XXIII.—*The Condensation of Furfuraldehyde with Sodium Succinate.*

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IN the course of an investigation on the higher acids of the succinic series, the authors, in seeking new methods of synthesis, selected furfuraldehyde as a starting point with the intention of converting it into acids of the type $C_4H_3O \cdot CH:CH \cdot [CH_2]_n \cdot CO_2H$, and these into suberic acid and its homologues, by processes similar to those by which Baeyer obtained *n*-pimelic acid, $CO_2H \cdot [CH_2]_5 \cdot CO_2H$, from furylacrylic acid, $C_4H_3O \cdot CH:CH \cdot CO_2H$ (*Ber.*, 1877, 10, 695, 1358).

It was anticipated that β -furfurylidenepropionic acid (furylisocrotonic acid), $C_4H_3O \cdot CH:CH \cdot CH_2 \cdot CO_2H$, the simplest compound of the above type, would be readily formed, according to Fittig's method, by the condensation of furfuraldehyde with sodium succinate in the presence of acetic anhydride (*Annalen*, 1883, 216, 97 ; 1889, 255, 1—142).

A considerable number of experiments, which have been carried out under a great variety of conditions, show beyond doubt, however, that furfuraldehyde behaves abnormally. Neither furylparaconic acid nor furylisocrotonic acid could be isolated, but two unexpected derivatives, $C_{13}H_{10}O_4$ and $C_{14}H_8O_5$, were obtained, but in such comparatively small yields that their investigation has been attended with considerable difficulty.

In dealing with the two compounds resulting from the condensation, it was at first suspected that the anomalous results might be due to the acetic anhydride having taken part in the reaction, but further investigation disproved this assumption, and it was ultimately shown that one of the products, $C_{13}H_{10}O_4$, could be obtained, in the absence of acetic anhydride, by the interaction of furfuraldehyde, sodium succinate, and succinic anhydride.

The compound $C_{14}H_8O_5$, which crystallises in long, dark orange-coloured needles melting at 187° , has the properties of a substituted succinic anhydride, and the other, $C_{13}H_{10}O_4$, which forms yellow, crystalline plates melting at 213° , was found to be a monobasic acid ; both substances, which are distinctly unsaturated, are produced by the

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condensation of 2 molecules of furfuraldehyde with 1 molecule of sodium succinate; the orange-coloured compound being difurfurylidenesuccinic anhydride, $\text{C}_4\text{H}_3\text{O} \cdot \text{CH} : \text{C} \cdot \text{CO} > \text{O}$, whilst the yellow compound is $\alpha\gamma$ -difurfurylidenepropionic acid (α -furfurylidenefuryliscrotonic acid), $\text{C}_4\text{H}_3\text{O} \cdot \text{CH} : \text{CH} \cdot \text{C} \cdot \text{CO}_2\text{H}$.

Since the orange-coloured compound is insoluble in cold aqueous alkali hydroxides, whilst the yellow compound dissolves in these solutions, the separation of the two products is readily effected. Unfortunately, their production is accompanied by large quantities of resinous substances having both acid and neutral properties, a fact which renders the purification very tedious.

In spite of a large number of experiments carried out under widely differing conditions, no evidence was obtained of the formation of the monofurfurylidene derivatives. The interaction of furfuraldehyde and sodium succinate in the presence of acetic anhydride may be represented as occurring in the following stages :

The dicarboxylic acid is liberated from the sodium salt by the acetic acid, resulting from the action of the eliminated water on a portion of the acetic anhydride, the excess of the latter reagent then converting the dicarboxylic acid into its anhydride. At the same time, carbon dioxide is removed from another portion of the dicarboxylic acid, giving rise to the monobasic acid :

The final product of the reaction contains, therefore, in addition to a certain amount of the unchanged reagents, the orange-coloured anhydride, the yellow acid and its sodium salt, sodium acetate, acetic and succinic acids, some succinic anhydride,* and traces of furylacrylic

* It has been shown beyond question, by separate experiments, that succinic anhydride and sodium acetate are formed when sodium succinate and acetic anhydride are heated together. A double decomposition of this nature was assumed by Fittig and Ott (*Annalen*, 1885, **227**, 79) to take place between sodium *isobutyrate* and acetic anhydride, giving rise to *isobutyric* anhydride and sodium acetate, but although the results obtained by these authors could only be interpreted on this assumption, the change was not demonstrated experimentally.

acid. Carbon dioxide is steadily disengaged during the course of the reaction, especially if the temperature is allowed to rise, and whilst the production of yellow acid increases at higher temperatures, that of the orange-coloured anhydride decreases to a corresponding extent.

