CHEMISTRY OF $\beta$-ARYL GLUTACONIC ACIDS.—Part I.

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A New Method of Synthesis.

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It is well known that in $\beta\gamma$ unsaturated acids, the double bond wanders to the $\alpha \beta$ position, thus producing a stable system of conjugated double-bonds. In glutaconic acid, however, owing to the presence of activating carboxylic groups at both the ends of the three carbon system, the double-bond is not fixed, and this results in the mobility of a hydrogen atom in the methylene group,

$$\text{CO}_2\text{H} \cdot \text{CH} = \text{CH} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}.$$  

This gives rise to a number of isomerides of peculiar properties in the various substitution products of glutaconic acid, and has attracted the attention of workers like Perkin, Thorpe, Feist, Ingold, Kon, etc., since the beginning of this century. Glutaconic acids where only the $\beta$-position has been substituted, possess a special interest, in that the mobility of the mobile hydrogen atom in the methylene group, is unhampered by any substitution. Only two such $\beta$ substituted glutaconic acids are known—$\beta$-methyl and $\beta$-phenyl, but the investigators were handicapped by their very poor yields; very little work having been done especially in the latter case (Rogerson and Thorpe, J. C. S., 1905, 1691; Bland and Thorpe, J. C. S., 1912, 856). Owing to, as Prof. Kon says in his recent publication (Gidwani and Kon, J. C. S., 1932, 24) "the difficulties attending the preparation of $\beta$-phenylated glutaconic acid derivatives," there was no method of general application for synthesis of these important group of compounds. This paper deals with a new method, by which it has been found possible to introduce a variety of aromatic groups in the $\beta$-position of glutaconic acid.

Limaye and Bhave have recently shown (J. Ind. C. S., 8, 137, 1931) that $\beta$-4-methoxy-phenyl glutaconic acid could be obtained by the condensation of anisole with acetone-dicarboxylic acid, the nuclear carbon atom occupying the para position to the methoxy group. The present author in extending Limaye and Bhave's method to meta- and para-cresol-methyl ethers, found that their condensation with acetone-dicarboxylic acid...
acid proceeded comparatively smoothly, but the acetone-dicarboxylic acid residue was observed to go to the ortho position to the methoxy group, which in the case of the resulting glutaric acid from p-cresol-methyl-ether i.e., \( \beta \)-\((2\text{-methoxy}-5\text{-methyl-phenyl})\) glutaric acid was proved by its transformation by means of concentrated sulphuric acid into the corresponding 6-methyl-coumarin-4-acetic acid, a known compound (Dey, J. C. S., 1915, 1606).

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\text{CH}_3\quad \text{CH}_2\text{-COOH} \quad \overset{\text{H}_2\text{SO}_4}{\rightarrow} \quad \text{CH}_3\quad \text{CH}_2\text{-COOH} + \text{MeOH}
\]

The action of sulphuric acid in this case could be supposed to consist in the demethylation of the methoxy group in the glutaric acid and subsequent closing of the coumarin ring by elimination of a molecule of water between the newly generated phenolic hydroxyl and one of the carboxylic groups of the glutaric acid. Consequently, it was thought that the reversion of this process may be employed for the synthesis of such \( \beta \)-methoxy-phenyl glutaric acids of the ortho series from the corresponding coumaryl-4-acetic acids, the opening of the coumarin ring of these latter compounds being the first step to be achieved.

This ring opening is known to happen in the case of simple coumarins, by the action of strong alkalis, the products being either coumarinic or coumaric acids, according to conditions (Fries and Klostermann, Annalen 1908, 362, 1-29; Fries and Volk, Annalen, 1911, 379, 90-110). Previous attempts to apply this reaction in the case of coumaryl-4-acetic acids failed, the compounds precipitating unchanged, on acidification after the treatment with alkali. (Dey, J. C. S., 1915, 1606; Fries and Volk, Annalen, 1911, 379, 1617-18.) In some cases, however, it was found possible to isolate the disilver salts of the expected glutaric acids, but these when decomposed by hydrogen sulphide, were found to give the original coumaryl-4-acetic acids unchanged. This shows that alkalis do open the coumarin ring in the coumaryl-4-acetic acids, but this again gets closed during acidification. To prevent this, treating the strongly alkaline solution, obtained after boiling the coumaryl-4-acetic acids with alkalis, with dimethyl sulphate before acidification, was thought would be the most suitable method; the phenolic hydroxy group would then be methylated first and thus be protected from taking part in the ring closure.

