

125. ω -2'-Furylalkane Derivatives.

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The use of palladised strontium carbonate as a catalyst permits the hydrogenation of the alkene side chain in 2'-furylalkenes without reduction of the nucleus. Application of this reaction to the preparation of some ω -2'-furyl derivatives is described.

THE synthesis of ω -2'-furylalkane derivatives from furfuraldehyde through alkenes of the type $C_4H_3O \cdot [CH:CH]_n \cdot CH_2X$ is hindered by the instability of the furan nucleus (cf. Jones and Taylor, *Quart. Reviews*, 1950, **4**, 196). It has now been found that hydrogenation in the presence of palladised strontium carbonate proceeds without attack on the nucleus, except in such compounds as ethyl β -2'-furylacrylate which contain a cationoid system. The potassium salt of the corresponding acid is, however, reducible in aqueous solution with the same catalyst to the desired ω -2'-furylalkane acid uncontaminated with tetrahydrofuryl derivatives.

Besides its ease of reduction the furan nucleus has great sensitivity to acids, thionyl chloride, and phosphorus, aluminium, and stannic halides. For this reason the Friedel-Crafts reaction has not been used with success; not many of the ω -furylalkyl halides have been prepared and the iodides appear to be unknown. By the action of sodium iodide on the toluene-*p*-sulphonates of the alcohols it has been possible to convert ω -2'-furylalkanols into the alkyl iodides in overall yields of 70%. A series of ω -2'-furylalkanecarboxylic acids has been prepared and converted into the amides. Previously only the anilides were known.

All the furyl derivatives prepared are unstable to acids. The apparent stability to

aqueous acids conferred by a long methylene chain is due to sparing solubility in the reagent: it disappears when aqueous-alcoholic acids are used.

Where the refraction was measured the observed values showed the "negative exaltation" characteristic of the furan nucleus. The melting points of the ω -furylalkane-carboxylic acids, $C_4H_3O \cdot [CH_2]_n \cdot CO_2H$, from furylpropionic to furylheptanoic, display a "reverse alternation," the acids with an odd total number of carbon atoms in the side chain being higher-melting than their next homologues: when $n = 2, 3, 4, 5$, or 6 , the melting points are 58° , (oil), 43° , 19° , 36° , respectively.

EXPERIMENTAL

Intermediates, Acids, etc.— β -2-Furylacraldehyde (cf. Röhmer, *Ber.*, 1898, **31**, 283). To sodium hydroxide (10 g.) in water (2 l.) furfuraldehyde (34 c.c.) was added, followed by acetaldehyde (100 c.c.), with vigorous swirling. The mixture was heated on a water-bath to 40° , then after 5 minutes cooled to 25° and extracted with chloroform. The aldehyde (35 g.; 70%, based on furfuraldehyde) boiled at 110 – $115^\circ/15$ mm. and solidified. Redistillation at 0.1 mm. and crystallisation from benzene-light petroleum gave needles, m. p. 53° (König, *Ber.*, 1925, **58**, 2559, gives m. p. 54°) (Found: C, 68.9; H, 5.3. Calc. for $C_7H_6O_2$: C, 68.8; H, 5.0%). The semicarbazone, plates from alcohol, melted at 212 – 213° (Found: N, 23.2. Calc. for $C_8H_9O_2N_3$: N, 23.5%); Röhmer gave m. p. 215 – 219° .

Burdick and Adkins's procedure (*J. Amer. Chem. Soc.*, 1934, **56**, 441) gave only 45% yields but was preferred for large-scale preparations.

5-2'-Furylpenta-2:4-dienal. This was prepared by the method of Hinz, Meyer, and Schücking (*Ber.*, 1943, **76**, 676) by adding acetaldehyde slowly to a cold, well-stirred alkaline suspension of furfuraldehyde. The fraction of the product boiling at 130 – $160^\circ/15$ mm. crystallised from light petroleum in pale yellow needles, m. p. 65 – 66° (yield, 20%). Hinz, Meyer, and Schücking record m. p. 66° .