The succinic anhydride formed as a secondary product in the reaction does not appear to play any special part in the formation of the orange-coloured anhydride, such as might at first be suspected. There can be no doubt that it is the sodium salt alone which enters into action with the aldehyde, as with other condensations of this order (Fittig, *loc. cit.*), for furfuraldehyde could not be made to condense with succinic anhydride in the absence of sodium succinate, either by varying the temperature or by adding acetic anhydride or other dehydrating agents.

Difurfurylidenesuccinic anhydride has a bright scarlet colour resembling that of azobenzene; it is stable towards hydrolytic agents, and is attacked only slowly by boiling aqueous sodium hydroxide, yielding the sodium salt of the corresponding dicarboxylic acid. The acid itself is a pale yellow powder which melts at 185° , regenerating the original orange-coloured anhydride. The marked stability of the latter is comparable with that of pyrocinchonic anhydride and the tetra-alkylsuccinic anhydrides, and there can be little doubt that the

cyclic structure, $\begin{array}{c} \text{C} \cdot \text{C} \\ | \quad \diagup \\ \text{C} \cdot \text{C} \end{array} > \text{O}$, in the orange-coloured compound is more closely allied to the furan nucleus than to the ring present in succinic anhydride. This configuration is, moreover, present in the two furyl groups, and the colour of the compound must in some way be associated with this peculiarity in constitution, and possibly with a special structure in the furan nucleus, having chromogenic characters, like the quinonoid grouping in the benzene nucleus. The chromogenic intensity becomes enhanced when bromine is added to the molecule, and the tetrabromide has marked fluorescent properties (see p. 190).

During this investigation, large quantities of furfuraldehyde were used up in abortive attempts to increase the yields of the yellow and orange-coloured compounds, but although the conditions were varied as far as possible, the yields never exceeded 5 per cent. of the calculated amount, except in one instance when an 8 per cent. yield of the yellow substance was obtained. In many other experiments, traces only were produced.

EXPERIMENTAL.

Action of Furfuraldehyde on Sodium Succinate in presence of Acetic Anhydride. Formation and Separation of Difurfurylidene-succinic Anhydride and α -Difurfurylidene- γ -propionic Acid.

An intimate mixture of furfuraldehyde, thoroughly dried sodium succinate, and freshly distilled acetic anhydride, contained in a flask fitted with an air condenser, was cautiously heated in a paraffin-bath. The reaction commenced at 100° and proceeded so vigorously above this temperature that occasionally, when large quantities were employed, it became uncontrollable, and gave rise to black, resinous products. The most favourable yields were obtained by heating together at 90–100° for 6 hours, 20 grams of furfuraldehyde, 30 grams of sodium succinate and 45 grams of acetic anhydride. It was found necessary to employ the sodium salt in the form of a very fine powder, which was dried at 140° just before the experiment.

During the condensation, small quantities of carbon dioxide were evolved and the contents of the flask darkened, the final semi-solid product having a dark greenish-brown colour. The relative proportion of orange-coloured anhydride and yellow acid produced varied considerably with the conditions (time and temperature), but in general the yellow acid increased at the expense of the anhydride if the temperature was allowed to rise above 100° and if the heating continued for more than 6 hours, whilst in many cases under these circumstances the anhydride was not isolated. It was, moreover, impossible to obtain the anhydride exclusively by working at lower temperatures. These two products were isolated and separated by one or other of the following methods.

1. *Ether Extraction*.—The contents of the flask were treated with ether, and the solid residue, after filtering, further extracted in a Soxhlet apparatus for 4 or 5 hours, this treatment being necessary owing to the sparing solubility of the yellow and orange-coloured substances in ether. The dark ethereal extracts, on evaporation, slowly yielded these two compounds, together with succinic acid and succinic anhydride, the mother liquor containing acetic acid and its anhydride, furfuraldehyde and resin. The crystals, which were much discoloured, assumed a bright orange colour after draining on a porous plate. They were now treated with dilute ammonia, in which the orange-coloured anhydride remained undissolved as a granular powder. This product was purified by recrystallising from hot glacial acetic acid, and finally from hot benzene. The highest yield of difurfurylidene-succinic anhydride thus obtained, after about thirty separate syntheses

had been carried out in order to ascertain the best conditions of treatment, was about 5 per cent. of the calculated amount.

