321. *A New Method for the Synthesis of Depsides.*

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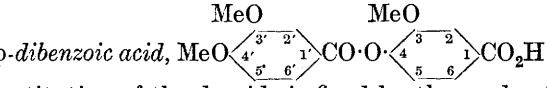
THE method consists in condensing an acid chloride with the sodium salt of a hydroxy-aldehyde and oxidising the resulting aldehyde with permanganate in methyl-alcoholic solution. It has several advantages over Fischer's method (condensation of the acid chloride directly with the disodium salt of the hydroxy-acid) : the yields are very good and there is no complication introduced by the simultaneous formation of depside and acid anhydride, separation of these being tedious and difficult owing to the low solubility of the feebly acidic depside in bicarbonate solution. The process seems to be of general application and it is hoped to extend it to the synthesis of polydepsides.

Didepsides derived from veratroyl chloride or anisoyl chloride and various hydroxy-aldehydes are now described. The positions of substituents in the ring carrying the carboxyl group are indicated by the numbers 1, 2, 3, etc., and those in the other ring by 1′, 2′, 3′, etc. ; p-*diprotocatechuic acid trimethyl ether*, for instance, is designated 3:3′:4′-*trimethoxy*-p-*dibenzoic acid*,  .

In each case the constitution of the depside is fixed by the mode of synthesis and confirmed by analysis. The free components of the depside—veratric acid, anisic acid, *p*-hydroxybenzoic acid, etc.—were shown not to be present by the absence of the characteristic colour tests for the phenolic acids with ferric chloride solution.

Condensation of the acid chloride with the sodium hydroxy-aldehyde usually proceeded quickly and was complete after two hours' shaking at room temperature. The depside aldehyde was always isolated from alkaline solution and was therefore free from acid, acid chloride, or hydroxy-aldehyde. The aldehydes crystallised readily from either dilute alcohol or dilute acetone and the yields were upwards of 70% of the theoretical.

Oxidation of the aldehydes was straightforward and the depsides were readily isolated. The crude 3′ : 4′-dimethoxy-*p*-dibenzoic, 4′-methoxy-*p*-dibenzoic, and 4′-methoxy-*m*-dibenzoic acids were gelatinous. Recrystallisation was effected in all cases by dilute acetone or dilute alcohol. The yields, after purification, were upwards of 70%.

p-*Diprotocatechualdehyde Trimethyl Ether* (3 : 3′ : 4′-*Trimethoxy*-p-*dibenzaldehyde*).—Solutions of vanillin (1·52 g.; 1 mol.) in Me_2CO (15 c.c.) and *N*-NaOH

(1 mol.) and of veratroyl chloride (2·1 g.; slight excess of 1 mol.) in Me_2CO (15 c.c.) were mixed, kept alkaline, and shaken for 2 hrs. After dilution with H_2O (6 vols.) and 12 hrs.' standing in the cold, the ppt. was collected, washed, and recrystallised from dil. EtOH; stout colourless needles, m. p. 124° (yield, 90%) [Found: C, 64·0; H, 5·1; OMe, 28·6. $C_{14}H_7O_3(OMe)_3$ requires C, 64·6; H, 5·1; OMe, 29·4%].

p-*Diprotocatechuic Acid Trimethyl Ether* (3 : 3′ : 4′-*Trimethoxy*-p-*dibenzoic Acid*).—To a boiling solution of *p*-diprotocatechualdehyde trimethyl ether (6 g.) in MeOH (100 c.c.), sat. $KMnO_4$ aq. (100 c.c.) was added drop by drop, the action being allowed to complete itself between each addition. The liquid was filtered hot, cooled, diluted with H_2O (5 vols.), and acidified with a few drops of AcOH. The cryst. ppt. was collected after 1 hr., washed, and recrystallised from dil. Me_2CO; colourless plates or prisms, m. p. 216—218° to a dark liquid (yield, 90%), slowly sol. in alkali bicarbonates but readily in dil. caustic soda [Found: C, 61·3; H, 4·9; OMe, 28·4. $C_{14}H_7O_4(OMe)_3$ requires C, 61·5; H, 4·8; OMe, 28·0%].