7-2'-Furylhepta-2:4:6-trienal could not be isolated from the mixture obtained by condensing 3-2'-furylacraldehyde and crotonaldehyde in presence of piperidine acetate (cf. Schmidt, *Annalen*, 1941, **547**, 270), but the reaction yields 11-2'-furylundeca-2:4:6:8:10-pentaenal. Extraction of the crude product (20 g., from 20 g. of furylacraldehyde and 25 g. of crotonaldehyde) with boiling toluene gave 6–7 g. of the deep red undecapentaenal, m. p. 107 – 110° , the remainder being tar.

β -2-Furylacrylic acid (*Org. Synth.*, 1945, **25**, 51) melted at 141° .

5-2'-Furylpent-2-enoic acid, made from β -2-furylpropaldehyde, malonic acid, pyridine, and a trace of piperidine (yield 79%), had b. p. 160 – $170^\circ/0.3$ mm., and formed needles, m. p. 75 – 76° , from light petroleum (b. p. 40 – 60°) (Found: C, 65.2; H, 6.1. $C_9H_{10}O_3$ requires C, 65.1; H, 6.1%).

5-2'-Furylpenta-2:4-dienoic acid. By Röhmer's method (*loc. cit.*) β -2-furylacrylic acid (11 g.), sodium acetate, and acetic anhydride at 175 – 180° gave only 0.1 g. of acid, m. p. 153° . By Hinz, Meyer, and Schücking's method (*loc. cit.*) furylacraldehyde, ethyl acetate, and sodium ethoxide gave an ester (62%), b. p. 145 – $150^\circ/10$ mm., m. p. 22 – 23° (Found: C, 68.9; H, 7.0. Calc. for $C_{11}H_{12}O_3$: C, 68.8; H, 6.3%). Hinz, Meyer, and Schücking give m. p. 14 – 15° . This ester was rapidly hydrolysed by aqueous-alcoholic potassium hydroxide to the acid, m. p. 153 – 154° (85% yield).

7-2'-Furylhepta-2:4:6-trienoic acid. 5-2'-Furylpenta-2:4-dienal (54 g., 0.3 mole) in anhydrous ethyl acetate (100 c.c.) was added dropwise during 2 hours to a vigorously stirred suspension of powdered sodium (10.0 g., 0.43 g.-atom) in ethyl acetate (150 c.c.) containing ethanol (1 c.c.) at -10° to -15° , and the mixture stirred for 3 hours. The resulting ester boiled at 135 – $140^\circ/0.1$ mm. and crystallised from 90% alcohol as yellow needles, m. p. 81 – 82° (47 g., 59%) (Found: C, 71.9; H, 6.7. $C_{13}H_{14}O_3$ requires C, 71.5; H, 6.4%). The derived acid melted at 194 – 196° . Hausser, Kuhn, Smakula, and Deutsch (*Z. physikal. Chem.*, 1935, **B**, **29**, 378) give m. p. 195 – 200° (corr.). The amide, pale yellow needles from 90% alcohol, melted at 210 – 211° (Found: N, 7.1. $C_{11}H_{11}O_2N$ requires N, 7.4%).

ω -2'-Furylalkanols.—3-2'-Furylpropanol. β -2-Furylacraldehyde by the Meerwein-Ponndorf method gave, in 6 hours, 3-2'-furylprop-2-enol (90%), b. p. 74 – $76^\circ/0.2$ mm., n_D^{20} 1.5445 (Found: C, 67.6; H, 6.7. Calc. for $C_7H_8O_2$: C, 67.8; H, 6.5%). The colourless liquid gave a 1-naphthylurethane, m. p. 93 – 94° . Bray and Adams (*J. Amer. Chem. Soc.*, 1927, **49**, 2101) give n_D^{20} 1.5520 and 1-naphthylurethane, m. p. 93 – 93.5° .

