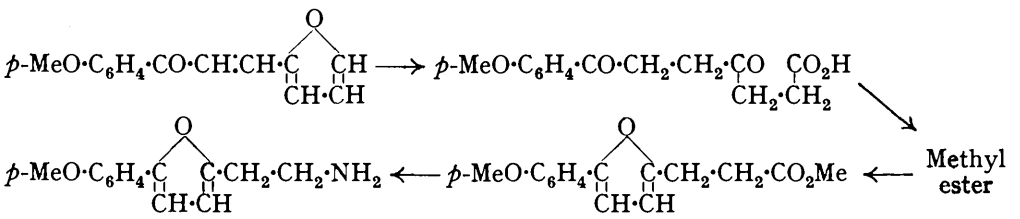
355. β-*Phenylfurylethylamine and Analogous Derivatives of Thiophen and Pyrrole.*

By Sir Robert Robinson and W. M. Todd.

4 : 7-Diketo-7-arylheptoic acids have been converted into furan, thiophen and pyrrole derivatives and then by Curtius degradation into β-substituted ethylamines. The processes involved are illustrated by the following example :



The bases have been prepared in order that their physiological properties may be investigated.

Histamine, isolated from ergot of rye (Barger and Dale, J., 1910, **97**, 2592), was shown to be 4(or 5)-β-aminoethyliminazole, and was synthesised by Pyman (J., 1911, **99**, 668). On account of its remarkable physiological effects, particularly on the blood pressure and the uterine muscle (Dale and Laidlaw, *J. Physiol.*, 1910, **41**, 318), it was considered desirable to prepare compounds possessing the ethanamine chain linked to heterocyclic rings other than iminazole.

Several such bases have already been obtained, notably β-2-furylethylamine (Windaus and Dalmer, *Ber.*, 1920, **53**, 2306), β-3-indolylethylamine (Ewins, J., 1911, **99**, 270; Majima and Hoshino, *Ber.*, 1925, **58**, 2042) and β-2-thienylethylamine (Barger and Easson, J., 1938, 2100).

The discovery by Kehrer and Igler (*Ber.*, 1899, **32**, 1178; 1901, **34**, 1263) that furfurylideneacetone and furfurylideneacetophenone are convertible into diketo-acids $R{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H$ rendered accessible a series of convenient intermediates for the syntheses of substituted pyrryl-, furyl-, or thienyl-propionic acids. Thus 4 : 7-diketo-7-phenylheptoic acid, from furfurylideneacetophenone, has been transformed by suitable ring closures and subsequent application of the Curtius degradation (*Ber.*, 1894, **27**, 778) into β-2-(5-*phenylfuryl*)*ethylamine hydrochloride* and β-2-(5-*phenylthienyl*)*ethylamine hydrochloride* in good yield, and into β-2-(5-*phenylpyrryl*)*ethylamine hydrochloride* in poor yield owing to the reactivity of the pyrrole nucleus.

Starting with *p*-methoxyacetophenone, β-2-(5-p-*methoxyphenylfuryl*)*ethylamine hydrochloride* and β-2-(5-p-*methoxyphenylthienyl*)*ethylamine hydrochloride* have been prepared in a similar manner.

Attempts to extend the work to the series from 4 : 7-diketo-octoic acid have not been successful, but have brought to light some points of interest mentioned in the experimental section.

It was found impossible to obtain the thienyl compounds directly from the diketo-acids themselves, because treatment of these with phosphorus pentasulphide in benzene solution afforded furan derivatives. The methyl esters gave the desired results when treated with phosphorus pentasulphide.

β-2-(5-*Phenyltetrahydrofuryl*)*ethylamine hydrochloride* has been prepared by catalytic hydrogenation of β-2-(5-phenylfuryl)ethylamine hydrochloride.

The physiological properties of the new bases are under examination by Professor J. A. Gunn.

Experimental.

