158. *Studies in the Polyene Series. Part VI. The Preparation of Ethinylcarbinols from αβ-Unsaturated Aldehydes.*

By E. R. H. Jones and J. T. McCombie.

αβ-Unsaturated aldehydes are readily converted into ethinylcarbinols by reaction with sodium acetylide in liquid ammonia, a method which, when applied to benzaldehyde, gives an 82·5% yield of phenylethinylcarbinol. The aldehydes now studied include crotonaldehyde (60% yield of carbinol), acraldehyde (35%), 2-methylcrotonaldehyde (50%), tiglic aldehyde (75%), 2-ethylhex-2-enal (80%), furfuraldehyde (65%), and cinnamaldehyde (2%). The carbinols have been characterised by the preparation of crystalline derivatives, particularly the *naphthylurethanes*, and also by complete hydrogenation to the known saturated secondary alcohols.

In view of current general interest in acetylenic carbinols and more particularly because of their potential importance for the synthesis of vitamin A and analogues (see preceding paper) a detailed investigation of the preparation and properties of the acetylenic carbinols derived from αβ-unsaturated aldehydes has been initiated. This paper deals with the preparation and characterisation of the ethinylcarbinols of certain αβ-unsaturated aldehydes (the literature is surveyed in the preceding paper). Accounts of their interesting reactions and also of investigations which are being made with other types of acetylenic carbinols formed from unsaturated aldehydes, and also with ethinylcarbinols from polyene aldehydes, will appear in subsequent publications in this series.

The method involves the preparation of sodium acetylide (from sodium) in liquid ammonia solution, followed by addition of the appropriate aldehyde, usually in ethereal solution, acetylene being passed into the reaction mixture throughout the whole time of reaction (cf. Campbell, Campbell, and Eby, *J. Amer. Chem. Soc.*, 1938, **60**, 2882). The sodium acetylide was prepared according to Vogt's method (U.S.P.

2,200,941), whereby no appreciable dissolved excess of sodium is ever present in the solution. When the above procedure was employed with benzaldehyde, an 82·5% yield of phenylethinylcarbinol was achieved (Campbell, Campbell, and Eby, *loc. cit.*, obtained only a 45% yield), and in order to investigate the formation of crystalline derivatives from these ethinylcarbinols the *phenylurethane*, p-*nitrophenylurethane*, β-*naphthylurethane*, and the *acid phthalate* were prepared.

Propenylethinylcarbinol was readily obtained from crotonaldehyde in 50—65% yields and was characterised by its *phenylurethane*, β-*naphthylurethane*, and *acetyl* derivative. Complete hydrogenation in the presence of palladium–norit yielded ethylpropylcarbinol (*phenylurethane*), which was oxidised to ethyl propyl ketone. Acraldehyde yielded vinylethinylcarbinol in only 36% yield, however, much solid polymeric material being formed under all conditions of experiment. This carbinol was characterised by the formation of a *phenylurethane* and an α-*naphthylurethane* and gave diethylcarbinol on complete hydrogenation. A 50% yield of iso*butenylethinylcarbinol* (*phenylurethane*, β-*naphthylurethane*) was obtained from 2-methylcrotonaldehyde, the constitution of the carbinol being proved by its complete hydrogenation to ethyl*iso*butylcarbinol (also oxidised to ethyl *iso*butyl ketone). 2-Ethylhex-2-enal gave the ethinylcarbinol (4-ethyloct-4-en-1-yn-3-ol) (α-*naphthylurethane*) in 85% yield (Kreimeier, U.S.P. 2,106,181, obtained the carbinol in 56% yield). From tiglic aldehyde a 75% yield of 4-*methylhex*-4-*en*-1-*yn*-3-*ol* (α-*naphthylurethane*) was obtained. 2-Furylethinylcarbinol was produced in 65% yield from furfuraldehyde (Macullum, U.S.P. 2,125,384, mentions a 30% yield), but from cinnamaldehyde only a 2% yield of *styrylethinylcarbinol* could be obtained, a large quantity of a solid polymer being simultaneously produced.

