liquid with a sweetish odour, b. p. 95—97°/100 mm., $n_{\mathrm{D}}^{18^\circ}$ 1·4902 (Found : C, 71·65; H, 9·9. C_5H_8O requires C, 71·45; H, 9·6%). The carbinol, like hexa-3 : 5-dien-2-ol, polymerises to a clear elastic material on standing. The α-*naphthylurethane* crystallised from light petroleum (b. p. 40—60°) in needles, m. p. 97·5° (Found : N, 5·55. $C_{16}H_{15}O_2N$ requires N, 5·55%).

n-*Amyl Alcohol.*—The above carbinol (1·8 g.) was completely hydrogenated in methyl acetate (50 c.c.) by means of a platinic oxide catalyst and gave *n*-amyl alcohol (0·75 g.), b. p. 134—138° (α-naphthylurethane, m. p. 68°, undepressed on admixture with an authentic specimen).

2-*Methylpenta*-2 : 4-*dien*-1-*ol* (VIII).—A mixture of *iso*propenylvinylcarbinol (10 g.) and sulphuric acid (100 c.c.; 2% w/v) together with a trace of quinol was shaken under nitrogen at 20° for 24 hours. After saturation with salt the product was isolated with ether, giving 2-*methylpenta*-2 : 4-*dien*-1-*ol* (4·6 g.), b. p. 97—99°/50 mm., 72—74°/15 mm., $n_{\mathrm{D}}^{13\cdot5^\circ}$ 1·5001 (Found : C, 73·25; H, 10·1. $C_6H_{10}O$ requires C, 73·4; H, 10·25%). Much rubbery polymer was formed during the preparation at 20° of the α-*naphthylurethane*, which crystallised from light petroleum (b. p. 40—60°) in needles, m. p. 59—60° (Found : N, 5·2. $C_{17}H_{17}O_2N$ requires N, 5·25%).

2-*Methylpentan*-1-*ol.*—The above dienol (3 g.) was fully hydrogenated in methyl acetate (50 c.c.) with platinic oxide (100 mg.) as catalyst and, after careful removal of solvent through a column, gave 2-methylpentan-1-ol (2·4 g.), b. p. 146—151°/776 mm., $n_{\mathrm{D}}^{15\cdot5^\circ}$ 1·4238 (cf. $n_{\mathrm{D}}^{25^\circ}$ 1·4180 given by Norris and Cortese, *J. Amer. Chem. Soc.*, 1927, **49**, 2644; $n_{\mathrm{D}}^{19^\circ}$ 1·4182 by Przewalski, *Chem. Zentr.*, 1909, II, 794; $n_{\mathrm{D}}^{19^\circ}$ 1·4230 by Terentjew, *Bull. Soc. chim.*, 1924, **35**, 1152, and the values for the isomeric 4-methylpentan-1-ol : $n_{\mathrm{D}}^{25^\circ}$ 1·4134, Norris and Cortese, *loc. cit.*; $n_{\mathrm{D}}^{20^\circ}$ 1·4142, Longinow, *Chem. Zentr.*, 1916, I, 1054). The crude α-naphthylurethane had m. p. 63—67°, but after several recrystallisations from light petroleum (b. p. 40—60°) it formed long needles, m. p. 79—80° (Found : N, 5·25, Calc. for $C_{17}H_{21}O_2N$: N, 5·15%) (Magnani and McElvain, *J. Amer. Chem. Soc.*, 1938, **60**, 819, give m. p. 75—76° for the derivative of 2-methylpentan-1-ol, and Huston and Agett, *J. Org. Chem.*, 1941, **6**, 128, give m. p. 60° for the derivative of the 4-methyl isomer).

γ-*Lactone of* 3-α-*Hydroxyethyl*-Δ^4-cyclo*hexene*-1 : 2-*dicarboxylic Acid* (X).—A mixture of hexa-3 : 5-dien-2-ol (5 g.), purified maleic anhydride (5 g.), and benzene (50 c.c.) was heated to about 80° for a few minutes to effect solution and then set aside for 3 days at 20°. In alcoholic solution the addition reaction is much more rapid. Crystallisation of the separated solid from benzene or water gave the above lactonic *acid* (5·5 g.) as prismatic needles, m. p. 157—158° (Found : C, 61·0; H, 6·05. $C_{10}H_{12}O_4$ requires C, 61·2; 6·15%). The *methyl* ester, prepared by using diazomethane in ethereal solution, crystallised from water in flat needles, m. p. 140·5—141·5° (Found : C, 63·1; H, 6·75. $C_{11}H_{14}O_4$ requires C, 62·85; H, 6·7%). Heating the lactone with *p*-toluidine at 220° for 20 minutes gave the p-*toluidide* as leaflets from aqueous alcohol, m. p. 172° (Found : C, 71·5; H, 6·9. $C_{17}H_{19}O_3N$ requires C, 71·55; H, 6·7%).