β-2-(5-*Phenylpyrryl*)*propionic Acid* (Kehrer and Igler, *Ber.*, 1902, **35**, 2009).—This acid was best obtained by heating an intimate mixture of diketophenylheptoic acid (10 g.) and ammonium

acetate (50 g.) until a homogeneous brown liquid resulted. This was poured into water, and the product crystallised from water, forming characteristic dendritic, crystalline aggregates, m. p. 140—141° (yield, 87%).

Ethyl β-2-(5-*Phenylpyrryl*)*propionate*.—A mixture of β-2-(5-phenylpyrryl)propionic acid (10 g.), alcohol (100 c.c.), and concentrated sulphuric acid (4 g.) was refluxed for 4 hours. The *product*, isolated by means of ether, crystallised from methyl alcohol in small, pinkish-white needles, m. p. 103° (yield, 82%) (Found: N, 5·8. $C_{15}H_{17}O_2N$ requires N, 5·8%).

β-2-(5-*Phenylpyrryl*)*propionhydrazide*.—Ethyl β-2-(5-phenylpyrryl)propionate was refluxed with a small excess of hydrazine hydrate for an hour. The *product* separated, on cooling, as a whitish crystalline solid. This crystallised from hot water in fine white needles, m. p. 137° (yield, 80%) (Found: N, 18·6. $C_{13}H_{15}ON_3$ requires N, 18·3%).

β-2-(5-*Phenylpyrryl*)*ethylamine Hydrochloride*.—β-2-(5-Phenylpyrryl)propionhydrazide (7 g.) and sodium nitrite (4 g. in 10 c.c. of water) were covered with a layer of ether, and 2N-hydrochloric acid (30 c.c.) then added with good stirring and ice-cooling. A considerable amount of decomposition occurred and the azide passed into the ethereal layer, which was separated and dried over sodium sulphate. Methyl alcohol (70 c.c.) was then added to the ethereal solution, and the ether removed. After refluxing for 2 hours on the steam-bath, the excess of methyl alcohol was removed, and the methylurethane was obtained as a sticky, reddish-brown oil. This was refluxed with a saturated solution of barium hydroxide in methyl alcohol (100 c.c.) for 36 hours. After filtration from barium carbonate, water was added, and the solution extracted with ether. Dry hydrogen chloride was passed into the dried ethereal solution with cooling in ice. The *amine hydrochloride* separated as a salmon-pink crystalline solid contaminated with oily impurity; it was collected, purified by solution in dry alcohol (charcoal) and reprecipitation with ether, and obtained as a faintly pink, crystalline solid, m. p. 225°. The yield was unsatisfactory (Found: C, 64·8; H, 6·9; N, 12·6. $C_{12}H_{14}N_2$,HCl requires C, 64·7; H, 6·7; N, 12·6%).

β-2-(5-*Phenylfuryl*)*propionic Acid*.—A mixture of 4 : 7-diketo-7-phenylheptoic acid (20 g.), phosphoric anhydride (15 g.), and benzene (300 c.c.) was refluxed on the steam-bath for 2 hours. The benzene solution was then decanted, and the solvent removed, finally under reduced pressure. The *product* crystallised on cooling (yield, 88%). A sample, recrystallised from toluene, afforded white, elongated, hexagonal plates, m. p. 116° (Found: C, 72·6; H, 5·8. $C_{13}H_{12}O_3$ requires C, 72·2; H, 5·5%).

Ethyl β-2-(5-*Phenylfuryl*)*propionate*.—(A) A mixture of β-2-(5-phenylfuryl)propionic acid (10 g.), alcohol (120 c.c.), and concentrated sulphuric acid (4 g.) was refluxed for 4 hours. The *ester*, isolated in the usual manner, had b. p. 165—167°/2—3 mm. (yield, almost theoretical). A portion redistilled for analysis solidified in the ice chest; m. p. 20—21°, $n_D^{28°}$ 1·5508 (Found: C, 73·7; H, 6·4. $C_{15}H_{16}O_3$ requires C, 73·8; H, 6·5%).