When the above ethinylcarbinols react with methylmagnesium iodide in Zerewitinoff determinations the temperature has to be raised to 90° before reaction with the acetylenic hydrogen atom is complete. The preferential reaction with the active hydrogen atom of the hydroxyl group is proved by the fact that the acetate of propenylethinylcarbinol gave practically no methane at 20°.

EXPERIMENTAL.

Absorption spectra were determined in alcoholic solutions. All distillations were carried out in a nitrogen atmosphere. Except where stated otherwise, light petroleum refers to that fraction of b. p. 40—60°.

Phenylethinylcarbinol.—Purified acetylene was rapidly passed into liquid ammonia (1000 c.c.) with stirring and cooling, and sodium (23 g.) added in small pieces in such a manner that the blue colour never persisted for more than a few moments. A solution of benzaldehyde (106 g.) in ether (100 c.c.) was then added during an hour, and the mixture stirred and cooled for a further 3 hours with continued introduction of acetylene. The ammonia was allowed to evaporate overnight and ether and dilute sulphuric acid (ice) were added to the residue. Isolation of the product in the usual manner gave phenylethinylcarbinol (110 g.), as prisms, m. p. 22°, b. p. 115—116°/16 mm., $n_D^{21°}$ 1·5482 (Campbell, Campbell, and Eby, *loc. cit.*, gave b. p. 114°/12 mm., $n_D^{20°}$ 1·5508). *Active hydrogen* (Zerewitinoff): The carbinol (130 mg.) gave 44·5 c.c. of methane at 22°/761 mm. (after heating to 85°), equivalent to 1·9 active hydrogen atoms per molecule. *Phenylurethane:* Equimolecular quantities of the carbinol and phenyl *iso*cyanate were set aside at 20° for several days in a sealed tube. The crystalline mass was washed with light petroleum and two crystallisations of the residue from light petroleum (b. p. 60—80°) gave the *phenylurethane* in needles, m. p. 81—82° (Found: N, 5·55. $C_{16}H_{13}O_2N$ requires N, 5·55%). p-*Nitrophenylurethane:* The reagents were heated together in dry xylene for an hour, the dinitrophenylurea removed, and after standing at 0° for several days the derivative separated. Recrystallisation from xylene gave the p-*nitrophenylurethane* in pale yellow needles, m. p. 132° (Found: N, 9·0. $C_{16}H_{12}O_4N_2$ requires N, 8·95%). *β-Naphthylurethane:* The mixed reagents were heated for an hour at 100° and after standing overnight at 20° the crude product was extracted with boiling petroleum (b. p. 100—120°); on cooling and after recrystallisation from the same solvent the *β-naphthylurethane* was obtained in needles, m. p. 120° (Found: N, 4·55. $C_{20}H_{15}O_2N$ requires N, 4·65%). *Acid phthalate:* Equimolecular quantities of the carbinol and phthalic anhydride were heated in pyridine solution at 100° for 2 hours and the derivative, removed from ethereal solution with N-ammonia, was isolated by means of chloroform. The crude product was purified both by adsorption on alumina from benzene solution, and by extraction with hot light petroleum (b. p. 60—80°); crystallisation from the latter solvent gave the *acid phthalate* in needles, m. p. 98—99° (Found: C, 73·1; H, 4·7. $C_{17}H_{12}O_4$ requires C, 72·9; H, 4·3%). The *acetyl* derivative, prepared by heating the carbinol with acetic anhydride at 100—115° for 2½ hours, had b. p. 124°/18 mm., $n_D^{20°}$ 1·5155 (Found: C, 76·2; H, 6·05. $C_{11}H_{10}O_2$ requires C, 75·9; H, 5·8%). The mercury compound separated from alcohol in aggregates of needles, m. p. 167—168°.