In order to isolate the yellow acid ($\alpha\gamma$ -difurfurylidene- β -propionic acid) which accompanies the anhydride, the ammoniacal filtrate from the latter was acidified with hydrochloric acid. A dirty yellowish-brown precipitate of the impure acid was deposited, which was found to be very difficult to purify, owing to the presence of brown, oily resins having an acid nature, these substances were also precipitated, and rendered it almost impossible to dry the product. When gently warmed, the impure material melted to a black tar, which could not be effectually purified. By repeated crystallisation of the dried precipitate from hot benzene, however, it was at length found possible to separate the less fusible, yellow, crystalline acid in a fairly pure condition from the oily resins.

An alternative, and much more satisfactory method of purification was ultimately devised, depending on the fact that the sodium salt of the yellow acid is not very soluble in water and crystallises readily, whilst the sodium salts of the impurities are more soluble and do not crystallise. The impure product, obtained by acidifying the above ammoniacal solution, was therefore washed, dissolved in a slight excess of sodium hydroxide solution, and the resulting dark brown solution of the sodium salts concentrated carefully on the water-bath until crystals commenced to separate. On cooling, the entire mass became crystalline, and the sodium salt, when collected at the pump and dried on a porous plate, was obtained in large, transparent, orange-yellow plates. The mother liquor generally yielded a second crop of crystals.

The $\alpha\gamma$ -difurfurylidene- β -propionic acid obtained from this sodium salt by the action of hydrochloric acid was absolutely pure and melted 5° higher than that obtained by the foregoing method of crystallisation from benzene. The maximum yield was about 5.5 per cent. of theory, this being obtained only by carrying out the original reaction at 110° , so as to diminish the production of the orange-coloured compound.

2. *Treatment with Water.*—A method of treatment similar to that employed by Fittig (*loc. cit.*) was adopted by the authors in a number of experiments made in endeavouring to isolate furylparaconic and furyl-isocrotonic acids. These acids could, however, not be detected. The steam distillate contained only furfuraldehyde; the residue in the flask contained a large quantity of oily resin, which was filtered off whilst hot. The filtrate was yellow, and on cooling became turbid, and in the course of two to three days a bright yellow, micro-crystalline powder appeared in the form of crusts on the surface of the liquid and sides of the vessel; this substance melted at about 200° , and was fairly pure $\alpha\gamma$ -difurfurylidene- β -propionic acid. It was crystallised

repeatedly from benzene. The aqueous filtrate from the yellow crusts contained only acetic acid, succinic acids, and their sodium salts.

The tarry matter was also examined, and, although it was found to contain a relatively considerable proportion of the yellow $\alpha\gamma$ -difurfurylidene- β -propiolic acid (which was extracted by repeated treatment with hot water, in which this acid is appreciably soluble), no other acid, except the resin acids, could be obtained from it. The quantity of tarry matter or pitch obtained in all the experiments was very great, and at once explained the very small yields, but it was impossible under any conditions to prevent its formation, although by carefully regulating the temperature at which the condensation was effected its quantity could be more or less minimised. The resin was closely investigated and, by repeated solution in alkali and reprecipitation with acids, was obtained in the form of a brown, amorphous powder, which was distinctly unsaturated, had slightly acid characters, and exhibited properties analogous to the yellow, crystalline $\alpha\gamma$ -difurfurylidene- β -propiolic acid. It had, however, no definite melting point, and evidently consisted of a mixture of several substances (probably polymerised derivatives), and, although numerous attempts were made to separate them by means of solvents, definitely pure compounds could not be isolated. The mixture was instantly oxidised by cold potassium permanganate, giving large quantities of oxalic acid. This investigation was accordingly abandoned.

This acid crystallises in fine, silky needles from benzene, but forms thick prisms when separating slowly from glacial acetic acid; it melts at 187° .

0.1123 gave 0.2684 CO_2 and 0.0351 H_2O . C = 65.18; H = 3.47.

0.0872 „ 0.2080 CO_2 „ 0.0270 H_2O . C = 65.05; H = 3.43.