(B) A mixture of 4 : 7-diketo-7-phenylheptoic acid (24 g.), alcohol (250 c.c.), and concentrated sulphuric acid (7 c.c.) was refluxed for 4 hours, and the product worked up in the usual way by ether extraction. The main portion of the product (18 g.) distilled between 160° and 190°/2—3 mm. and was the required ester, the sulphuric acid present having been sufficient to cause ring closure. A small fraction, b. p. 200—210°/2—3 mm., was also collected and eventually solidified to a mass of needles. The substance gave an orange precipitate on treatment with Brady's reagent. A sample crystallised from light petroleum (b. p. 40—60°) in white needles, m. p. 23—25°, and analysis showed it to be *ethyl* 4 : 7-*diketo*-7-*phenylheptoate* (Found: C, 68·8; H, 6·8. $C_{15}H_{18}O_4$ requires C, 68·7; H, 6·9%).

β-2-(5-*Phenylfuryl*)*propionhydrazide*.—Ethyl β-2-(5-phenylfuryl)propionate (10 g.) was refluxed with a slight excess of hydrazine hydrate until a clear liquid was obtained. The product solidified, on cooling, as a white crystalline mass (yield, theoretical). The *hydrazide* crystallised from hot water in fine, white, feathery needles, m. p. 110° (Found: N, 12·1. $C_{13}H_{14}O_2N_2$ requires N, 12·2%).

Methyl β-2-(5-*Phenylfuryl*)*ethylcarbamate*.—β-2-(5-Phenylfuryl)propionhydrazide (10 g.), once crystallised, was covered with concentrated hydrochloric acid and a layer of ether. An aqueous solution of sodium nitrite (6 g.) was added with rapid stirring and ice-cooling; the azide passed into the ethereal layer, which was separated and dried. Methyl alcohol (100 c.c.) was added, the ether removed, and the solution refluxed for 2 hours. The methyl alcohol was distilled, finally under diminished pressure; the brown oily residue solidified on cooling (yield, 80—90%). The *urethane* crystallised from light petroleum (b. p. 60—80°) in white feathery aggregates, m. p. 59—60° (Found: N, 6·0. $C_{14}H_{15}O_3N$ requires N, 5·7%).

β-2-(5-*Phenylfuryl*)*ethylamine Hydrochloride*.—The above urethane was refluxed with a

saturated solution of methyl-alcoholic barium hydroxide (150 c.c.) for 24 hours. The product was worked up as described for the pyrryl base and the *hydrochloride* was obtained from the ethereal solution as a white crystalline solid (yield, 50—60%). The salt crystallised from chloroform in fine white plates with a nacreous lustre, m. p. 205—206°, easily soluble in water and hot alcohol and insoluble in acetone (Found : C, 64·4; H, 6·1; N, 6·2. $C_{12}H_{13}ON,HCl$ requires C, 64·4; H, 6·3; N, 6·3%). Aqueous sodium hydroxide liberated the free base as an oil.

The orange-yellow *picrate*, crystallised from alcohol, had m. p. 200° (Found : N, 13·7. $C_{12}H_{13}ON,C_6H_3O_7N_3$ requires N, 13·5%). The *benzoyl* derivative crystallised from aqueous alcohol in fine white needles, m. p. 121° (Found : N, 4·8. $C_{19}H_{17}O_2N$ requires N, 4·8%), and the *acetyl* derivative in white, diamond-shaped plates, m. p. 72° (Found : N, 6·2. $C_{14}H_{15}O_2N$ requires N, 6·1%).