Reduction of the propenol (27 g.) in ethanol (80 c.c.) with hydrogen at 4 atm. in presence of

palladised strontium carbonate (2 g., from 1 g. of palladium chloride on 35 g. of commercial strontium carbonate) was complete in 10 minutes, giving the propanol (22 g.), b. p. 122°/15 mm., n_D^{20} 1.4795, d_4^{20} 1.0660, $[R_L]_D^{20}$ 33.8 (Calc. : 34.56) (Found : C, 66.7; H, 8.0. Calc. for $C_3H_8O_2$: C, 66.8; H, 7.9%). Bray and Adams (*loc. cit.*) give b. p. 201—208°/747 mm., n_D^{25} 1.4760, d_4^{20} 1.0613 (1-naphthylurethane, m. p. 49°).

For 4-2'-furylbutanol, see Hofmann, Bridgwater, and Axelrod, *J. Amer. Chem. Soc.*, 1949, **71**, 1253.

5-2'-Furylpentanol. (a) 5-2'-Furylpenta-2 : 4-dienal (26.5 g.) in isopropanol (500 c.c.) with distilled aluminium isopropoxide (6.3 g.) gave, in 3.5 hours, the unsaturated alcohol (21.1 g., 80%) free from aldehyde. This (a pale yellow solid), crystallised from benzene-light petroleum, had m. p. 50—51°. The colourless crystals rapidly formed a dark gum, and a satisfactory analysis could not be obtained. The freshly distilled 5-2'-furylpenta-2 : 4-dienol was reduced in 6 minutes with hydrogen at 4 atm. (Pd-SrCO₃). 5-2'-Furylpentanol (yield 93%) had b. p. 125—127°/15 mm., n_D^{20} 1.4798, d_4^{20} 1.023, $[R_L]_D^{20}$ 42.8 (Calc. 43.8) (Found : C, 70.2; H, 9.3. $C_9H_{14}O_2$ requires C, 70.1; H, 9.2%). The 1-naphthylurethane, colourless needles from light petroleum (b. p. 40—60°), melted at 58—59°. Hofmann (*J. Amer. Chem. Soc.*, 1945, **67**, 421) gives m. p. 58—58.5° (he did not purify the pentanol). (b) 5-2'-Furylpenta-2 : 4-dienal (23.5 g.) in ethanol (70 c.c.) was reduced with hydrogen at 160°/164 atm. and copper chromite (Connors, Folkers, and Adkins, *J. Amer. Chem. Soc.*, 1932, **54**, 1139). Reduction was complete in 10 minutes. The product, which was free from aldehydes (Schiff and Angeli-Rimini tests), had n_D^{20} 1.4798 (Found : C, 70.1; H, 9.1%). (c) Reduction of 5-2'-furylpenta-2 : 4-dienal with hydrogen at 4 atm. and Raney nickel gave, in 11 minutes at room temperature, a product showing positive tests for the aldehyde group and also a high percentage of hydrogen (Found : C, 68.9; H, 11.3. 5-2'-Tetrahydrofurylpentanol, $C_9H_{18}O_2$, requires C, 68.3; H, 11.5%). It was inferred that nuclear reduction had occurred.

7-2'-Furylheptanol. (a) Attempts to produce this alcohol by reduction of the crude mixture of polyene aldehydes from the condensation of furylacraldehyde and crotonaldehyde led only to a small yield of an impure product. (b) Reduction of 7-2'-furylheptanoic acid (see below) in ether with lithium aluminium hydride gave in 45 minutes an alcohol, b. p. 92—94°/0.2 mm., n_D^{20} 1.4797, d_4^{20} 0.987, $[R_L]_D^{20}$ 52.45 (Calc. : 53.05) (Found : C, 72.2; H, 9.8. $C_{11}H_{18}O_2$ requires C, 72.5; H, 10.0%). The 1-naphthylurethane, needles from light petroleum (b. p. 40—60°), melted at 70—71° (Found : N, 4.0. $C_{22}H_{25}O_3N$ requires N, 4.0%).