This expectation was amply fulfilled in the case of the coumaryl-4-acetic acid from \( \beta \)-cresol, i.e. 6-methyl-coumarin-4-acetic acid, the expected \( \beta \) (2-
methoxy-5-methyl-phenyl) glutaric acid having been obtained, as a result of the application of the above process, along with some unchanged 6-methyl coumarin-4-acetic acid.

The solubilities of the coumarin acid and the glutaric acid were so near each other that it was found impossible to separate them by ordinary methods such as fractional crystallisation, fractional precipitation, etc. By treating the mixture with acetic anhydride, only the glutaric acid was transformed into its hydroxy-anhydride, the coumarin acid remaining unchanged. These two substances, having widely different properties, were easily separated by ordinary methods. In similar manner the \( \beta \) (2-methoxy-4-methyl-phenyl) glutaric acid was synthesised from 7-methyl-coumarin-4-acetic acid (m-cresyl-coumarin-4-acetic acid), and was found to be identical with that obtained by condensing the methyl-ether of meta-cresol with acetone dicarboxylic acid.

On application of this method of hydrolysis and methylation to the coumaryl-4-acetic acid from \( \alpha \)-naphthol, a mixture of the expected glutaric acid and the unchanged coumarin acid was obtained as usual. These two compounds differed very much as regards their solubilities and were easily separated. The methyl-ether of \( \alpha \)-naphthol, unlike the methyl-ethers of \( m \) and \( p \) cresols, however, when condensed with acetone-dicarboxylic acid at low temperatures, was found to give a different glutaric acid, evidently of the para series. Here the para position of the acetone-dicarboxylic acid residue with respect to the methoxy group in the naphthol ring, was proved by oxidation of this glutaric acid to the corresponding naphthyl carboxylic acid, a known compound (Gattermann, *Annalen*, 244, 72). These reactions are represented as:

\[
\text{Hydrolysis} \quad \xrightarrow{} \quad \text{Methylation and acidification}
\]
When the reaction was extended to the coumaryl-4-acetic acid from β-naphthol, it was discovered that on careful fractional crystallisation of the reaction product, two isomeric glutaric acids could be separated, the less soluble melting at 186°C. (decomp.), and the other at 162°C. (decomp.). That these two acids were stereoisomeric and not structurally isomeric followed from the fact that both of them, when treated with equi-molecular proportions of aniline at a temperature slightly above their melting points, gave the same hydroxy-anil (I) by loss of two molecules of water. Further, both the forms when decomposed in a paraffin bath at their melting points, lost a molecule of water, and were converted into the same hydroxy-anhydride (III) m.p. 135°C, and a new substance m.p. 172°C isomeric with the anhydride.

It has been observed that these two substances are interconvertible simply by the action of different solvents and appear to be tautomeric. However they have distinctly different physical and chemical properties, and are quite stable as such, and hence this appears to be a new kind of tautomerism. An account of detailed study of this tautomerism as well as of the
determination of the structure of the product m.p. 172°C. has been reserved for a future communication. That the compound m.p. 155°C. represents the true hydroxy-anhydride is, however, supported by the formation from it of a semianilide (II), when treated in benzene solution with equivalent amount of aniline. This semianilide, when decomposed at its melting point, gave a hydroxy-anil identical with that produced from the glutaconic acid and aniline, as described above.