Propenylethinylcarbinol.—To sodium acetylide, prepared from sodium (230 g.) as above, in liquid ammonia (6000 c.c.) in a 10-litre 3-necked flask, crotonaldehyde (700 g.) was added during 2 hours with stirring and cooling. After the addition of ammonium chloride (525 g.) the ammonia was allowed to evaporate overnight; water and ice (1 kg.) were then added, and the carbinol distilled in steam. The steam-distillate was saturated with salt and after isolation with ether and distillation through a Widmer column propenylethinylcarbinol (565 g.) (in experiments on a somewhat smaller scale, yields up to 65% were obtained) was obtained as a colourless oil, b. p. 154—156°, 102—103°/111 mm., 75°/24 mm., $n_D^{23°}$ 1·4651 (Lespieau and Lombard, *Bull. Soc. chim.*, 1935, **2**, 369, give b. p. 153°, 58—59°/13 mm., $n_D^{23°}$ 1·4650) (Found: C, 75·1; H, 8·0. Calc. for C_6H_8O: C, 75·0; H, 8·4%). The carbinol gives white silver and mercury compounds, the latter forming small prisms, m. p. above 360°. It exhibits no absorption in the ultra-violet with $E_{1\,cm.}^{1\%}$ greater than 35, between 2150—5000 A. *Active hydrogen* (Zerewitinoff): The carbinol (99·2 mg.) evolved 27·2 c.c. of methane at 20°/773 mm., after heating to 90°, equivalent to 1·9 active hydrogen atoms per molecule. *Phenylurethane:* After standing at 20° for 14 days, the reaction mixture crystallised at 0° and formed needles from light petroleum, m. p. 65° (Found: N, 6·55. $C_{13}H_{13}O_2N$ requires N, 6·5%). The *β-naphthylurethane*, prepared as described above, crystallised in needles, m. p. 89°, from light petroleum or aqueous methyl alcohol (Found: N, 5·3. $C_{17}H_{15}O_2N$ requires N, 5·3%). *Acetyl derivative:* A mixture of propenylethinylcarbinol (96 g.) and acetic anhydride (120 g.) was heated at 110° for 4 hours. Isolation in the usual manner yielded the *acetyl* derivative (111·5 g.), b. p. 110—112°/100 mm., $n_D^{20.5°}$ 1·4463 (Found: C, 69·8; H, 7·2. $C_8H_{10}O_2$ requires C, 69·6; H, 7·25%). This compound exhibits practically no absorption in the 2150—5000 A. range. *Active hydrogen* (Zerewitinoff): The acetate (157 mg.) gave 29·1 c.c. of methane at 19·5°/766 mm., after heating to 90°, corresponding to 1·1 active hydrogen atoms per molecule.

Ethylpropylcarbinol.—A solution of propenylethinylcarbinol (5 g.) in methyl alcohol (50 c.c.) was shaken with hydrogen in the presence of palladium–norit (1·5 g.; 10%) until absorption was complete. The catalyst was filtered off, and the solvent removed through a column; the residual ethylpropylcarbinol had b. p. 134—136° (Völker, *Ber.*, 1875, **8**, 1019, gives b. p. 135°). A synthetic specimen of this alcohol made by treating ethylmagnesium bromide with butaldehyde had b. p. 135—136°, the *phenylurethane* of either specimen crystallised from light petroleum in needles, m. p. 49—50°, and no depression was observed on admixture (Found: N, 6·4. $C_{13}H_{19}O_2N$ requires N, 6·35%). A small portion of each specimen of the alcohol was oxidised to the ketone with chromic anhydride in dilute sulphuric acid. No depressions in m. p. were observed on admixture of the 2 : 4-dinitrophenylhydrazones, m. p. 134—135° (purified by adsorption on alumina) (Allen, *J. Amer. Chem. Soc.*, 1930, **52**, 2958, gives m. p. 130°) or the semicarbazones, m. p. 112° (Pickard and Kenyon, J., 1913, **103**, 1942, give m. p. 112°) of the two ketones.