11-2'-Furylundecanol. 11-2'-Furylundeca-2 : 4 : 6 : 8 : 10-pentaenal (the crude mixture of unsaturated aldehydes described above; 22.0 g.) was finely powdered and reduced in 3 batches with ethanol (80 c.c.), palladised strontium carbonate (2.0 g.), and hydrogen at 5 atm. for each batch. The colourless distillates of b. p. 105—125°/0.1 mm. (9.1 g.) were combined and immediately reduced (Meerwein-Ponndorf) giving 7.0 g. of the alcohol. Distillation gave the alcohol, b. p. 132—135°/0.03 mm., n_D^{20} 1.4795, d_4^{20} 0.949, $[R_L]_D^{20}$ 71.3 (Calc. : 71.50) (Found : C, 75.6; H, 11.1. $C_{15}H_{26}O_2$ requires C, 75.6; H, 11.0%). The 1-naphthylurethane, needles from light petroleum (b. p. 40—60°), melted at 73—74° (Found : N, 3.3. $C_{26}H_{33}O_3N$ requires N, 3.4%).

ω-2'-Furylalkyl Halides.—1-Bromo-3-2'-furylpropane. To a solution of 3-2'-furylpropanol (10.5 g., 0.085 mole) in boiling dry ether (100 c.c.), phosphorus tribromide (4.0 g., 0.015 mole) in ether (50 c.c.) was added dropwise during 30 minutes. The dark solution was then refluxed for 3 hours and left overnight at room temperature; a dark mass of acid phosphorus esters separated. From the ethereal layer the bromide (4.0 g., 27%) was obtained, having b. p. 88—91°/15 mm., n_D^{20} 1.5011 (Found : Br, 42.1. C_7H_9OBr requires Br, 42.3%).

1-Bromo-5-2'-furylpentane was similarly prepared from the pentanol (10.0 g., 0.064 mole) and phosphorus tribromide (8.6 g., 0.032 mole) but the mixture was refluxed for 8.5 hours. The product (41% yield) had b. p. 124—127°/15 mm., n_D^{20} 1.4996 (Found : Br, 36.7. $C_9H_{13}OBr$ requires Br, 36.8%).

1-2'-Furyl-3-iodopropane. To 3-2'-furylpropanol (20.5 g., 0.17 mole) in dry pyridine (120 c.c.) at -15°, toluene-*p*-sulphonyl chloride (38.1 g., 0.2 mole) was added in 3 portions (temp. held below 0°) and the mixture kept for 3 hours in an ice-salt bath (cf. Tipson, *J. Org. Chem.*, 1944, **9**, 235). Water (10 × 2 c.c.) was added and the mixture then slowly poured into ice-water (600 c.c.) containing concentrated hydrochloric acid (200 c.c.). The pink oil which separated was extracted with the aid of sodium chloride and ether (4 × 200 c.c.); it (45.4 g., 79%) did not crystallise.

To a solution of dried sodium iodide (35 g., 0.2 mole) in dry acetone (250 c.c.) the toluene-*p*-sulphonate (45 g., 0.18 mole) was added and the mixture left at room temperature for 48 hours. After a few minutes sodium toluene-*p*-sulphonate began to separate. This salt was collected

and dried at 140° (24.5 g., 98%). After the acetone had been removed (12' Dufton column), water (200 c.c. saturated with sodium chloride) was added and the mixture extracted with ether. The extracts, washed with 1% thiosulphate solution and then dried (MgSO₄), yielded the iodide (27.7 g., 91%), b. p. 94—96°/15 mm., n_D^{20} 1.55, d_4^{20} 1.577 (Found: I, 54.1. C₇H₉OI requires I, 53.8%). The overall yield from the alcohol was 72%.

1-2'-Furyl-5-iodopentane. Similar methods gave the crude pentyl toluene-*p*-sulphonate (87%) and thence the iodide (92%), b. p. 124—126°/16 mm., n_D^{20} 1.5331, d_4^{20} 1.489, $[R_L]_D^{20}$ 54.7 (Calc.: 55.07) (Found: I, 47.4. C₉H₁₃OI requires I, 48.1%).

1-2'-Furyl-11-iodoundecane. This iodide (60% yield from the undecanol) could not be distilled or crystallised.

ω -2'-Furylalkyl Cyanides.—1-Bromo-3-2'-furylpropane with aqueous-alcoholic potassium cyanide gave 3-2'-furylpropyl cyanide, b. p. 104—108°/10 mm., n_D^{20} 1.4712 (70% yield) (Found: N, 10.3. C₈H₉ON requires N, 10.4%).