The two isomers, however, are differentiated by the action of acetic anhydride on them, the acid m.p. 162°C. being readily transformed into the hydroxy-anhydride described above, whereas the acid m.p. 186°C. remains unchanged when boiled with a slight excess of the reagent. This showed that the acid m.p. 162°C. is the cis variety and the other melting at 186°C. the trans one, and is further supported by the fact that, only the form melting at 182°C. is obtained by hydration of the hydroxy-anhydride under mild conditions. To explain the formation of the same hydroxy anhydride or the same hydroxy-anil from both these glutaconic acids, it has to be assumed that at the temperature of its melting point, the trans is first converted into the cis variety, before further action. Reference to literature showed that whereas cis and trans forms of very few substituted glutaconic acids have been isolated, no glutaconic acid of the "β-aryl" series has been shown to exist in any such geometrical isomers, the present β (β-methoxy-naphthyl) glutaconic acid being the first to be separated into two such forms. A further detailed study about the isomerism, the determination of the condition of interconversion of the isomers etc., is in progress, an account of which is reserved for a future communication.
The original β-naphthyla-coumarin-4-acetic acid may be represented by two structures (IV) and (V), according as the acetone dicarboxylic acid residue occupies the α or γ position in the β-naphthol, and consequently the present β (β-methoxy-naphthyl) glutaconic acids, which are derived from it might have either of the constitution (VI) or (VII): To settle this point, both the cis and trans forms of the β (β-methoxy-naphthyl) glutaconic acid were subjected to the action of various oxidising agents but in no case any definite oxidation product could be isolated, the molecule as a whole being decomposed. This is quite in conformity with Dey's inability to oxidise the parent β-naphthyl-coumarin-4-acetic acid to any naphthol carboxylic acid (Dey, J. C. S., 1915, 1615). The author is, however, led to believe the constitutions (V) and (VII) for the β-naphthyl-coumarin-4-acetic acid and β (β-methoxy-naphthyl) glutaconic acid respectively, especially as a result of oxidation of the internal condensation product of the latter, which will be reported in due course.

Quite contrary to expectations, the methyl-ether of β-naphthol was not found to condense with acetone-dicarboxylic acid at all under any temperature, every time the substance being recovered unchanged.

Experimental.

Preparation of β (2-methoxy-5-methyl-phenyl) glutaconic acid from 6-methyl-coumarin-4-acetic acid:—

6-methyl-coumarin-4-acetic acid (10 gm.) was dissolved in 50 c.c. of 20 per cent. aqueous sodium hydroxide, and the solution refluxed for about an hour. After cooling and filtering, dimethyl sulphate (20 c.c.) was gradually added and the whole heated in a water-bath at 80-90°C. As the reaction started, the contents began to boil, which came to an end in about half an hour. To decompose any ester formed, more alkali was added and the solution again refluxed for about fifteen minutes. On cooling and filtering, the solution was carefully acidified, when a semi-solid mass gradually separated, and solidified to a crystalline mass on rubbing and keeping for a couple of hours. After filtering and drying, this was mixed with 15 c.c. of acetic anhydride, and the mixture heated to boiling until the whole just went in solution. The excess of acetic anhydride was evaporated on a boiling water-bath and then in a vacuum desiccator over solid potash, and the residue extracted with boiling benzene. On evaporating away the benzene from the benzene extract, the anhydride of the glutaconic acid was obtained almost pure. It was recrystallised from a mixture of petrol and benzene. Colourless needles m.p. 117°C. (Found: C, 67·12 %; H, 5·08 %; Equivalent 234. C₁₃H₁₂O₄ requires C, 67·24 %; H, 5·17 %; Equivalent 232.)
The glutaconic acid was obtained from the above anhydride by hydrolysis with dilute alkalis or water—rectangular prisms from dilute acetic acid, m.p. 189°C. (decomp.). This was found identical with the one obtained by directly condensing the methyl-ether of p-cresol with acetone-dicarboxylic acid. (Found: C, 62.27%; H, 5.52%; Equivalent 125. C₁₃H₁₄O₅ requires C, 62.4%; H, 5.6%; Equivalent 125.)

