XX.—*Studies in the Phenylsuccinic Acid Series. Part X. Racemisation Phenomena observed during the Action of Water and Bases on the Optically Active Diphenylsuccinic Anhydrides.*

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THE optically active diphenylsuccinic anhydrides are converted by hot water into diphenylsuccinic acids of similar sign which contain about 8% of optically inactive material from which *meso*diphenylsuccinic acid can be isolated in small amount (Wren and Still, J., 1915, **107**, 1451). With cold ethyl alcohol and the *l*-anhydride a rather more complex result is obtained, the product containing about 20% of optically inactive material consisting, in part at any rate, of ethyl hydrogen *r*- and *meso*-diphenylsuccinates (*loc. cit.*; also Wren and Williams, J., 1918, **113**, 832). The greater extent of the racemisation under the milder experimental conditions appeared to indicate a profound influence of the particular reagent effecting the opening of the diphenylsuccinic anhydride ring and has led to the further observation of the behaviour of water and bases under varied conditions. The production of substituted amic acids from the active anhydrides and aniline, *p*-toluidine, α- or β-naphthylamine in presence of cold benzene is accompanied by not more than slight, if any, racemisation; it may be noted that Wren and Williams (*loc. cit.*) failed to find any evidence of the production of *meso*-forms when the *r*-anhydride reacted with amines. On the other hand, the optical activity of the diphenylsuccinic acids resulting from the action of water on the active diphenylsuccinic anhydrides is influenced in an extraordinary degree by the presence of a mutual solvent. Homogeneous *d*-diphenylsuccinic acid has $[\alpha]_D^{17^\circ}$ + 397·3° in acetone (Wren and Still, J., 1915, **107**, 449). The acid produced from the *l*-anhydride and aqueous acetic acid is only slightly racemised. In ether saturated with water the *d*-anhydride yields an acid having $[\alpha]_D$ + 232·7° (in acetone), whereas in aqueous acetone and pyridine the activity of the acid falls to + 116·5° and + 22·4° respectively. Determination of the proportion of *meso*diphenylsuccinic acid in the products has been effected according to the method of Anschütz and Bendix (*Annalen*, 1890, **259**, 81), which depends on the widely differing solubilities of barium *r*- and *meso*-diphenylsuccinates in water; the presence of optically active acid in the product is without influence on the analytical procedure, since the solubilities of the barium salts of the racemic and the active acids are closely similar (compare J., 1915, **107**, 1449). In every case the production of a small proportion of the *meso*-acid has been established. Since a high degree of accuracy could scarcely be expected with the small amounts of material available from the active anhydrides, control experiments have been performed with larger quantities of the more accessible *r*-anhydride under identical conditions. The fundamental assumption that the latter substance in dilute solution behaves as a mixture of the *d*- and *l*-forms is not, however, universally true. In aqueous ether, acetone, and pyridine the results afforded by the two sets of data are reasonably concordant. In aqueous acetic acid, on the other hand, the product obtained from the *r*-anhydride contains somewhat more than 20% of the *meso*-acid, whereas the *l*-acid derived from the *l*-anhydride contains about 6% of optically inactive material.

EXPERIMENTAL.

The *d*- and *l*-diphenylsuccinic anhydrides, prepared according to the method of Wren and Still (J., 1915, **107**, 1449), had $[\alpha]_D^{14^\circ}$ + 278·8° and $[\alpha]_D$ − 286·5° in benzene.

Interaction of Amines and Optically Active Diphenylsuccinic Anhydrides.—(a) *α-Naphthylamine.* α-Naphthylamine (0·5482 g.), dissolved in benzene, was mixed with *l*-diphenylsuccinic anhydride (0·966 g.) in benzene solution. Reaction was complete within a few minutes, after which the solvent was removed at atmospheric temperature and the residual solid dried in a vacuum until constant in weight. The product obtained had $[\alpha]_D^{19.5^\circ}$ − 200·3° in acetone (l = 2, c = 0·9412, $\alpha_D^{19.5^\circ}$ − 3·77°). Crystallisation of it from 80% alcohol gave homogeneous *l*-diphenylsuccin-α-naphthylamic acid, m. p. 206—207°, $[\alpha]_D^{18^\circ}$ − 207·3° in acetone (compare Wren and Wright, preceding paper).