5-2'-Furylpentyl cyanide, similarly prepared in 87% yield, had b. p. 147—149°/20 mm., n_D^{20} 1.4731 (Found: N, 8.5. C₁₀H₁₃ON requires N, 8.6%). The cyanide from crude 1-2'-furyl-11-iodoundecane was not purified.

ω -2'-Furyl-carboxylic Acids and Their Amides.— β -2-Furylpropionic acid. A solution of β -2-furylacrylic acid (13.8 g., 0.1 mole) in water (60 c.c.) containing potassium hydroxide (8.0 g.) and palladised strontium carbonate (2.0 g.) was reduced in 3 hours at room temperature with hydrogen at 4—5 atm. The solution was poured on crushed ice (10.0 g.) and vigorously stirred while hydrochloric acid was added until the mixture was acid to Congo-red. The precipitated solid was quickly filtered off; after being dried it was distilled, and then crystallised from light petroleum (b. p. 40—60°); it melted at 57—58°. The yield was 91% (Found: C, 59.8; H, 5.5. Calc. for C₈H₈O₃: C, 60.0; H, 5.7%). Amstutz and Plucker (*J. Amer. Chem. Soc.*, 1941, 63, 206) give m. p. 56.5—57.6°. To the acid (1 g.) in ether (5 c.c.) distilled phosphorus trichloride (0.4 g.) in ether (1 c.c.) was added and the mixture left for 1 hour at room temperature. The ether was removed and the liquid poured immediately with vigorous stirring into aqueous ammonia (20 c.c.; d 0.880) and crushed ice (10 g.). The amide (75%), crystallised from water containing a little ethanol, melted at 107—108° (Found: N, 9.5. C₇H₉O₂N requires N, 10.0%).

γ -2-Furylbutyric acid. Hydrolysis of 3-2'-furylpropyl cyanide with aqueous-alcoholic potassium hydroxide for 8 hours gave the oily acid (80%), b. p. 108—110°/0.4 mm., n_D^{20} 1.4796, d_4^{20} 1.1307, $[R_L]_D^{20}$ 38.7 (calc.: 39.19) (Hofmann, Bridgwater, and Axelrod, *J. Amer. Chem. Soc.*, 1949, 71, 1253, give b. p. 94—117°/0.03 mm.) (Found: C, 62.3; H, 6.8. Calc. for C₈H₁₀O₃: C, 62.3; H, 6.5%). The amide, made as above, crystallised from water with a little ethanol in plates, m. p. 88—89° (Found: N, 9.4. C₈H₁₁O₂N requires N, 9.2%).

δ -2-Furylvaleric acid. (a) Hydrogenation of potassium 5-2'-furylpenta-2:4-dienoate in water (with Pd-SrCO₃) at 4—5 atm. was complete in 40 minutes at room temperature and gave a solid acid (88%), m. p. 42—43° after crystallisation from light petroleum (Hofmann, *J. Amer. Chem. Soc.*, 1944, 66, 51, gives m. p. 42—43°) (Found: C, 64.4; H, 7.3. Calc. for C₉H₁₂O₃: C, 64.3; H, 7.2%). The amide, plates from very dilute alcohol, melted at 116—117° (Found: N, 8.1. C₉H₁₃O₂N requires N, 8.4%). (b) β -2-Furylacraldehyde, malonic acid, pyridine, and piperidine acetate gave 4-2'-furylbuta-1:3-diene-1:1-dicarboxylic acid (53%), m. p. 190—195° (decomp.). Hofmann (*loc. cit.*) gives m. p. 190—195°. The dipotassium salt of this acid was reduced with hydrogen and palladised strontium carbonate to a syrup which, on decarboxylation in pyridine, gave δ -2-furylvaleric acid, m. p. 42—43°. (c) 5-2'-Furylpent-2-enoic acid was reduced in aqueous potassium hydroxide with hydrogen (Pd-SrCO₃) in 1 hour, giving a 73% yield of needles, m. p. 42—43°. (d) 1-2'-Furyl-3-iodopropane and ethyl sodiomalonate gave diethyl 4-2'-furylbutane-1:1-dicarboxylate, b. p. 105—112°/0.1 mm. Hydrolysis and decarboxylation at 100°/15 mm. gave the valeric acid, b. p. 120—130°/0.1 mm., m. p. 42—43°.