Synthesis of β (2-methoxy-4-methyl-phenyl) glutaconic acid from 7-methyl-coumarin-4-acetic acid:—

7-methyl-coumarin-4-acetic acid (10 gm.) was boiled with 75 c.c. of 30% solution of potassium hydroxide for an hour under reflux. Dimethyl sulphate (20 c.c.) was then gradually added, keeping the alkali solution at a temperature between 80–90°C. in a water-bath during the addition. The rest of the method followed was exactly as above. The anhydride of the β (2-methoxy-4-methyl-phenyl) glutaconic acid, crystallises from alcohol or benzene as colourless short needles, m.p. 147°C. (Found: C, 67.17%; H, 5.12%; Equivalent 235. C₁₃H₁₂O₄ requires C, 67.24%; H, 5.17%; Equivalent 232.)

The corresponding glutaconic acid obtained from this hydroxy anhydride crystallised from water in prisms, m.p. 174°C. (decomp.). (Found: C, 62.32%; H, 5.49%; Equivalent 125. C₁₃H₁₄O₅ requires C, 62.4%; H, 5.6%; Equivalent 125.)

Hydrolysis and methylation of a-naphtha-coumarin-4-acetic acid. Formation of β (1-methoxy-naphthyl-2-) glutaconic acid:—

α-naphtha-coumarin-4-acetic acid (10 gm.) was dissolved in 75 c.c. of 30% sodium hydroxide solution, and boiled under reflux for two hours. On cooling, it was kept in a water-bath maintained at a temperature between 80–90°C., and dimethyl sulphate (40 c.c.) was gradually run in under continuous mechanical stirring. After the addition of dimethyl sulphate was over, after about half an hour, 15 c.c. more of 30 per cent. sodium hydroxide solution were added, and the whole again boiled for further half an hour. On cooling, the sodium sulphate which separated was filtered out, and the filtrate washed with ether. It was then cooled in ice and carefully acidified with dilute hydrochloric acid, under constant stirring, when a yellow oil gradually separated, which, on rubbing
and keeping overnight, solidified to a crystalline cake. It was filtered, dried and rubbed in a mortar with about 70 c.c. of cold alcohol, when most of the unchanged α-naphtha-coumarin-4-acetic acid remained undissolved. This was filtered out, and the alcoholic solution concentrated to 30 c.c. This was cooled in ice and 100 c.c. of ice water added slowly under continuous stirring when the glutaconic acid separated first as an oil which soon solidified to a yellow crystalline mass, on rubbing and keeping. This was recrystallised from 30 per cent. methyl alcohol or 5 per cent. acetic acid, using animal charcoal—colourless plates, m.p. 161°C. (decomp.). (Found : C, 66.9 %; H, 4.7 %; Equivalent 145. \( \text{C}_{16}\text{H}_{14}\text{O}_{2} \) requires C, 67.1 %; H, 4.9 %; Equivalent 143.)

**Hydroxy-anhydride of β-(1-methoxy-naphthyl-2-) glutaconic acid:**—

This is obtained by boiling the glutaconic acid with acetic anhydride for a few minutes. The hydroxy-anhydride separated on cooling the acetic anhydride solution in ice and scratching, as grey needles. It was filtered, washed with ether and crystallised from benzene or acetic acid (using animal charcoal)—yellowish needles, m.p. 158°C. More of this hydroxy-anhydride could be recovered from the acetic anhydride filtrate, on removing the acetic anhydride in a vacuum desiccator over potash; and crystallising the residue from benzene.

The hydroxy-anhydride dissolves readily in cold dilute alkalis but gives a coloured solution and hence could not be titrated. It could be recovered unchanged from its cold alkali solution, even after standing for an hour. The sodium salt of the hydroxy-anhydride separates when strong alkali is added to its solution in dilute alkali. The hydroxy-anhydride gives the characteristic phenolic colouration with ferric chloride, in cold alcoholic solution. (Found : C, 71.3%; H, 4.38%. \( \text{C}_{16}\text{H}_{12}\text{O}_{4} \) requires C, 71.6%; H, 4.47%.)

