CLIX.—*Studies in the Phenylsuccinic Acid Series.*
Part II. Some Derivatives of the Optically
Active Diphenylsuccinic Acids.

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IN a previous communication (this vol., p. 444), the resolution of *r*-diphenylsuccinic acid into its optically active components has been described, the *d*- and *l*-acids being obtained by fractional crystallisation of the brucine salts. The work was undertaken primarily with the object of elucidating the configuration of the stereoisomeric diphenylsuccinic acids, but the high optical activity of the acids obtained (the *d*-acid has $[\alpha]_D^{14} + 397.9^\circ$ in acetone solution), the extensive investigation to which the inactive derivatives have been subjected, and the comparatively limited knowledge of the chemistry of the active derivatives of these or similarly constituted substances appeared to render an examination of their derivatives a matter of interest. Certain salts, esters, and

anhydrides of *d*- and *l*-diphenylsuccinic acids are therefore described in the present communication.

The barium salts of *r*- and *meso*-diphenylsuccinic acids are of particular importance, since their widely differing solubilities in water afford a ready means of separating the parent acids. The former crystallises with two or four molecules of water, and is soluble in 312 parts of water at 17–18°; the latter has seven molecules of water, and dissolves in 4.742 parts of water (Anschütz and Bendix, *Annalen*, 1890, **259**, 81). Barium *d*-diphenylsuccinate separates from its aqueous solution in well-defined prisms, which contain five molecules of water of crystallisation, four of which are lost at 100–105°, the fifth being expelled at 200–210°. It is soluble in 330 parts of water at 7°, and thus, in this respect, closely resembles the corresponding salt of the *r*-acid. In each case, the solubilities are calculated for the anhydrous salt.

The diphenylsuccinic acids are readily esterified by methyl alcohol and sulphuric acid, the methyl esters of the *meso*-, *r*-, and active acids melting at 218.5–219.5°, 173.5–174°, and 165–166° respectively. By the action of an ethereal solution of iodine on a methyl-alcoholic solution of ethyl phenylacetate and sodium methoxide, Komnenos (*Annalen*, 1910, **375**, 254) has obtained a substance, melting at 210°, which is regarded as methyl *r*-diphenylsuccinate, since, when hydrolysed, it yields *r*-diphenylsuccinic acid; in view of the fact that the latter substance is obtained in considerable quantity by the action of potassium hydroxide on ethyl *meso*-diphenylsuccinate (Wren and Still, *loc. cit.*), this line of reasoning scarcely appears valid, and it would seem that the product prepared by Komnenos is a mixture of the *r*- and *meso*-esters; this supposition gains in probability from the fact that the corresponding ethyl esters are formed simultaneously when ethereal solutions of iodine and ethyl phenylacetate react in the presence of solid sodium ethoxide.

In accordance with expectations, the optically active phenylsuccinic acids react considerably less readily with ethyl than with methyl alcohol; esterification by the Fischer-Speier method leads to a mixture of acid and normal esters, the former of which separate in the form of sparingly soluble sodium salts when the crude product is shaken with dilute sodium carbonate solution. The normal ethyl esters of the active acids melt at 104–105°, the values for the corresponding *meso*- and *r*-derivatives being 140–141° and 82–83.5° respectively. With the ethyl esters, therefore, the melting points of the active substances are higher than that of the racemic compound, whilst with the methyl esters the reverse is the case.

d-Diphenylsuccinic acid is not appreciably racemised by prolonged treatment with an excess of aqueous potassium hydroxide at the temperature of the boiling-water bath. This result appears at first sight rather unexpected (compare Rothe, *Ber.*, 1914, **47**, 843; also McKenzie and Widdows, this vol., p. 702), since the acid contains two hydrogen atoms in neighbouring positions to the carboxyl groups, but probably the mobility of these atoms is considerably restricted by their proximity to groups of rather high molecular weight (compare Meyer, *Annalen*, 1888, **250**, 124). On the other hand, considerable racemisation occurs during the hydrolysis of the optically active esters with aqueous alcoholic potassium hydroxide. Apparently in this instance, as in the case of tartaric acid investigated by Winther (*Zeitsch. physikal. Chem.*, 1905, **56**, 466, 720), one asymmetric carbon atom is first affected, since *meso*-diphenylsuccinic acid can be isolated from the product of the reaction, although the effect of alkali is known to tend towards the conversion of the *meso*- into the *r*-acid.

