# XIX.—*Studies in the Phenylsuccinic Acid Series. Part IX. The Resolution of* r-*Diphenylsuccin-α- and -β-naphthylamic Acids into their Optical Antipodes.*

By HENRY WREN and EDWARD WRIGHT.

IN continuation of the work of Wren and Burrows (J., 1924, **125**, 1934), the resolution of *r*-diphenylsuccin-α- and -β-naphthylamic acids has been effected by the alkaloidal method. The active acids, like the corresponding anilic and *p*-toluidic acids (*loc. cit.*), exhibit the high optical activity characteristic of simple derivatives of the active diphenylsuccinic acids. Conversion of the acids into the substituted imides is accompanied by very marked diminution in specific rotation, the optical effect of the change thus resembling that of the transformation of the active diphenylsuccinic acids into their anhydrides (Wren and Still, J., 1915, **107**, 1457). The influence of the aryl group on the specific rotation of the substituted diphenylsuccinamic acids and the diphenylsuccinimides appears quite irregular; for the former group the substituents fall into the descending sequence β-naphthyl, phenyl, *p*-tolyl, α-naphthyl, whereas for the latter group the order is α-naphthyl, *p*-tolyl, phenyl, β-naphthyl.

## EXPERIMENTAL.

*Resolution of* r-*Diphenylsuccin-α-naphthylamic Acid into its Optical Antipodes.*—r-*Diphenylsuccin-α-naphthylamic acid*, m. p. 217—219° (decomp.), was prepared by mixing solutions of equivalent quantities of *r*-diphenylsuccinic anhydride and α-naphthylamine in cold benzene and purified by crystallisation from rectified spirit (Found: C, 79·0; H, 5·4. $C_{26}H_{21}O_3N$ requires C, 79·0; H, 5·4%).

A solution of *r*-diphenylsuccin-α-naphthylamic acid (25·1 g.) and quinine (24·1 g.) in boiling absolute ethyl alcohol (175 c.c.) was filtered and preserved in an ice-chest during 3 days. The ill-defined crystals which separated (26·5 g.) were crystallised repeatedly from the same solvent, 5 c.c. of the latter being used for each gram of material. The course of the resolution was followed by observing the specific rotations in acetone of the acids isolated from the successive filtrates, the following values being obtained: − 155·5°, − 61·4°, + 93·4°, and + 154·9°. The residual quinine salt (9·6 g.) was decomposed with dilute sulphuric acid and ether, and the crude d-*diphenylsuccin-α-naphthylamic acid* crystallised from 80% alcohol until its specific rotation remained constant. It formed small needles, m. p. 206—207° (Found: C, 78·8; H, 5·4%). In acetone ($l = 2$, $c = 0{\cdot}8432$) $\alpha_D^{16°}$ + 3·47°, whence $[\alpha]_D^{16°}$ +205·8°.

*l*-Diphenylsuccin-α-naphthylamic acid ($[\alpha]_D$ − 123·2° in acetone;

16·7 g.), from the crude lævorotatory mixture of acids obtained from the first filtrates of the quinine salt (see above), and cinchonidine (13 g.) were dissolved in boiling ethyl alcohol (120 c.c.). The salt, which separated very slowly from the cold solution, was recrystallised from alcohol and decomposed in the usual manner, yielding l-*diphenylsuccin-α-naphthylamic acid* having $[\alpha]_D$ − 194·3° in acetone. Crystallisation of the crude acid from 80% alcohol afforded the homogeneous acid, which exactly resembled its optical antipode in appearance, solubility and melting point. It had $[\alpha]_D^{17°}$ − 206·6° in acetone solution ($l = 2$, $c = 0·9484$, $\alpha_D^{17°}$ − 3·92°) (Found: C, 79·2; H, 5·4%).

d-*Diphenylsuccin-α-naphthil*, m. p. 145°, was prepared by the action of boiling ethyl-alcoholic hydrogen chloride (3%) on the corresponding acid. The crude product had $[\alpha]_D$ + 136·8° in acetone, thus showing that appreciable racemisation had not occurred during the course of the change. After crystallisation from absolute alcohol containing a little hydrogen chloride, the compound was optically homogeneous. In acetone ($l = 2$, $c = 1·0916$) $\alpha_D^{16°}$ + 3·04°, whence $[\alpha]_D^{16°}$ + 139·2°; in chloroform ($l = 2$, $c = 1·2608$), $\alpha_D^{17°}$ + 3·11°, whence $[\alpha]_D^{17°}$ + 123·3° (Found: C, 82·9; H, 5·2. $C_{26}H_{19}O_2N$ requires C, 82·7; H, 5·1%).

*d*-Diphenylsuccin-α-naphthil is unusually readily racemised by sodium ethoxide in alcoholic solution. Crystallisation of the active material from boiling alcohol was occasionally accompanied by complete racemisation. The danger was avoided by the use of alcohol containing a trace of hydrogen chloride.

*Resolution of* r-*Diphenylsuccin-β-naphthylamic Acid into its Optical Antipodes.*—*r*-Diphenylsuccin-β-naphthylamic acid (m. p. 201—202°; prepared in almost quantitative yield in the same manner as the α-acid and purified by crystallisation from rectified spirit) (49·8 g.) and quinine (23·6 g.) were dissolved in boiling absolute alcohol and the solution was preserved in an ice-chest during 3 days. The needles (27·8 g.) which slowly separated were repeatedly crystallised from the same solvent, 20 c.c. of which were used for each gram of salt. The acid recovered from the successive filtrates had $[\alpha]_D$ − 96·3°, − 56·4°, + 44·0°, + 126·2° and + 210°, respectively, in acetone. The crude dextrorotatory acid isolated from the residual salt was crystallised from 80% alcohol until successive crops had a constant specific rotation. d-*Diphenylsuccin-β-naphthylamic acid* crystallises in small needles, m. p. 188° (Found: C, 78·8; H, 5·4. $C_{26}H_{21}O_3N$ requires C, 79·0; H, 5·4%). In acetone ($l = 2$, $c = 0·7288$) $\alpha_D^{15·5°}$ + 5·64°, whence $[\alpha]_D^{15·5°}$ + 386·9°.

Preparation of the homogeneous *l*-acid from the crude lævorotatory mixture of acids isolated from the initial filtrates obtained in the foregoing resolution could not be effected by crystallisation or by means of cinchonine, cinchonidine, or brucine.

d-*Diphenylsuccin-β-naphthil*, prepared in the same manner as the α-compound, separated from alcohol, containing a trace of hydrogen chloride, in slender needles, m. p. 178—179° (Found: C, 82·9; H, 5·1. $C_{26}H_{19}O_2N$ requires C, 82·7; H, 5·1%). In acetone ($l = 2$, $c = 0{\cdot}8792$) $\alpha_D^{18°} + 1{\cdot}845°$, whence $[\alpha]_D^{18°} + 104{\cdot}9°$.

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MUNICIPAL COLLEGE OF TECHNOLOGY,
BELFAST.

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