Methyl 4 : 7-*Diketo*-7-*phenylheptoate*.—Powdered diketophenylheptoic acid (20 g.) was covered with ether, cooled in ice, and treated with a slight excess of the calculated quantity of diazomethane (from 25—30 g. of nitrosomethylurea) in ethereal solution. After the brisk evolution of nitrogen ceased, the solution was kept for an hour at room temperature. It was then shaken with dilute hydrochloric acid to remove the excess of diazomethane, and with aqueous sodium carbonate to remove any unchanged acid. The ethereal solution was dried over sodium sulphate, the ether removed, and the oily product distilled as a light yellow oil, b. p. 194—198°/2 mm. The *ester* eventually crystallised in four-sided plates, m. p. 41° (yield, 88%). A fraction for analysis had b. p. 197°/2 mm., $n_D^{28°}$ 1·5180 (Found : C, 67·8; H, 6·4. $C_{14}H_{16}O_4$ requires C, 67·8; H, 6·4%).

Methyl β-2-(5-*Phenylthienyl*)*propionate*.—An intimate mixture of methyl diketophenylheptoate (10 g.) and phosphorus pentasulphide (10 g.) was heated to 95° and stirred until evolution of hydrogen sulphide had ceased (about 1 hour). The product, a thick brown syrup, solidified after a few hours. The whole was extracted with ether, the filtered solution shaken with aqueous sodium carbonate and dried, and the ether removed; the residue solidified on cooling. It crystallised from a small amount of alcohol (charcoal) in white plates with a nacreous lustre, m. p. 75° (yield of crude ester, *ca.* 50%) (Found : C, 65·8; H, 5·7; S, 12·4. $C_{14}H_{14}O_2S,0·5H_2O$ requires C, 65·9; H, 5·5; S, 12·5%).

β-2-(5-*Phenylthienyl*)*propionic Acid*.—The methyl ester was hydrolysed for 2 hours with boiling aqueous sodium hydroxide, and the solution cooled and acidified. The *product* crystallised from benzene in white plates, m. p. 148° (Found : C, 64·3; H, 5·1. $C_{13}H_{12}O_2S,0·5H_2O$ requires C, 64·7; H, 5·3%).

β-2-(5-*Phenylthienyl*)*propionhydrazide*, prepared from the corresponding methyl ester in the usual way (yield, theoretical), crystallised from alcohol in long, white prisms, m. p. 151° (Found : N, 11·5. $C_{13}H_{14}ON_2S$ requires N, 11·4%).

Methyl β-2-(5-*phenylthienyl*)*ethylcarbamate*, obtained from the hydrazide in a manner exactly analogous to that already described for the furanoid urethane, separated from light petroleum (b. p. 100—120°) in white crystals, m. p. 100° (Found : N, 5·3. $C_{14}H_{15}O_2NS$ requires N, 5·4%).

β-2-(5-*Phenylthienyl*)*ethylamine Hydrochloride*.—Unlike the salts already described, this compound could be obtained from the urethane by prolonged hydrolysis with concentrated hydrochloric acid. It was more convenient, however, to adopt the method of hydrolysis by methyl-alcoholic baryta previously described. The *hydrochloride* crystallised from alcohol in white, rhombic plates with a nacreous lustre, m. p. 266° with previous softening (yield from the urethane, 50—60%) (Found : C, 60·4; H, 5·7; N, 6·2. $C_{12}H_{13}NS,HCl$ requires C, 60·1; H, 5·9; N, 5·9%).

The *picrate* crystallised from alcohol in scarlet rods, m. p. 217° (Found : N, 12·6. $C_{12}H_{13}NS,C_6H_3O_7N_3$ requires N, 12·9%). The *benzoyl* derivative had m. p. 141° (Found : N, 4·8. $C_{19}H_{17}ONS$ requires N, 4·6%), and the *acetyl* derivative m. p. 128° (Found : N, 5·7. $C_{14}H_{15}ONS$ requires N, 5·7%), both crystallised from aqueous alcohol.

Furfurylidene-p-*methoxyacetophenone*.—A mixture of freshly distilled furfuraldehyde (42 g.) and *p*-methoxyacetophenone (64 g.) was added to methyl-alcoholic sodium methoxide (100 c.c. of 1%) with shaking and cooling in ice-water and was then kept for 2—3 hours at room temperature. The crystalline *product* induced to separate by seeding or scratching (yield, dry, 80—90%) formed straw-yellow needles, m. p. 79°, from light petroleum (b. p. 60—80°) (Found : C, 73·7; H, 5·3. $C_{14}H_{12}O_3$ requires C, 73·7; H, 5·3%).