The inactive diphenylsuccinic anhydrides have been the subject of some controversy. According to Tillmanns (*Annalen*, 1890, **258**, 90), the *r*- and *meso*-acids are transformed by acetyl chloride into distinct anhydrides, which, though closely similar in melting point (111–112° and 112° respectively), are distinguished by yielding *r*- and *meso*-diphenylsuccinic acids when treated with water. Anschütz and Benedix (*Annalen*, 1890, **259**, 73), on the other hand, found that *r*-diphenylsuccinic acid reacts with acetyl chloride at the ordinary temperature to yield an anhydride, melting at 115–116°, which is converted by hot water into a mixture of *r*-acid (about 96 per cent.) and *meso*-acid (about 4 per cent.), whilst a rather greater proportion of the latter acid is formed when potassium hydroxide solution is employed. The *meso*-acid itself reacts less readily with acetyl chloride; in two experiments, the anhydride formed gave 70.6 and 81.8 per cent. of *r*-acid and 26.1 and 18.5 per cent. of *meso*-acid when treated with water. The optically active diphenylsuccinic acids react fairly readily with acetyl chloride or thionyl chloride, yielding the corresponding anhydrides, which melt at 105.5–106.5° after slight previous softening, and have $[\alpha]_D \pm 287.7^\circ$ in benzene solution. When treated with hot water, they pass into diphenylsuccinic acids of the same sign, which contain about 8 per cent. of optically inactive material, and from which *meso*-diphenylsuccinic acid can be isolated in very small quantity. With cold ethyl alcohol, a rather complex action appears to take place. The ethyl hydrogen ester which is formed contains approximately 80 per cent. of the active material. Attempts to isolate a pure substance from the product

of the reaction were, however, unsuccessful. After crystallisation from light petroleum, a small quantity of material was obtained which was not completely molten below 146° . Since ethyl hydrogen *l*-diphenylsuccinate melts at $113.5\text{--}114.5^{\circ}$, and the racemic compound at 140° (Franchimont, *Ber.*, 1872, **5**, 1050), it seems probable that the corresponding *meso*-derivative is also present. In a somewhat similar experiment, in which *r*-diphenylsuccinic anhydride was dissolved in chloroform containing ethyl alcohol, Anschütz and Bendix (*loc. cit.*) obtained a product, analyses of which gave results in agreement with those required for the ethyl hydrogen ester, but the physical constants (m. p. of crop, $164\text{--}168^{\circ}$; m. p. of substances from mother liquor, $156\text{--}174^{\circ}$) appear to show that the material was not uniform.

The specific rotations of the substances described have been observed in a number of solvents. In general, the high optical activity of the parent acids is shared by their derivatives, but otherwise little regularity is displayed. In acetone, methyl and ethyl alcohols, ethyl acetate or chloroform solution, the esters have closely similar specific rotations; in carbon tetrachloride solution, however, a not inconsiderable exaltation is observed. The anhydrides are less active than the corresponding acids, whilst also the rotation in carbon tetrachloride is lower than in ethyl acetate solution.

EXPERIMENTAL.

Preparation of Barium d-Diphenylsuccinate.

Pure *d*-diphenylsuccinic acid (1 gram) was suspended in hot water and exactly neutralised with aqueous barium hydroxide. After concentration and cooling, *barium d-diphenylsuccinate* separated in well-defined prisms, which were purified by crystallisation from hot water:

0.3818* gave 0.1790 BaSO_4 . Ba = 27.6.

0.2380 lost 0.0349 at $100\text{--}105^{\circ}$ and 0.0423 at $200\text{--}210^{\circ}$.