$\text{C}_{14}\text{H}_8\text{O}_5$ requires C = 65.62; H = 3.12 per cent.

A determination of its molecular weight was carried out by the ebullioscopic method in benzene solution.

	Solute.	Solvent.	Rise of b. p.	M. W.
I.	0.1524	34.168	0.045	264
II.	0.2926	34.168	0.090	254

$\text{C}_{14}\text{H}_8\text{O}_5$ requires M. W. = 256.

Difurfurylidenesuccinic anhydride is only very sparingly soluble in the usual organic solvents, but the solutions have a bright orange colour. In benzene, it is fairly readily soluble in the hot, but only slightly so in the cold solvent (1 part in 350 at 14°).

It is insoluble in and unaffected by water, aqueous sodium carbonate, ammonia, &c.; also by cold aqueous sodium hydroxide, but in a boiling solution of this alkali it is slowly attacked and disappears, forming a pale yellow solution of the sodium salt of the corresponding dicarboxylic acid.

Attempts made to reduce difurfurylidenesuccinic anhydride by zinc dust and glacial acetic acid, and other reducing agents gave no satisfactory results, mainly owing to insufficiency of material.

On cautiously oxidising the substance with nitric acid, potassium permanganate, or chromic acid, oxalic acid was formed, this result being due to the presence of the furan nucleus. An appreciable quantity of a syrupy acid was simultaneously formed, but this substance could not be purified or identified owing to its small amount.

Action of Bromine on Difurfurylidenesuccinic Anhydride.

Owing to the markedly unsaturated character of the anhydride and the presence of two furyl groups, bromine interacts with great vigour and its chloroform solution is instantly decolorised. It is probable that the first action consists in adding two and then four atoms of the halogen at the points of double union outside the furyl groups thus :

further addition then taking place in the furan nucleus. The action is further complicated by the fact that substitution simultaneously occurs, with evolution of hydrogen bromide and formation of viscous bromo-derivatives. When, however, the bromine is carefully added, comparatively little substitution occurs until four atoms of bromine have been introduced. Experiments were then made with the view of introducing bromine in successive stages corresponding with 2, 4, 6, and more atoms. A saturated solution of the orange-coloured anhydride in chloroform was treated with the requisite volume of a solution of bromine in the same solvent added drop by drop; the solvent was then allowed to evaporate and the residue purified. It was found impossible to isolate in a pure condition any product other than the tetrabromide. In the experiments in which two atoms of bromine only had been added, a mixture of granular and viscous substances remained which were found to contain the tetrabromide and unchanged difurfurylidenesuccinic anhydride, but no dibromide. From those experiments, also, in which an excess of

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bromine had been used, the chief product isolated was the tetrabromide, the remainder being a syrupy mixture from which no definite substance could be isolated.

αα₁ββ₁-Tetrabromo-s-difurfurylsuccinic Anhydride,

This compound was obtained in largest quantity by the addition of four atoms of bromine to difurfurylidenesuccinic anhydride. The residue, after removing the chloroform, had a brown, vitreous appearance; it was washed several times with cold alcohol and recrystallised from benzene, being then obtained in micro-crystalline, yellow needles melting at 195—196°.

0.1736 gave 0.2270 AgBr. Br = 55.16.

$\text{C}_{14}\text{H}_8\text{O}_5\text{Br}_4$ requires Br = 55.55 per cent.

The tetrabromo-derivative is fairly readily soluble in chloroform, benzene or acetone, but only sparingly so in alcohol; its solutions have a yellow fluorescence, which is destroyed by alkalis and restored by acids.

An attempt was made to obtain the dibromo-derivative by using glacial acetic acid as a solvent for the bromine. On adding water to the product of reaction, a yellow powder was deposited, which, when dissolved in acetic acid and reprecipitated with water, melted indefinitely at about 112° and contained 33.46 per cent. of bromine. The dibromide, $\text{C}_{14}\text{H}_8\text{O}_5\text{Br}_2$, requires Br = 38.46 per cent. By further treatment with acetic acid and water, it was obtained apparently pure, and melted at 135°, but unfortunately the quantity was too small for analysis.