**Semianilide.**—The hydroxy-anhydride was dissolved in warm benzene, the equivalent amount of aniline added, and the solution heated to boiling for a few minutes. On cooling and scratching, the semianilide separated from the benzene solution as a white precipitate. It was crystallised from dilute alcohol—colourless needles m.p. 180°C. (decomp.). It titrates as a monocarboxylic acid. (Found : C, 72.5%; H, 5.1%. \( \text{C}_{28}\text{H}_{19}\text{O}_{4}\text{N} \) requires C, 73.1%; H, 5.25%.)

**Hydroxy-anil.**—The glutaconic acid was finely powdered and heated with a slight excess over the equivalent amount of aniline, in an oil-bath at a temperature between 150–160°C. The reaction started with vigorous decomposition and evolution of water vapour. After an hour's heating the temperature was increased to 180°C. for a short time. On cooling, the red
sticky reaction mixture was rubbed first with dilute hydrochloric acid and then with alcohol, when it turned into a yellowish powder. This was filtered and rapidly crystallised from glacial acetic acid—short needles, m.p. 199-200°C. The hydroxy-anil is very sparingly soluble in ordinary organic solvents. It dissolves in cold dilute alkalis. (Found: C, 76.5%; H, 4.91%. C_{22}H_{19}O_3N requires C, 76.9%; H, 5.0%.)

Condensation of α-naphthol-methyl-ether with acetone-dicarboxylic acid; formation of β (1-methoxy-naphthyl-4-) glutaric acid:

Citric acid (25 gm.) was finely powdered and heated with concentrated sulphuric acid (40 c.c. of sp. gr. 1.84) at a temperature of 70°C. for 15 minutes with repeated shaking. The clear orange solution thus obtained was cooled in a pecking of ice and salt, and α-naphthol-methyl-ether (13 gm.) was gradually introduced, shaking vigorously the mixture during each addition. The mixture was kept at a temperature not exceeding 5°C., for 2½ hours and then poured in large amount of ice water. A red sticky mass separated which turned into a yellow precipitate on standing overnight. This was filtered, washed with water and taken up in 10% cold sodium carbonate solution. This sodium carbonate solution was washed with ether, and carefully acidified, when the glutaric acid came out as granular mass. It was filtered, washed and crystallised from alcohol (animal charcoal);—parallelomeric colourless plates. It softens at 193°C. and decomposes with blackening at 199°C. This glutaric acid unlike the other members of this series, is sparingly soluble in alcohol or acetic acid, but dissolves readily in acetone. It gives an insoluble barium salt in cold. Yield 13 gm. (Found: C, 66.8%; H, 4.74%; Equivalent 143. C_{16}H_{14}O_5 requires C, 67.1%; H, 4.9%; Equivalent 143.)

Hydroxy-anhydride.—This is obtained as usual by heating the glutaric acid with acetic anhydride; crystallisation from benzene and then from acetic acid yields prismatic needles m.p. 156°C. The sodium salt of this hydroxy-anhydride is insoluble in cold water or alkalis, but dissolves on boiling. It thus separates as colourless plates when a hot solution of the hydroxy-anhydride in dilute sodium hydroxide or sodium carbonate is cooled. The hydroxy-anhydride is comparatively more stable towards alkalis; and could be recovered unchanged on acidification of its solution in hot alkalis. The hydroxy-anhydride gives the characteristic colouration with ferric chloride in cold alcoholic solution. (Found: C, 71.1%; H, 4.38%. C_{16}H_{12}O_4 requires C, 71.6%; H, 4.47%.)

Semianilide.—Prepared as usual from the hydroxy-anhydride and aniline in benzene solution—colourless needles from alcohol, m.p. 176-177°C. (decomp). This titrates as a monobasic acid. (Found: C, 72.6%; H, 5.14%. C_{22}H_{19}O_4N requires C, 73.1%; H, 5.25%).
Chemistry of β-Aryl Glutaconic Acids

Hydroxy-anil.—Obtained as usual by heating the glutaconic acid with equivalent amount of aniline at 160°C., or decomposing the above semi-anilide at its melting point: crystallised from glacial acetic acid: short prismatic needles, m.p. 223–224°C. It readily dissolves in cold dilute alkalis. (Found: C, 76.6%; H, 4.84%. C22H17O5N requires C, 76.9%; H, 5.0%).