$4\text{H}_2\text{O} = 14.66$; $5\text{H}_2\text{O} = 17.77$.

$\text{C}_{16}\text{H}_{12}\text{O}_4\text{Ba}, 5\text{H}_2\text{O}$ requires Ba = 27.7; $4\text{H}_2\text{O} = 14.55$; $5\text{H}_2\text{O} = 18.18$
per cent.

27.287 Grams of aqueous solution, saturated at 7° , left 0.0824 gram of barium salt after desiccation at $200\text{--}205^{\circ}$, equivalent to 1 part of anhydrous salt in 330 parts of water.

Esterification of the Diphenylsuccinic Acids by Methyl Alcohol.

The diphenylsuccinic acids are readily esterified by methyl alcohol and concentrated sulphuric acid according to the Fischer-

* Air-dried.

Speier method, the initially clear solution gradually depositing the ester during the process; in the case of the *meso*-acid, however, separation of the ester commences before the acid has completely dissolved, so that a homogeneous mixture is not obtained at any point. After removal of the bulk of the alcohol, the ester is most conveniently dissolved in chloroform, shaken with dilute sodium carbonate solution, and subsequently crystallised from methyl alcohol.

Methyl d-diphenylsuccinate separates from methyl alcohol in shining platelets, which melt at 165—166°. It is sparingly soluble in the boiling solvent, very sparingly in the cold. It dissolves readily in cold acetone, chloroform, or ethyl acetate, less readily in ether or carbon disulphide. It is readily soluble in boiling benzene, moderately so in boiling ethyl alcohol or light petroleum (b. p. 60—80°), from which it can easily be recrystallised. For analysis and determination of specific rotation, the ester was dried in a vacuum over calcium chloride until constant in weight:

0.1517 gave 0.4026 CO₂ and 0.0845 H₂O. C=72.4; H=6.2.

C₁₈H₁₈O₄ requires C=72.5; H=6.1 per cent.

The following determinations of the specific rotation were made:

In acetone solution:

$$l=2, c=1.0820, \alpha_D^{15.2} + 7.4^\circ, [\alpha]_D^{16.2} + 341.9^\circ.$$

In chloroform solution:

$$l=2, c=1.0615, \alpha_D^{15.8} + 8.00^\circ, [\alpha]_D^{15.8} + 376.8^\circ.$$

Methyl l-diphenylsuccinate exactly resembles its optical antipode in preparation and solubility. It melts at 165—166°:

0.1837 gave 0.4869 CO₂ and 0.1004 H₂O. C=72.3; H=6.1.

C₁₈H₁₈O₄ requires C=72.5; H=6.1 per cent.

The specific rotation was determined in a number of solvents.

In acetone solution:

$$l=2, c=1.3505, \alpha_D^{15.6} - 9.24^\circ, [\alpha]_D^{15.6} - 342.1^\circ.$$

In ethyl acetate solution:

$$l=2, c=1.6095, \alpha_D^{14.2} - 11.76^\circ, [\alpha]_D^{14.2} - 365.3^\circ.$$

In carbon tetrachloride solution:

$$l=2, c=1.3315, \alpha_D^{16.3} - 11.50^\circ, [\alpha]_D^{16.3} - 431.8^\circ.$$

Methyl r-diphenylsuccinate separates from boiling methyl alcohol, in which it is considerably less soluble than the corresponding optically active esters, in transparent, rhombic platelets. It dissolves readily in cold chloroform, rather less readily in cold acetone, ethyl acetate, or benzene. It is moderately soluble in boiling ethyl alcohol or light petroleum (b. p. 70—80°), sparingly so in boiling ether. It melts at 173.5—174°:

0.1841 gave 0.4876 CO₂ and 0.1005 H₂O. C=72.2; H=6.1.

C₁₈H₁₈O₄ requires C=72.5; H=6.1 per cent.