4 : 7-*Diketo*-7-p-*methoxyphenylheptoic Acid*.—Furfurylidene-*p*-methoxyacetophenone (150 g.) was treated with hot alcoholic hydrochloric acid as described for furfurylideneacetophenone by Kehrer and Igler (*loc. cit.*). The *acid* crystallised in long, straw-yellow needles (yield, 50—55%).

A sample recrystallised from hot water formed white needles, m. p. 119° (Found: C, 63·6; H, 5·9. $C_{14}H_{16}O_5$ requires C, 63·7; H, 6·1%).

β-2-(5-p-*Methoxyphenylpyrryl*)*propionic Acid.*—This was prepared analogously to β-2-(5-phenylpyrryl)propionic acid; the yield was 80%. Some difficulty was experienced in preparing an analytically pure sample, but this was eventually accomplished by esterification of the crude acid and hydrolysis of the purified derivative. The *acid* crystallised from dilute acetic acid in plates, m. p. 170—171° (Found: C, 68·5; H, 6·1; N, 6·1. $C_{14}H_{15}O_3N$ requires C, 68·6; H, 6·1; N, 5·7%).

The acid was esterified by means of boiling 5% alcoholic sulphuric acid. *Ethyl* β-2-(5-p-*methoxyphenylpyrryl*)*propionate*, obtained in excellent yield, solidified to a mass of needles and crystallised from a small amount of methyl alcohol in hexagonal prismatic needles, m. p. 103° (Found: C, 69·9; H, 7·0; N, 5·4. $C_{16}H_{19}O_3N$ requires C, 70·2; H, 7·0; N, 5·2%).

β-2-(5-p-*Methoxyphenylpyrryl*)*propionhydrazide*, obtained from the ester in the usual way, in theoretical yield, separated from hot water in white crystals, m. p. 169° (Found: N, 16·2. $C_{14}H_{17}O_2N_3$ requires N, 16·2%). Attempts to convert this hydrazide into the azide and thence into the urethane and amine were unsuccessful owing to profound decomposition in the first stage of the process.

β-2-(5-p-*Methoxyphenylfuryl*)*propionic Acid.*—A mixture of 4 : 7-diketo-7-*p*-methoxyphenylheptoic acid (20 g.), phosphoric anhydride (15 g.), and benzene (300 c.c.) was refluxed for 2 hours on the steam-bath. The product, obtained by decanting and then removing the benzene under reduced pressure, formed a crystalline mass (yield, 70—75%). The *acid* crystallised from benzene in long, colourless, hexagonal plates, m. p. 141° (Found: C, 68·3; H, 5·6. $C_{14}H_{14}O_4$ requires C, 68·3; H, 5·7%).

The *ethyl* ester, prepared in the usual way, crystallised from aqueous methyl alcohol in small, white, feathery needles, b. p. 189—195°/2 mm., m. p. 52° (Found: C, 70·2; H, 6·2. $C_{16}H_{18}O_4$ requires C, 70·1; H, 6·5%). Yield, 80—90%.

The *hydrazide* crystallised from hot water in white needles, m. p. 136° (Found: N, 11·1. $C_{14}H_{16}O_3N_2$ requires N, 10·8%).

Methyl β-2-(5-p-*Methoxyphenylfuryl*)*ethylcarbamate.*—This was prepared like the phenylfuryl analogue. The thick brown oil decomposed on attempted distillation; it partly solidified and was purified with some difficulty by crystallisation, first from light petroleum (b. p. 100—120°) and then from light petroleum (b. p. 60—80°). The *substance* was obtained in white, feathery clusters, m. p. 89° (Found: N, 5·4. $C_{15}H_{17}O_4N$ requires N, 5·1%).