p-*Diprotocatechuyl Chloride Trimethyl Ether* (3 : 3′ : 4′-*Trimethoxy*-p-*dibenzoyl Chloride*).—*p*-Diprotocatechuic acid trimethyl ether (6 g.; 1 mol.) and thionyl chloride (5 g.; slight excess of 2 mols.) were heated under reflux for 2—3 hrs., the excess of the latter removed under reduced press., and the residue crystallised from Me_2CO–ligroin; stout yellowish needles, m. p. 129° (yield, 83%) [Found: Cl, 10·4; OMe, 25·9. $C_{14}H_6O_3Cl(OMe)_3$ requires Cl, 10·1; OMe, 26·6%].

The following aldehydes and acids were prepared by the methods described above.

3′ : 4′-*Dimethoxy*-o-*dibenzaldehyde* (from salicylaldehyde and veratroyl chloride), m. p. 102° (yield, 90%) [Found: C, 66·3; H, 5·0; OMe, 21·2. $C_{14}H_8O_3(OMe)_2$ requires C, 67·1; H, 4·9; OMe, 21·7%]. 3′ : 4′-*Dimethoxy*-o-*dibenzoic acid*, fine needles, m. p. 152° (yield, 80%) [Found: C, 63·5; H, 4·7; OMe, 20·1. $C_{14}H_8O_4(OMe)_2$ requires C, 63·6; H, 4·64; OMe, 20·5%].

3′ : 4′-*Dimethoxy*-m-*dibenzaldehyde*, needles, m. p. 120° (yield, 95%) (Found: C, 66·2; H, 5·0; OMe, 21·6%). 3′ : 4′-*Dimethoxy*-m-*dibenzoic acid*, plates, m. p. 167° (yield, 95%) (Found: C, 62·5; H, 4·7; OMe, 19·8%).

3′ : 4′-*Dimethoxy*-p-*dibenzaldehyde*, needles, m. p. 109° (yield, 85%) (Found: C, 67·0; H, 5·0; OMe, 21·2%). 3′ : 4′-*Dimethoxy*-p-*dibenzoic acid*, hair-like needles, m. p. 211—212° (yield, 70%) (Found: C, 62·8; H, 4·6; OMe, 19·9%).

4′-*Methoxy*-o-*dibenzaldehyde*, prisms, m. p. 85° (yield, 90%) [Found: C, 69·0; H, 4·7; OMe, 12·0. $C_{14}H_9O_3(OMe)$ requires C, 70·4; H, 4·7; OMe, 12·1%]. 4′-*Methoxy*-o-*dibenzoic acid*, stout needles, m. p. 132° (yield, 70%) [Found: C, 65·2; H, 4·5; OMe, 11·1. $C_{14}H_9O_4(OMe)$ requires C, 66·2; H, 4·4; OMe, 11·4%].

4′-*Methoxy*-m-*dibenzaldehyde*, needles, m. p. 102° (probably somewhat low) (yield, 68%) (Found: C, 69·8; H, 4·8; OMe, 11·9%). 4′-*Methoxy*-m-*dibenzoic acid*, hair-like needles, m. p. 196° (yield, 80%) (Found: C, 66·1; H, 4·45; OMe, 11·8%).

4′-*Methoxy*-p-*dibenzaldehyde*, prisms, m. p. 113° (yield, 70%) (Found: C, 69·7; H, 4·7; OMe, 11·6%). 4′-*Methoxy*-p-*dibenzoic acid*, hair-like needles, m. p. 212° (yield, 70%) (Found: C, 65·5; H, 4·4; OMe, 11·0%).

3 : 4′-*Dimethoxy*-p-*dibenzaldehyde*, small prisms, m. p. 136° (yield, 85%)

(Found : C, 66·8; H, 5·0; OMe, 22·0%). 3 : 4′-*Dimethoxy*-p-*dibenzoic acid*, plates, m. p. 171° (yield, 80%) (Found : C, 63·2; H, 4·8; OMe, 21·0%).

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