(b) *β-Naphthylamine.* β-Naphthylamine (0·5229 g.) was treated with the equivalent amount of *l*-diphenylsuccinic anhydride in benzene, the same procedure being adopted as with the α-amine. The crude acid had $[\alpha]_D^{19°}$ $-$ 378·8° in acetone ($l = 2$, $c = 0{\cdot}8248$, $\alpha_D^{19°}$ $-$ 6·25°). Purification of the product from 80% alcohol gave l-*diphenylsuccin-β-naphthylamic acid,* which crystallised in small needles, m. p. 188—188·5° (Found : C, 79·0; H, 5·4. $C_{26}H_{21}O_3N$ requires C, 79·0; H, 5·4%). In acetone solution ($l = 2$, $c = 0{\cdot}7355$) $\alpha_D^{17{\cdot}5°}$ $-$ 5·72°, whence $[\alpha]_D^{17{\cdot}5°}$ $-$ 388·2°. For *d*-diphenylsuccin-β-naphthylamic acid the m. p. 188° and $[\alpha]_D^{15{\cdot}5°}$ + 386·9° (in acetone) are recorded by Wren and Wright (*loc. cit.*).

(c) *Aniline.* Freshly distilled aniline (0·429 g.) and the equivalent amount of the *l*-anhydride in benzene yielded *l*-diphenylsuccinanilic acid having $[\alpha]_D^{10°}$ $-$ 325·0° in acetone ($l = 2$, $c = 0{\cdot}8070$, $\alpha_D^{10°}$ $-$ 5·24°), whereas Wren and Burrows (J., 1924, **125**, 1934) record $[\alpha]_D^{10{\cdot}2°}$ $-$ 338·2° for the homogeneous acid.

(d) p-*Toluidine.* The *l*-diphenylsuccino-*p*-toluidic acid derived from 0·3433 g. of *p*-toluidine had $[\alpha]_D$ $-$ 319·5° in acetone ($l = 2$, $c = 0{\cdot}8544$, α_D $-$ 5·46°); the homogeneous acid has $[\alpha]_D^{18{\cdot}8°}$ $-$ 329·5° in the same solvent (Wren and Burrows, *loc. cit.*).

Interaction of Water and Optically Active Diphenylsuccinic Anhydrides in the Presence of Solvents.—(a) *Acetone.* A solution of *d*-diphenylsuccinic anhydride (0·7742 g.) in a mixture of acetone (20 c.c.) and water (5 c.c.) was preserved at laboratory temperature during 3 days. It was then allowed to evaporate spontaneously and the residue was dried in a vacuum desiccator until constant in weight. It had $[\alpha]_D^{17°}$ + 116·7° in acetone ($l = 2$, $c = 0{\cdot}9425$, $\alpha_D^{17°}$ + 2·20°), whereas the homogeneous acid has $[\alpha]_D^{17°}$ + 393·3°. The proportion of *meso*-acid in the product was 4·5%.

(b) *Pyridine.* The *d*-anhydride (1·1974 g.) was preserved in a solution of pyridine (24 c.c.) and water (6 c.c.) during 3 days. The mixture was treated with an excess of dilute hydrochloric acid, and the diphenylsuccinic acid removed by ether. In acetone, it had $[\alpha]_D^{17°}$ + 22·4° ($l = 2$, $c = 0{\cdot}8488$, $\alpha_D^{17°}$ + 0·38°); it contained 3·4% of *meso*-acid. Repetition of the experiment gave an acid with $[\alpha]_D$ + 21·1° in acetone.

(c) *Ether.* The *d*-anhydride (0·8336 g.) was dissolved in 30 c.c. of ether saturated with water; 4 c.c. of water were added, after which the solution was preserved at atmospheric temperature during 3 days. The *d*-acid obtained had $[\alpha]_D$ + 232·7° in acetone ($l = 2$, $c = 0{\cdot}9260$, α_D + 4·31°) and contained 2·8% of the *meso*-form.

(d) *Acetic acid.* The *l*-anhydride (0·9995 g.) was preserved in

85% acetic acid (35 c.c.) during 3 days. The bulk of the acetic acid was removed by distillation under diminished pressure below 40° and the remainder in a vacuum over soda-lime. The isolated *l*-diphenylsuccinic acid had $[\alpha]_{\mathrm{D}}^{19\cdot5^\circ} - 364\cdot7^\circ$ in acetone ($l = 2$, $c = 0\cdot8828$, $\alpha_{\mathrm{D}}^{19\cdot5^\circ} - 6\cdot44^\circ$) and contained 3·6% of the *meso*-form. A second experiment gave an acid with $[\alpha]_{\mathrm{D}} - 373\cdot3^\circ$ in acetone.

Interaction of Water and r-*Diphenylsuccinic Anhydride in the Presence of Solvents.*—The experiments were performed in exactly the same manner as the corresponding ones with the active anhydrides except that much larger quantities were employed. The percentage of *meso*-acid in the mixed acids obtained by use of aqueous acetone, pyridine, and ether was 2·0, 2·0, and 1·0 respectively. With acetic acid, however, the values 21·6, 22·3, and 20·6 were found in three successive experiments.

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