Vinylethinylcarbinol.—The crude condensation product from acraldehyde (58 g.) and sodium (25 g.) yielded amorphous polymeric material (40 g.). This was washed with ether and the aqueous solution, after saturation with salt, was thoroughly extracted. The combined ethereal extracts were washed with saturated brine and sodium bicarbonate solution, dried, and evaporated. Two distillations of the residual liquid gave vinylethinylcarbinol (30 g.), b. p. 83·5—84·5°/150 mm. (Lespieau and Lombard, *loc. cit.*, give b. p. 128·5—129·5°), $n_{\mathrm{D}}^{16^\circ}$ 1·4545. The carbinol is appreciably soluble in water and gives white silver and mercury compounds. It exhibits practically no absorption in the range 2150—5000 A. *Active hydrogen* (Zerewitinoff): Vinylethinylcarbinol (61 mg.) gave 37·5 c.c. of methane at 23°/768 mm., after heating to 90°, corresponding to 2·1 active hydrogen atoms per molecule. The *phenylurethane* formed needles, m. p. 37°, from light petroleum (Found: N, 7·1. $C_{12}H_{11}O_2N$ requires N, 6·95%). The *α-naphthylurethane* was obtained in needles, m. p. 127·5—128·5°, from light petroleum (Found: N, 5·45. $C_{16}H_{13}O_2N$ requires N, 5·6%). The carbinol (3·4 g.) was refluxed with acetic anhydride (5 g.) for 15 hours and isolation in the usual manner gave the *acetate* (4 g.), b. p. 87—88°/100 mm., $n_{\mathrm{D}}^{23^\circ}$ 1·4319 (Found: C, 67·6; H, 6·7. $C_7H_8O_2$ requires C, 67·75; H, 6·45%). This derivative shows no appreciable absorption in the range 2150—5000 A.

Diethylcarbinol.—Vinylethinylcarbinol (3 g.) in ether (150 c.c.) was shaken with platinic oxide (0·1 g.) and hydrogen until absorption ceased. The catalyst was separated, and the ether distilled through a column; the residual diethylcarbinol had b. p. 114—116°, $n_{\mathrm{D}}^{18^\circ}$ 1·4071 (Rosanow, *Chem. Zentr.*, 1923, I, 1490, gives b. p. 116·2°, $n_{\mathrm{D}}^{20^\circ}$ 1·4057). The α-naphthylurethane had m. p. 90—91° (Bicket and French, *J. Amer. Chem. Soc.*, 1926, **48**, 747, give m. p. 71—72°, presumably a misprint), and the 3 : 5-dinitrobenzoate had m. p. 98—99° (Conant and Blatt, *ibid.*, 1929, **51**, 1227, give m. p. 101°). No depressions were observed on admixture with authentic specimens.

iso*Butenylethinylcarbinol.*—Prepared by the standard method from 2-methylcrotonaldehyde (26 g.) and sodium (7·1 g.), iso*butenylethinylcarbinol* (17 g.) was obtained, b. p. 110—113°/100 mm., $n_{\mathrm{D}}^{20^\circ}$ 1·4657 (Found: C, 76·2; H, 9·2. $C_7H_{10}O$ requires C, 76·35; H, 9·1%). It exhibits no appreciable light absorption in the 2150—5000 A. range. The *phenylurethane*, prepared in the manner already described, crystallised in leaflets, m. p. 58—59°, from light petroleum (Found: C, 73·6; H, 6·7. $C_{14}H_{15}O_2N$ requires C, 73·35; H, 6·55%). The *β-naphthylurethane* formed leaflets, m. p. 76°, from light petroleum (Found: C, 77·85; H, 6·6. $C_{18}H_{17}O_2N$ requires C, 77·4; H, 6·1%).