6-2'-Furylhexanoic acid. (a) 5-2'-Furylpentyl cyanide, hydrolysed for 42 hours in aqueous-alcoholic potassium hydroxide, gave a pale yellow oil which was taken up in ether. The ethereal solution, shaken with *n*-sodium carbonate solution and then acidified at 0°, gave an acid, b. p. 160—180°/0.01 mm., m. p. 18—19°, n_D^{20} 1.4779, d_4^{20} 1.080, $[R_L]_D^{20}$ 47.75 (calc.: 48.42) (Found: C, 65.5; H, 8.0. C₁₀H₁₄O₃ requires C, 65.9; H, 7.8%). The amide, colourless plates from aqueous ethanol, melted at 81—82° (Found: N, 7.5. C₁₀H₁₅O₂N requires N, 7.7%). (b) To the Grignard reagent from 1-2'-furyl-5-iodopentane solid carbon dioxide was added, giving a 50% yield of acid, b. p. 114—116°/0.3 mm., n_D^{20} 1.4769, m. p. 18—19°.

7-2'-Furylheptanoic acid. (a) Hydrogenation of potassium 7-2'-furylhepta-2:4:6-trienoate in water (Pd-SrCO₃) gave the saturated acid which, crystallised from light petroleum, melted

at 35—36° (yield 86%) (Found : C, 67.2; H, 8.2. $C_{11}H_{16}O_3$ requires C, 67.3; H, 8.2%). The *amide*, lustrous plates from aqueous ethanol, melted at 96—97° (Found : N, 6.9. $C_{11}H_{17}O_2N$ requires N, 7.2%). (b) 1-Bromo-5-2'-furylpentane and ethyl sodiomalonate gave diethyl 6-2'-furylhexane-1 : 1-dicarboxylate (67%). Hydrolysis (68 hours) followed by decarboxylation gave needles (63%), m. p. 35—36°.

12-2'-Furyldodecanoic acid. 1-2'-Furyl-11-iodoundecane was converted into the nitrile, hydrolysis of which gave the *acid* in plates (from light petroleum), m. p. 41—42° (Found : C, 72.3; H, 9.9. $C_{16}H_{26}O_3$ requires C, 72.1; H, 9.8%). The *amide*, plates from aqueous ethanol, melted at 119—120° (Found : N, 5.0. $C_{16}H_{27}O_2N$ requires N, 5.3%).

1-2'-Furyl-3 : 3-dimethoxyprop-1-ene.—β-2-Furylacraldehyde (50 g.), dry methyl alcohol (90 c.c.), and phosphoric acid (0.4 g. of 100%) were kept for 12 hours at room temperature. After neutralisation with methyl-alcoholic sodium methoxide and addition of water, ether extracted the *acetal* (21 g., 30%), b. p. 112—114°/25 mm., n_D^{20} 1.5014 (Found : C, 64.1; H, 7.3. $C_9H_{12}O_3$ requires C, 64.3; H, 7.1%).

3 : 3-Diethoxy-1-2'-furylprop-1-ene.—The acraldehyde (42 g.) was dissolved in absolute ethanol (25 c.c.) containing ammonium nitrate (1.5 g.) (cf. Fischer and Baer, *Helv. Chim. Acta*, 1935, 18, 514) and ethyl orthoformate (72 g.). After 10 minutes' refluxing the solution was filtered while hot. To the cold filtrate ether and then excess of 10% aqueous ammonia were added. There were obtained 42 g. (66%) of unsaturated *acetal*, b. p. 110—114°/22 mm., n_D^{20} 1.4973 (Found : C, 67.5; H, 8.1. $C_{11}H_{16}O_3$ requires C, 67.3; H, 8.2%).