Oxidation of β (1-methoxy-naphthyl-4-) glutaconic acid:

The glutaconic acid (5 gm.) was dissolved in 40 c.c. of 10% sodium carbonate solution, the solution cooled in a mixture of ice and salt, and a 4% aqueous solution of potassium permanganate was gradually run in under continuous mechanical stirring, until the pink colour of a test portion persisted. A current of carbon-dioxide was continuously passed through the solution during the whole operation. On keeping overnight the manganese dioxide which separated, was filtered out under suction and washed with small amounts of distilled water, the washings being added to the filtrate. The filtrate was evaporated under reduced pressure to a small bulk, cooled in ice and acidified with dilute hydrochloric acid. The naphthyl carboxylic acid which separated, was twice crystallised from alcohol using animal charcoal: fine needles, m.p. 232–234°C. (Found: C, 71.1%; H, 4.82%. C12H10O3 requires C, 71.3%; H, 4.95%).

Hydrolysis and methylation of β-naphtha-coumarin-4-acetic acid, formation of β (2-methoxy-naphthyl-3-) glutaconic acid:

The coumarin acid (20 gm.) was heated under reflux with 150 c.c. of 30% sodium hydroxide solution for two hours. The deep-orange solution was kept at a temperature of 80–90°C. in a water-bath, and dimethyl sulphate (80 c.c.) was gradually run in under continuous mechanical stirring. After the addition was over in about half an hour, the solution turned faint yellow, and a considerable amount of salt separated. This was filtered out, more sodium hydroxide (5 gm.) was added and the whole refluxed for about 15 minutes. Still some more salt separated which was again filtered out, the filtrate washed with ether, cooled in ice, and acidified with dilute hydrochloric acid. A yellow viscous mass separated, but this did not solidify completely even on rubbing and keeping overnight. The supernatant liquid was drawn off and the mass was rubbed with small quantities of distilled water repeatedly, when it turned into a yellow granular precipitate. It was filtered and treated with 400 c.c of boiling 5% aqueous acetic acid when major part of the unchanged β-naphtha-coumarin-4-acetic acid remained undissolved (3 gm.). The product which crystallised out on cooling the acetic acid filtrate, was fractionally crystallised from 20% aqueous methyl alcohol, and separated into two pure acids:—(I) the more insoluble
hexagonal colourless plates, m.p. 186°C. (decomp.): Yield 4 gm. (II)

Rectangular prisms, m.p. 162°C. (decomp.): Yield 10 gm. (I) Found: C, 66.7%; H, 4.8%; Equivalent 146. C₁₅H₁₄O₅ requires C, 67.1%; H, 4.9%; Equivalent 144. (II) Found: C, 66.9%; H, 4.9%; Equivalent 144. C₁₅H₁₄O₅ requires C, 67.1%; H, 4.9%; Equivalent 144.

Thermal decomposition of the above glutaconic acids:—

Decomposition of acid m.p. 162°C.:—The glutaconic acid (10 gm.) was heated in a hard glass tube in an oil-bath at 170°C, when the decomposition started with vigorous evolution of water vapour. In about an hour the decomposition came to an end, and the dark red liquid in the tube solidified to a brittle red mass on cooling. On breaking the tube, this brittle mass was ground in a mortar with cold benzene (70 c.c.), when a light yellow precipitate came out. This was filtered and washed with small amounts of benzene, these washings being added to the original filtrate. Yield 5 gm. Crystalised from a mixture of acetone and benzene (1:4), with animal charcoal: short prismatic needles, m.p. 172°C with slight decomp.