β-2-(5-p-*Methoxyphenylfuryl*)*ethylamine Hydrochloride.*—The pure urethane was refluxed with an excess of saturated methyl-alcoholic barium hydroxide for 24 hours and the *hydrochloride* was isolated as previously described, but in this case the yield was unsatisfactory. The salt crystallised from alcohol in white, nacreous plates, m. p. 240° (Found: C, 61·7; H, 6·4. $C_{13}H_{15}O_2N$,HCl requires C, 61·5; H, 6·3%).

Methyl 4 : 7-*Diketo*-7-p-*methoxyphenylheptoate.*—4 : 7-Diketo-7-*p*-methoxyphenylheptoic acid (15 g.) was treated with an etheral solution of diazomethane (5—6 g.) with ice-cooling. The *product* was distilled, b. p. 200—220°/2 mm. (yield, 90%). The light yellow oil solidified in long, white needles, m. p. 48°. A portion was redistilled for analysis, b. p. 248°/3 mm. (Found: C, 64·8; H, 6·4. $C_{15}H_{18}O_5$ requires C, 64·7; H, 6·5%).

Methyl β-2-(5-p-*Methoxyphenylthienyl*)*propionate.*—An intimate mixture of methyl 4 : 7-diketo-7-*p*-methoxyphenylheptoate (10 g.) and phosphorus pentasulphide (10 g.) was heated to 90—100° and stirred (*ca.* 1 hour) until no more hydrogen sulphide was evolved. The dark brown product, which crystallised on keeping, was extracted with hot ethyl acetate, and the solvent removed from the filtered solution, finally under reduced pressure; the cooled residue was a crystalline mass (yield, 50—60%). The *ester* crystallised from alcohol in white plates, m. p. 94° (Found: C, 65·5; H, 5·6. $C_{14}H_{14}O_3S$ requires C, 65·2; H, 5·8%).

β-2-(5-p-*Methoxyphenylthienyl*)*propionic Acid.*—The methyl ester was hydrolysed by refluxing with an excess of aqueous sodium hydroxide for 2 hours. The *acid* crystallised from benzene in white, glistening plates, m. p. 178° (Found: C, 64·5; H, 5·8. $C_{14}H_{14}O_3S$ requires C, 64·2; H, 5·4%).

β-2-(5-p-*Methoxyphenylthienyl*)*propionhydrazide*, prepared from the methyl ester in theoretical yield, crystallised from alcohol, in which it was sparingly soluble, in clusters of white, rhombic plates, m. p. 165° (Found: N, 10·1. $C_{14}H_{16}O_2N_2S$ requires N, 10·0%).

Methyl β-2-(5-p-*methoxyphenylthienyl*)*ethylcarbamate*, obtained as usual, separated from light petroleum (b. p. 100—120°) as a light yellow powder, m. p. 112° (yield, 80%) (Found: N, 5·0. $C_{15}H_{17}O_3NS$ requires N, 4·8%).

β-2-(5-p-*Methoxyphenylthienyl*)*ethylamine Hydrochloride*.—Hydrolysis of the urethane could be effected either by means of concentrated hydrochloric acid or by boiling alcoholic baryta during 24 hours. The latter method proved the more satisfactory, although it only gave good results when the pure urethane was used. The *hydrochloride* crystallised from alcohol in white plates with a characteristic nacreous lustre, m. p. 283° (yield, 60%) (Found : C, 57·8; H, 5·8; N, 5·5. $C_{13}H_{15}ONS,HCl$ requires C, 57·9; H, 5·9; N, 5·2%), easily soluble in hot water and very sparingly soluble in acetone.

The *acetyl* derivative separated from dilute acetic acid in white crystals, m. p. 145° (Found : N, 4·8. $C_{15}H_{17}O_2NS$ requires N, 5·1%).