Methyl mesodiphenylsuccinate crystallises in fine needles, which are more sparingly soluble than the isomeric esters. It dissolves readily in cold chloroform or in boiling benzene, moderately in boiling ethyl acetate or acetone, sparingly in boiling methyl and ethyl alcohol or ether, and very sparingly in boiling light petroleum (b. p. 70—80°). It is conveniently crystallised from a considerable volume of ethyl alcohol or acetone. It melts at 218.5—219.5°:

0.1425 gave 0.3787 CO₂ and 0.0776 H₂O. C=72.5; H=6.1.

C₁₈H₁₈O₄ requires C=72.5; H=6.1 per cent.

Action of Alkali on d-Diphenylsuccinic Acid and its Esters.

Methyl *d*-diphenylsuccinate ($[\alpha]_D + 338.8^\circ$ in acetone, 0.9 gram) was heated with boiling aqueous alcoholic potassium hydroxide (0.52*N*, 50 c.c.) during two hours. The solution was evaporated nearly to dryness on the water-bath, the residue diluted with water, acidified, and the liberated diphenylsuccinic acid extracted with ether. Its specific rotation was determined in acetone solution:

$$l=2, c=2.429, \alpha_D + 14.35^\circ, [\alpha]_D + 295.4^\circ.$$

Pure *d*-diphenylsuccinic acid has $[\alpha]_D^{17} + 397.3^\circ$ when dissolved in acetone.

In order to examine the influence of the concentration of the alkali on the process of racemisation, and also to determine whether *mesodiphenylsuccinic acid* is formed, the experiment was repeated with a larger quantity of material and with a more concentrated solution of alkali, the ethyl ester being used in this instance.

Pure ethyl *d*-diphenylsuccinate (3 grams) was boiled for two hours with 50 c.c. of aqueous alcoholic potassium hydroxide (0.978*N*). The resulting solution was heated in an open dish until the alcohol was expelled, water being added from time to time so that the volume of the solution remained practically constant. After acidification with dilute sulphuric acid, the liberated acids were extracted with ether in a Hagemann's apparatus. The ether was removed, and the mixture of acids polarimetrically examined in acetone solution:

$$l=2, c=1.7765, \alpha_D + 7.78^\circ, [\alpha]_D + 218.9^\circ.$$

The acids were suspended in hot water and neutralised by aqueous barium hydroxide. The solution was concentrated and cooled, and the crystalline crop of barium salts removed. The filtrate was evaporated to dryness on the water-bath, and the

residue (0.57 gram) treated with hot water (3 c.c.) in quantity rather more than sufficient to dissolve an equal weight of barium *mesodiphenylsuccinate*. After cooling, the undissolved portion was separated; the filtrate was acidified with hydrochloric acid, whereby a bulky, white precipitate was obtained, from which, after purification from boiling ethyl alcohol, *mesodiphenylsuccinic acid*, melting at 227—229°, was isolated in small quantity.

d-Diphenylsuccinic acid is scarcely affected by prolonged treatment with an excess of hot aqueous alkali. In one experiment, *d*-diphenylsuccinic acid ($[\alpha]_D + 391.0^\circ$ in acetone, 0.96 gram) was dissolved in 100 c.c. of aqueous potassium hydroxide solution (0.772*N*). A portion of this solution when examined in a 2-dcm. tube had $\alpha_D + 5.55^\circ$. The solution was heated during eleven hours on the boiling-water bath; at the end of this period, the activity of the solution was found to be unchanged, whilst the recovered acid had $[\alpha]_D + 379.5^\circ$ ($l=2$, $c=2.8695$, $\alpha_D + 21.88^\circ$) in acetone solution.

Esterification of d- and l-Diphenylsuccinic Acids with Ethyl Alcohol.

The esterification of the optically active diphenylsuccinic acids with ethyl alcohol, according to the Fischer-Speier method, proceeds considerably less rapidly than with methyl alcohol, and is not fully effected by protracting the duration of heating or increasing the quantity of mineral acid beyond the customary limits. When the ethereal solution of the mixture of esters is shaken with dilute sodium carbonate solution, the sodium salt of the acid ester separates as a voluminous, white precipitate. The normal esters are readily purified by crystallisation from ethyl alcohol or light petroleum (b. p. 40—60°).