*Ethyl*iso*butylcarbinol.*—A solution of *iso*butenylethinylcarbinol (8·5 g.) in acetic acid (80 c.c.) was shaken with hydrogen and platinic oxide (0·1 g.). When absorption was complete the catalyst was removed, and the filtrate neutralised with sodium hydroxide solution and extracted with ether. The ethyl*iso*butylcarbinol isolated had b. p. 93—96°/105 mm., $n_{\mathrm{D}}^{20^\circ}$ 1·4128 (Wagner, *Bull. Soc. chim.*, 1884, **42**, 330, gives b. p. 147—148°). The α-naphthylurethane had m. p. 72—73° (Levene and Walti, *J. Biol. Chem.*, 1931, **94**, 367, give m. p. 74—75°). Oxidation with chromic anhydride in dilute sulphuric acid yielded ethyl *iso*butyl ketone, which gave a semicarbazone, m. p. 150° (Rhinesmith, *J. Amer. Chem. Soc.*, 1936, **58**, 596, gives m. p. 149—150°), and a 2 : 4-dinitrophenylhydrazone, m. p. 73° (Allen, *ibid.*, 1930, **52**, 2955, gives m. p. 75°).

4-*Ethyloct*-4-*en*-1-*yn*-3-*ol.*—Prepared by the standard method from 2-ethylhex-2-enal (86 g.) and sodium (15·7 g.), 4-ethyloct-4-en-1-yn-3-ol (88 g.) was obtained, b. p. 96·5—97°/14 mm., $n_{\mathrm{D}}^{20^\circ}$ 1·4678 (Kreimeier, *loc. cit.*, records b. p. 115—115·5°/34 mm.). The carbinol exhibits no appreciable light absorption in the 2150—5000 A. range. The *α-naphthylurethane* formed needles, m. p. 57—58°, from light petroleum (Found: N, 4·4. $C_{21}H_{23}O_2N$ requires N, 4·35%).

4-*Methylhex*-4-*en*-1-*yn*-3-*ol.*—Condensation of tiglic aldehyde (54 g.) with sodium acetylide (from 15 g. of sodium) in liquid ammonia in the usual manner gave 4-*methylhex*-4-*en*-1-*yn*-3-*ol* (55 g.), b. p. 96—97°/50 mm., $n_{\mathrm{D}}^{24^\circ}$ 1·4673 (Found: C, 76·2; H, 9·2. $C_7H_{10}O$ requires C, 76·35; H, 9·1%). The carbinol shows no appreciable absorption in the range 2150—5000 A. The *α-naphthylurethane* crystallised from light petroleum (b. p. 60—80°) in needles, m. p. 105° (Found: C, 77·45; H, 6·2. $C_{18}H_{17}O_2N$ requires C, 77·4; H, 6·1%).

2-*Furylethinylcarbinol.*—Prepared by the standard procedure from furfuraldehyde (96 g.) and sodium (23 g.), 2-furylethinylcarbinol (79 g.) was obtained as an almost colourless oil, b. p. 83—85°/2 mm. (Macullum, *loc. cit.*, gives b. p. 100—103°/25 mm.). The carbinol is fairly sensitive to oxidation and slowly darkens even in a nitrogen atmosphere. *Active hydrogen* (Zerewitinoff): The carbinol (104 mg.) gave 36·5 c.c. of methane at 20·5°/762 mm., after heating to 90°, equivalent to 1·9 active hydrogen atoms per molecule.

Styrylethinylcarbinol.—When cinnamaldehyde (132 g.) was condensed with sodium acetylide (from sodium, 23 g.) in the normal manner, the crude product contained polymeric material (more than 100 g.), insoluble in ether. The ether-soluble portion of the product was distilled, yielding an oil (3 g.), b p. 130—140°/12 mm., which crystallised on cooling, yielding *styrylethinylcarbinol* in needles, m. p. 66—67°, from light petroleum (Found: C, 83·6; H, 6·5. $C_{11}H_{10}O$ requires C, 83·5; H, 6·3%). *Light absorption:* Maximum, 2510 A.; log $\epsilon = 4{\cdot}31$.

The authors are indebted to Professor I. M. Heilbron, D.S.O., F.R.S., for his interest in this work and to the Rockefeller Foundation and I.C.I. (Dyestuffs) Ltd. for grants.

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

[*Received, September* 21*st*, 1942.]