4 : 7-*Diketo-octoic Acid* (Kehrer and Igler, *Ber.*, 1899, **32**, 1176).—This was prepared, not as described, but in a manner exactly analogous to that used in the preparation of diketophenylheptoic acid. As the acid did not separate completely from water, the solution was concentrated to a small volume. The crude acid so obtained was purified by solution in benzene, decantation from an insoluble residue, and precipitation with light petroleum (b. p. 60—80°). The light yellow solid was freed from hydrogen chloride by gentle warming in a current of air (yield, 20—25%). The acid crystallised from ether in white, hexagonal plates, m. p. 75°.

β-2-(5-*Methylfuryl*)*propionic Acid*.—A mixture of 4 : 7-diketo-octoic acid (20 g.), phosphoric anhydride (15 g.), and benzene (300 c.c.) was refluxed for 2 hours. The benzene solution was decanted, and the benzene removed; the residue solidified (yield, 50%), and crystallised from hot water in white needles, m. p. 54—55° (Found : C, 61·9; H, 6·5. $C_8H_{10}O_3$ requires C, 62·3; H, 6·5%).

Ethyl β-2-(5-*Methylfuryl*)*propionate*.—A mixture of β-2-(5-methylfuryl)propionic acid (10 g.), alcohol (120 c.c.), and concentrated sulphuric acid (5 g.) was refluxed for 4 hours. On distillation of the isolated product two fractions were collected : (1) b. p. 97°/2—3 mm., $n_D^{21°}$ 1·457 (Found : C, 63·6; H, 7·5. Calc. for $C_{10}H_{14}O_3$: C, 65·9; H, 7·7%); (2) b. p. 136°/2—3 mm., $n_D^{21°}$ 1·445 (75% of the product) (Found : C, 60·0; H, 8·0. Calc. for $C_{10}H_{16}O_4$: C, 60·0; H, 8·0%). The lower fraction was obviously an impure sample of the desired ester, but the esterification conditions evidently caused the furyl ring to open, yielding the diketo-ester. This was in contrast to the esterification of 4 : 7-diketo-7-phenylheptoic acid, where such conditions gave, largely, a ring-closed product.

When 4 : 7-diketo-octoic acid itself was esterified by refluxing with 5% alcoholic sulphuric acid, a mixture of diketo-ester and furyl ester was again obtained, the diketo-ester, however, predominating. Wichterle (*Coll. Czech. Chem. Comm.*, 1939, **11**, 171) has made similar observations on the esterification of 4 : 7-diketo-octoic acid.

Methyl β-2-(5-*Methylfuryl*)*propionate*.—In view of the mixed products obtained by the usual esterification methods, diazomethane was employed in this preparation. β-2-(5-Methylfuryl)propionic acid (10 g.) was covered with ether and treated with diazomethane (from 15 g. of nitrosomethylurea) in ether at 0°. The product (7·8 g.) had b. p. 83°/2—3 mm., $n_D^{20°}$ 1·465 (Found : C, 64·1; H, 7·2. $C_9H_{12}O_3$ requires C, 64·3; H, 7·2%).

Methyl 4 : 7-*diketo-octoate*, prepared from the acid by the action of diazomethane in ethereal solution, had b. p. 145°/5 mm., (redistilled) b. p. 140°/4 mm., $n_D^{28°}$ 1·4458 (Found : C, 57·8; H, 7·8. $C_9H_{14}O_4$ requires C, 58·1; H, 7·5%).

β-2-(5-*Phenyltetrahydrofuryl*)*ethylamine Hydrochloride*.—A mixture of β-2-(5-phenylfuryl)-ethylamine hydrochloride (1 g.), dissolved in the minimum quantity of alcohol, and palladised charcoal (17 c.c. of a 10% alcoholic suspension) was gently heated and shaken in an atmosphere of hydrogen. After 6·7 hours the required volume of hydrogen (200 c.c.) was absorbed. The filtered solution was concentrated and the separated solid was crystallised by dissolution in alcohol and precipitation with ether. The white crystals had m. p. 122° (Found : C, 63·0; H, 8·3. $C_{12}H_{17}ON,HCl$ requires C, 63·3; H, 7·9%). This *salt*, obtained in good yield, is freely soluble in water.

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