The orange-coloured anhydride was digested with about twice the theoretical quantity of a 30 per cent. solution of pure sodium hydroxide in a silver vessel at 100° for several hours until the last traces of orange-coloured needles had disappeared. A slightly yellow solution resulted, which, after cooling, was acidified with hydrochloric acid. A pale yellow, crystalline precipitate was gradually deposited, the total yield being theoretical. The acid was purified by dissolving in aqueous sodium carbonate and reprecipitating with acid. The pure substance melted at 185—187°, but at 185° it rapidly assumed a deep orange colour and then melted to a blood-red liquid, evolving steam and yielding the anhydride (m. p. 187°).

0.0724 gave 0.1639 CO_2 and 0.0244 H_2O . $\text{C} = 61.73$; $\text{H} = 3.74$.

$\text{C}_{14}\text{H}_{10}\text{O}_6$ requires $\text{C} = 61.31$; $\text{H} = 3.64$ per cent.

The acid is fairly readily soluble in alcohol and acetone; it dissolves very easily in glacial acetic acid, but is insoluble in benzene and chloroform. It forms a yellow, crystalline sodium salt and a bright yellow, insoluble silver salt.

When the acid is warmed with acetyl chloride, it dissolves, and the colour of the solution rapidly changes from yellow to blood-red, then almost instantaneously the pure anhydride separates as a net-work of bright orange-coloured needles melting at 187° .

α -Difurfurylidene- β -propionic Acid (α -Furfurylidene-furylisocrotonic Acid),

The isolation of this compound from the product of interaction of furfuraldehyde, sodium succinate, and acetic anhydride has already been described. An 8 per cent. yield of this acid was obtained by using succinic anhydride as dehydrating agent instead of acetic anhydride. By this method, the formation of difurfurylidene-succinic anhydride was prevented. The use of large quantities was avoided, the preparation being carried out on a small scale. Eight grams of sodium succinate (dried at 140°), 6 grams of succinic anhydride, and 5 grams of furfuraldehyde were intimately mixed and heated at 120° in a paraffin bath for 4–5 hours. The solid product, which had darkened considerably, was pulverised in a mortar and digested with aqueous sodium carbonate at 40° for about 2 hours. A considerable quantity of brown, insoluble, resinous matter remained, which was filtered off, and the yellow solution, after cooling, acidified with hydrochloric acid. The yellow precipitate, which was somewhat oily, was washed thoroughly and purified by conversion into its sodium salt (compare p. 187), the acid being subsequently liberated by treatment with hydrochloric acid. The purest specimen of the acid obtained in this manner melted at 213° . A number of specimens in the earlier experiments, which had been purified by recrystallisation from benzene and other solvents, melted at 205° , evidently owing to traces of adherent resinous matter.

m. p. 205° . 0.1096 gave 0.2702 CO_2 and 0.0423 H_2O . $\text{C} = 67.23$; $\text{H} = 4.28$.

m. p. 205° . 0.1858 gave 0.4569 CO_2 and 0.0732 H_2O . $\text{C} = 67.21$; $\text{H} = 4.39$.

m. p. 213° . 0.2169 gave 0.5419 CO_2 and 0.0865 H_2O . $\text{C} = 68.07$; $\text{H} = 4.43$.

$\text{C}_{13}\text{H}_{10}\text{O}_4$ requires $\text{C} = 67.83$; $\text{H} = 4.34$ per cent.

α -Difurfurylidenepropionic acid is practically insoluble in water, slightly soluble in ether, cold alcohol or benzene, but may be crystallised from its hot solution in the last two solvents in long, yellow needles; it is readily soluble in glacial acetic acid, and is reprecipitated by water as a bright yellow precipitate. The acid at once dissolves in aqueous alkali hydroxides, including ammonia, and is slowly soluble in sodium carbonate solution, being reprecipitated from these solutions by mineral acids or acetic acid.

The *sodium* salt is sparingly soluble in water and crystallises in large, transparent, orange-yellow plates, which at 100° lose water and crumble to an opaque, bright yellow powder.

The *silver* salt is precipitated from neutral solutions on adding silver nitrate as a bright yellow, colloidal precipitate.

0.0720 gave 0.0232 Ag. $\text{Ag} = 32.22$.

$\text{C}_{13}\text{H}_9\text{O}_4\text{Ag}$ requires $\text{Ag} = 32.05$ per cent.

In pure water, the salt is fairly soluble, forming a pale yellow solution.

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