The combined benzene filtrates were evaporated to 10 c.c. and cooled in ice, when the hydroxy-anhydride separated out as a crystalline mass, on scratching the sides of the container. It was filtered under a strong suction, washed with small amounts of ice-cold benzene, and crystallised rapidly from alcohol or benzene (animal charcoal). Colourless light needles from alcohol; colourless plates from benzene, m.p. 135°C. Yield 3 gm. (Found: C, 71.4%; H, 4.4%. C₁₅H₁₃O₄ requires C, 71.6%; H, 4.47%)

Both the compounds titrate as monobasic acids giving the same equivalent, and could be recovered unchanged on acidification of their alkali solution. The solution of the hydroxy-anhydride in cold alcohol or acetone gives the characteristic colouration with ferric chloride, which is not given by the solution of the compound m.p. 172°C in cold acetone. The hydroxy-anhydride is very easily soluble in benzene while the compound m.p. 172°C. is practically insoluble in benzene.

Decomposition of the acid m.p. 186°C.:—The glutaconic acid (5 gm.) was decomposed at a temperature of 190°C., and the decomposition product treated with cold benzene exactly as above, when the same compound m.p. 172°C. and the hydroxy-anhydride m.p. 135°C. were separated in yields of 0.7 gm. and 2 gm. respectively. After the hydroxy-anhydride crystallised out, the benzene filtrate on evaporating off the benzene, gave a considerable amount of dark red viscous substance from which nothing crystalline could be separated.

Action of acetic anhydride on the β (β-methoxy-naphthyl) glutaconic acids:—

The glutaconic acid m.p. 162°C. (5 gm.) was boiled with acetic anhydride (6 c.c.) for a short time when a homogeneous green solution was obtained,
from which no hydroxy-anhydride crystallised out even on cooling and scratch- 
ing. The hydroxy-anhydride only crystallised out on cooling in ice and salt, 
and seeding with a pure sample of the same. Yield 2 gm. On remov- 
ing the acetic anhydride from the filtrate over potash, more of the hydroxy- 
anhydride was obtained. The glutaconic acid m.p. 186°C. similarly went 
in solution in boiling acetic anhydride but even on cooling the solution in 
ice and salt and seeding with pure hydroxy-anhydride, no hydroxy-anhydride 
crystallised out. On removing the hydroxy-anhydride over potash from 
the solution, and treating the residue with benzene the original glutaconic 
acid was obtained unchanged, being insoluble in benzene. Warming the 
hydroxy-anhydride with $\frac{N}{2}$ sodium hydroxide solution in a steam-bath for 
1½ hours, gave only the glutaconic acid m.p. 162°C.

Semianilide of $\beta$ (2-methoxy-naphthyl-3-) glutaconic acid :—

Obtained as usual from the hydroxy-anhydride m.p. 135° and equivalent 
amount of aniline in benzene solution. Colourless needles from alcohol, 
m.p. 172°C. It titrates as a monobasic acid. (Found : C, 72.7% ; 
H, 5.1%. $C_{28}H_{19}O_4N$ requires C, 73.1 % ; H, 5.25%.)

Hydroxy-anil.—This is obtained by three methods :—

(a) By the thermal decomposition of the semianilide at 170°C.

(b) By heating the glutaconic acid m.p. 162°C. with a slight excess 
over the equivalent amount of aniline 155–160°C. for half an hour.

(c) By heating the glutaconic acid m.p. 186°C. with aniline as above 
at 170–180°C. for half an hour.

In all the above methods the hydroxy-anil was separated as follows :—
when the frothing of the reaction mixture and the evolution of water vapour 
stopped, the containing tube was cooled and broken, and the red resinous 
mass was first ground in a mortar with dilute hydrochloric acid and then 
with cold alcohol, when the hydroxy-anil separated as a light yellow precipi-
tate. It was filtered, washed with alcohol and crystallised from a large 
amount of the same solvent. Light colourless plates m.p. 196–197°C. The 
hydroxy-anil is soluble in cold dilute alkalis. (Found : C, 76.7% ; 
H, 4.8%. $C_{22}H_{17}O_3N$ requires C, 76.9% ; H, 5%.)

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