Ethyl l-diphenylsuccinate crystallises in rectangular plates, which melt at 104—105°. It dissolves readily in cold ether, acetone, ethyl acetate, chloroform, carbon tetrachloride, or benzene. It is freely soluble in boiling ethyl alcohol, sparingly so in the cold solvent, and moderately soluble in boiling light petroleum (b. p. 40—60°):

0.2166 gave 0.5828 CO₂ and 0.1303 H₂O. C=73.4; H=6.7.

C₂₀H₂₂O₄ requires C=73.6; H=6.8 per cent.

The following determinations of the specific rotation were made:

In acetone solution:

$l=2$, $c=1.4265$, $\alpha_D^{15.4} - 7.98^\circ$, $[\alpha]_D^{15.4} - 279.7^\circ$.

In ethyl alcoholic solution:

$l=2$, $c=0.7370$, $\alpha_D^{13.4} - 4.24^\circ$, $[\alpha]_D^{13.4} - 287.6^\circ$.

In carbon tetrachloride solution:

$$l=2, c=1.5795, \alpha_D^{16.2} - 11.29^\circ, [\alpha]_D^{16} - 357.4^\circ.$$

Ethyl d-diphenylsuccinate melts at 104—105°, and resembles the *l*-isomeride in appearance and solubility:

0.1706 gave 0.4594 CO₂ and 0.1021 H₂O. C=73.5; H=6.7.

C₂₀H₂₂O₄ requires C=73.6; H=6.8 per cent.

The specific rotation was observed in a number of solvents.

In acetone solution:

$$l=2, c=2.0525, \alpha_D^{16} + 11.47^\circ, [\alpha]_D^{16} + 279.4^\circ.$$

In methyl-alcoholic solution:

$$l=2, c=0.8160, \alpha_D^{15.2} + 4.59^\circ, [\alpha]_D^{15.2} + 281.3^\circ.$$

In ethyl acetate solution:

$$l=2, c=3.6605, \alpha_D^{18} + 21.59^\circ, [\alpha]^{18} + 294.9^\circ.$$

In chloroform solution.

$$l=2, c=2.057, \alpha_D^{18.6} + 12.57^\circ, [\alpha]_D^{18.6} + 305.5^\circ.$$

Ethyl sodium d-diphenylsuccinate separated as a voluminous, white precipitate during the purification of the crude product obtained by esterifying *d*-diphenylsuccinic acid. It was purified by crystallisation from hot water, in which it is freely soluble, although very sparingly in the cold solvent. It forms pearly leaflets, which were dried on porous earthenware exposed to the air:

0.4061 lost 0.0768 at 100—102° and gave 0.0716 Na₂SO₄.
H₂O=18.91; Na=5.71.

0.5059 lost 0.0964 at 100—105°. H₂O=19.05.

C₁₈H₁₇O₄Na.4H₂O requires H₂O=18.4; Na=5.86 per cent.

When heated to 170°, the substance darkened in colour and evolved acrid fumes.

Ethyl hydrogen l-diphenylsuccinate was prepared by acidifying the corresponding *sodium* salt with dilute sulphuric acid, and extracting with ether. The slightly viscid residue which remained after removal of the ether was purified by repeated crystallisation from boiling light petroleum (b. p. 60—80°), from which it slowly separated as a voluminous, white powder, which became strongly electrified when gently rubbed with a spatula. It is sparingly soluble in boiling light petroleum, very readily so in cold acetone, and readily so in cold ethyl alcohol. It melts at 113.5—114.5°. For analyses and determinations of specific rotation, the substance was placed in a vacuum over paraffin wax until constant in weight:

0.3145 neutralised 14.9 c.c. of 0.072*N*-barium hydroxide. Calc.,
14.67 c.c.