γ-*Lactone of* 3-*Hydroxymethyl*-Δ^4-cyclo*hexene*-1 : 2-*dicarboxylic Acid.*—A warm solution of penta-2 : 4-dien-1-ol (0·8 g.) and purified maleic anhydride (1 g.) in benzene (8 c.c.) was set aside at 20° and a mass of crystals separated after 3 hours. Recrystallisation of these from water gave the lactonic *acid* as large prisms, m. p. 175—176° (Found : C, 59·55; H, 5·65. $C_9H_{10}O_4$ requires C, 59·35; H, 5·5%).

γ-*Lactone of* 3-*Hydroxymethyl*-3-*methyl*-Δ^4-cyclo*hexene*-1 : 2-*dicarboxylic Acid.*—The crystals which separated on keeping a solution of 2-methylpenta-2 : 4-dien-1-ol (3·5 g.) and purified maleic anhydride (3·5 g.) in dry benzene (8 c.c.) containing a trace of quinol at 20°, were recrystallised from water or sublimed at 115° (bath temp.)/10^{-4} mm., giving the lactonic *acid* (2·5 g.) as rectangular plates, m. p. 181—182° (Found : C, 61·25; H, 6·25. $C_{10}H_{12}O_4$ requires C, 61·2; H, 6·15%). The original benzene mother-liquors contained much rubbery polymeric material.

α-*Methylacraldehyde* (cf. D.R.P. 482,839; B.PP. 286,602, 457,174; Shriner and Sharp, *J. Amer. Chem. Soc.*, 1940, **62**, 2245; Hearne, Tamele, and Converse, *Ind. Eng. Chem.*, 1941, **33**, 805).—α-Methylallyl alcohol (46 g.) was added dropwise during 2 hours to a stirred suspension of selenium dioxide (35 g., freshly sublimed in oxygen) in dioxan (80 g.). The mixture was heated under gentle reflux during the addition in such a manner that the temperature at the head of the 24-cm. Dufton column fitted to the flask did not exceed 90°. When the addition was complete, more selenium dioxide (5 g.) was added, and heating was continued until the b. p. of the distillate rose above 90°. Some 50—75 c.c. of distillate were collected. The distillates from two such experiments were combined and carefully fractionated through a column packed with a 50 × 1·5 cm. section of single-turn glass helices. The fraction with b. p. 63·5—64° was dried, and on redistillation yielded α-methylacraldehyde (30 g.), b. p. 67—69°/770 mm., $n_{\mathrm{D}}^{18^\circ}$ 1·4166.

. iso*Propenylethynylcarbinol.*—A solution of α-methylacraldehyde (30 g.) in ether (50 c.c.) was added to a stirred solution of sodium acetylide (from sodium 8·5 g. *via* sodamide made *in situ* according to Vaughn, Vogt, and Nieuwland, *J. Amer. Chem. Soc.*, 1934, **56**, 2120) in liquid ammonia (500 c.c.). Stirring was continued for 2 hours, ammonium chloride added, and the solvent allowed to evaporate off overnight. Isolation in the usual manner gave *iso*propenylethynylcarbinol (25 g.), b. p. 74°/50 mm., $n_{\mathrm{D}}^{18\cdot5^\circ}$ 1·4629 (Kreimeier, U.S.P. 2,106,181, gives b. p. 141—144°, $n_{\mathrm{D}}^{25^\circ}$ 1·4589). The α-*naphthylurethane* crystallised from light petroleum (b. p. 40—60°) in long needles, m. p. 99—100° (Found : N, 5·2. $C_{17}H_{15}O_2N$ requires N, 5·3%).

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY, LONDON, S.W. 7.

[*Received, October* 19*th*, 1944.]