1 : 1-Dimethoxy-3-2'-furylpropane.—Hydrogenation of the dimethoxypropene (above) with hydrogen at 4 atm. and room temperature (Pd-SrCO₃) gave, in 10 minutes, the dimethoxypropane (93%), b. p. 109°/30 mm., n_D^{20} 1.4546 (Found : C, 63.7; H, 8.6. Calc. for $C_9H_{14}O_3$: C, 63.5; H, 8.3%). Wienhaus and Leonhardi (*Chem. Abs.*, 1930, 24, 2127) give b. p. 77°/4 mm., n_D^{20} 1.4550.

Similarly obtained, 1 : 1-diethoxy-3-2'-furylpropane had b. p. 110—115°/22 mm., n_D^{20} 1.4586. It decomposed rapidly and immediate analysis was essential (Found : C, 67.2; H, 9.1. $C_{11}H_{18}O_3$ requires C, 66.7; H, 9.2%).

β-2'-Furylpropaldehyde.—3-2'-Furyl-1 : 1-dimethoxypropane (8.5 g.) was rapidly hydrolysed in 30 c.c. of cold, aqueous-ethanolic hydrochloric acid (40 : 59 : 1 by vol.). After neutralisation with aqueous sodium carbonate the mixture yielded to ether β-2'-furylpropaldehyde (5.7 g., 90%), b. p. 80—85°/15 mm., n_D^{20} 1.4771 (Found : C, 67.5; H, 6.3. Calc. for $C_7H_8O_2$: C, 67.8; H, 6.5%). Wienhaus and Leonhardi (*loc. cit.*) give b. p. 59—61°/4 mm., n_D^{20} 1.4782. The diethyl acetal was similarly hydrolysed.

1-2'-Furylpentane.—1-2'-Furylpent-1-ol, prepared in 72% yield by the action of *n*-butylmagnesium bromide in ether on an ethereal solution of furfuraldehyde (Paul, *Bull. Soc. chim.*, 1935, 2, 2223), had b. p. 107—110°/15 mm., n_D^{20} 1.4752 (Found : C, 69.9; H, 8.8. Calc. for $C_9H_{14}O_2$: C, 70.0; H, 9.1%). Dehydration of this was best carried out by passing the vapour with the aid of carbon dioxide over alumina at 250—270° (Paul, *loc. cit.*); the yield was 34%. Other methods, refluxing with iodine or with copper sulphate, or stirring with phosphoric oxide, gave only tars. The olefin yielded a main fraction of b. p. 66—67°/16 mm., n_D^{20} 1.5007 (Found : C, 79.5; H, 8.9. $C_9H_{12}O$ requires C, 79.4; H, 8.9%), presumably 1-2'-furylpent-1-ene, but the position of the double bond was not determined.

The pentene (13.6 g.) in ethanol (60 c.c.) was completely hydrogenated at 4 atm. (Pd-SrCO₃; 1.0 g.) at room temperature. The product, b. p. 64—66°/23 mm., n_D^{20} 1.4478, was obtained in 88% yield (Found : C, 78.3; H, 10.3. Calc. for $C_9H_{14}O$: C, 78.2; H, 10.2%). Normant (*Ann. Chim.*, 1942, 17, 335) gives n_D^{19} 1.4482. This furylpentane appeared to be stable to aqueous acids, but its rapid polymerisation in warm aqueous-alcoholic hydrochloric acid showed that the sparing solubility had masked the reaction.

1-(Tetrahydro-2'-furyl)pentane.—When 1-2'-furylpent-1-ene (41 g.) in ethanol (80 c.c.) was shaken with hydrogen at 4 atm. in presence of Raney nickel (Mozingo, *Org. Synth.*, 1941, 21, 15) rapid absorption occurred during 8 minutes, followed by slower reduction, complete in 2 hours. The product gave a main fraction of tetrahydrofurylpentane, b. p. 78—80°/20 mm., n_D^{20} 1.4326 (30.5 g., 75%) (Found : C, 75.6; H, 12.6. Calc. for $C_9H_{18}O$: C, 76.0; H, 12.8%). Paul (*Bull. Soc. chim.*, 1938, 5, 1053) gives b. p. 70—71°/14 mm., n_D^{20} 1.4362. n_D^{20} (calc.) should be approx. 1.4322.

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