0.1165 gave 0.3107 CO₂ and 0.0637 H₂O. C=72.7; H=6.1.

C₁₈H₁₈O₄ requires C=72.5; H=6.1 per cent.

The following determinations of the specific rotation were made:

In acetone solution:

$$l=2, c=1.4496, \alpha_D^{16.5} - 9.53^\circ, [\alpha]_D^{16.5} - 328.7^\circ.$$

In ethyl-alcoholic solution:

$$l=2, c=0.5292, \alpha_D^{16.8} - 3.34^\circ, [\alpha]_D^{16.8} - 315.6^\circ.$$

In carbon tetrachloride solution:

$$l=2, c=0.6392, \alpha_D^{13} - 4.94^\circ, [\alpha]_D^{13} - 386.4^\circ.$$

Preparation of d- and l-Diphenylsuccinic Anhydrides.

Action of Acetyl Chloride on l-Diphenylsuccinic Acid.—*l*-Diphenylsuccinic acid ($[\alpha]_D - 380^\circ$ in acetone, 6.4 grams) was covered with acetyl chloride (19 c.c.) in a small flask provided with a calcium chloride tube. At 0°, a scarcely perceptible action occurred, and at the ordinary temperature hydrogen chloride was only very slowly evolved. The mixture was therefore very gradually heated to 30°, and maintained at this temperature until evolution of hydrogen chloride ceased. The clear solution which was thus obtained was evaporated in a vacuum over soda-lime, when the residue readily solidified. It was purified by repeated crystallisation from light petroleum (b. p. 60–80°) containing 10 per cent. of its volume of benzene. The crystals were washed with light petroleum (b. p. 40–60°), and kept in a vacuum over calcium chloride and paraffin wax.

l-Diphenylsuccinic anhydride forms oblique prisms, which melt at 105.5–106.5° after slight previous softening. It is readily soluble in cold benzene, chloroform, acetone, or ether, and sparingly so in cold ethyl alcohol or boiling light petroleum (b. p. 60–80°):

0.2986, after treatment with water, neutralised 34.7 c.c. of

0.0680*N*-barium hydroxide. Calc., 34.8 c.c.

0.1968 gave 0.5503 CO₂ and 0.0852 H₂O. C=76.3; H=4.8.

C₁₆H₁₂O₃ requires C=76.2; H=4.8 per cent.

The following determinations of the specific rotation were made:

In benzene solution:

$$l=2, c=1.6284, \alpha_D^{17.4} - 9.37^\circ, [\alpha]_D^{17.4} - 287.7^\circ.$$

In toluene solution:

$$l=2, c=1.4945, \alpha_D^{18.6} - 8.53^\circ, [\alpha]_D^{18.6} - 285.4^\circ.$$

In ethyl acetate solution:

$$l=2, c=1.465, \alpha_D^{20} - 7.71^\circ, [\alpha]_D^{20} - 263.1^\circ.$$

In carbon tetrachloride solution:

$$l=2, c=1.2985, \alpha_D^{20.4} - 6.43^\circ, [\alpha]_D^{20.4} - 247.6^\circ.$$

1458 STUDIES IN THE PHENYLSUCCINIC ACID SERIES. PART II.

Action of Acetyl Chloride on d-Diphenylsuccinic Acid.—*d*-Diphenylsuccinic anhydride was obtained by the action of acetyl chloride on the *d*-acid in the manner adopted for the *l*-isomeride. It melts at 105·5—106·5° after slight previous softening. In appearance and solubility it resembles the isomeric *l*-anhydride:

0·1906 gave 0·5324 CO₂ and 0·0819 H₂O. C=76·2; H=4·8.

C₁₆H₁₂O₃ requires C=76·2; H=4·8 per cent.

The specific rotation was determined in benzene and chloroform solution:

In benzene solution:

$$l=2, c=1\cdot2210, \alpha_D^{18\cdot5} + 6\cdot99^\circ, [\alpha]_D^{18\cdot5} + 286\cdot2^\circ.$$

In chloroform solution:

$$l=2, c=1\cdot3965, \alpha_D^{20\cdot2} + 6\cdot87^\circ, [\alpha]_D^{20\cdot2} + 246\cdot0^\circ.$$

Action of Thionyl Chloride on d-Diphenylsuccinic Acid.—*d*-Diphenylsuccinic acid (1·3 grams) was covered with thionyl chloride (6 c.c.). Practically no action occurred at the ordinary temperature. The mixture was therefore very slowly heated to 60°, when a clear solution was obtained, from which hydrogen chloride was not further evolved. Excess of thionyl chloride was removed over soda-lime, and the residue purified from a mixture of benzene and light petroleum (b. p. 60—80°). The *d*-diphenylsuccinic anhydride obtained in this way melted at 105·5—106·5° after slight previous softening. It was polarimetrically examined in benzene solution:

$$l=2, c=1\cdot4075, \alpha_D^{20} + 8\cdot10^\circ, [\alpha]_D^{20} + 287\cdot7^\circ.$$

Interaction of Water or Ethyl Alcohol and the Optically Active Diphenylsuccinic Anhydrides.

Action of Water on l-Diphenylsuccinic Anhydride.—*l*-Diphenylsuccinic anhydride (0·2986 gram) was heated on the boiling-water bath with water (about 100 c.c.) during three hours. The substance gradually passed into solution, and combination with water was shown to be complete by titration with standard aqueous barium hydroxide. The solution was acidified, the liberated acid extracted with ether, and, after desiccation at 100—105°, polarimetrically examined in acetone solution:

$$l=2, c=1\cdot4275, \alpha_D - 10\cdot34^\circ, [\alpha]_D - 362\cdot2^\circ.$$

For the pure isomeric *d*-acid, the value $[\alpha]_D^{17} + 397\cdot3^\circ$ has been determined.

Action of Water on d-Diphenylsuccinic Anhydride.—Pure *d*-diphenylsuccinic anhydride (1 gram) was heated with water (about 150 c.c.) on the boiling-water bath for three hours. The

cooled solution, from which a bulky precipitate had separated, was exhaustively extracted with ether in a Hagemann's apparatus. The acid, after removal of ether, was examined in acetone solution:

$$l=2, c=1.5585, \alpha_D + 11.35^\circ, [\alpha]_D + 364.1^\circ.$$

The crude mixture of acids was transformed into the barium salts, which were fractionally crystallised from water. On acidification of the most soluble portion, a very small quantity of *meso*-diphenylsuccinic acid was obtained, which, after being recrystallised from ethyl alcohol, melted at 228—230°.

Action of Ethyl Alcohol on l-Diphenylsuccinic Anhydride.—*l*-Diphenylsuccinic anhydride (0.7748 gram) was allowed to remain in contact with ethyl alcohol at the ordinary temperature during two days, at the end of which time it was completely dissolved. The solution was made up to 25 c.c. A portion of it, when examined in a 2-dcm. tube, had $\alpha_D^{20} - 19.07^\circ$, this value being unchanged after a further five hours. On the assumption that the anhydride is completely converted into the ethyl hydrogen ester, this corresponds with a specific rotation -260.3° for the latter ($c=3.6732$), whereas the pure acid ester has $[\alpha]_D^{16.8} - 315.6^\circ$ in ethyl-alcoholic solution ($c=0.6615$). The solution was evaporated to dryness at the ordinary temperature. The residue had $[\alpha]_D - 261.3^\circ$ in acetone solution ($c=1.280$), whilst the pure ester has $[\alpha]_D^{16.5} - 328.7^\circ$ under similar conditions. Attempts to isolate a uniform substance were unsuccessful; after two crystallisations from light petroleum (b. p. 60—80°), a product was obtained which softened from 90° onwards, the bulk melting at about 112°, but small portions remaining unmelted until 146°. When dissolved in acetone it had $[\alpha]_D - 247.1^\circ$ ($c=0.939$).

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