126. *The Resolution of β-Naphthylmethylcarbinol.*

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d- and *l*-β-Naphthylmethylcarbinols have been prepared, and their properties compared with those of the corresponding α-naphthyl compounds.

Optically active α-naphthylmethylcarbinol was prepared by Pickard and Kenyon (J., 1914, **105**, 1115, 2644), and it was considered of interest to compare its properties with those of the optically active β-naphthyl analogue.

dl-β-Naphthylmethylcarbinol, obtained by reduction of β-naphthyl methyl ketone, yields a hydrogen phthalic *ester*, the *cinchonidine* and *strychnine* salts of which on fractional crystallisation yield the *d*- and the *l*-hydrogen phthalic *ester* respectively. Saponification of these yields the optically pure *d*- and *l*-β-naphthylmethylcarbinols. Rotatory powers are given in Table I, and comparative data with those of corresponding derivatives of α-naphthylmethylcarbinol in Table II.

It will be noticed that the rotatory powers of both series of compounds are susceptible of very wide variations with change of solvent (and of temperature in the case of α-naphthylmethylcarbinol; the m. p. of the corresponding β-compound is too high for these determinations to be made).

It was shown by Pickard and Kenyon (*loc. cit.*, where the diagram is given) that the rotatory powers of *l*-α-naphthylmethylcarbinol and its derivatives despite their wide variation ($[\alpha]_{4358}$ from + 170° to − 200°) would all lie closely on a single characteristic diagram, the three straight lines (for λ 5893, 5461, 4358) of which intersected at about $[\alpha]_\lambda$ − 14°. It is now found that the rotatory powers of the β-naphthyl analogue and its derivatives will also lie on the same characteristic diagram.

It thus appears that both the *l*-α- and the *l*-β-derivatives of naphthalene are configuratively similar, and further, that the optical behaviour of both series of compounds is dominated by the naphthyl radical.

TABLE I.

Specific Rotatory Powers in Solvents at Room Temperature (l, 2).

Solvent.	*c*.	$[\alpha]_{6438}$.	$[\alpha]_{5893}$.	$[\alpha]_{5780}$.	$[\alpha]_{5461}$.	$[\alpha]_{4358}$.	$[\alpha]_{4358}/[\alpha]_{5461}$.
(a) d-*β-Naphthylmethylcarbinyl hydrogen phthalate.*							
C_5H_5N	5·001	+ 24·5°	+ 29·8°	+ 31·3°	+ 34·4°	+ 51·5°	—
AcOH	5·103	+ 8·1	+ 9·9	+ 11·9	+ 12·3	+ 12·4	—
$CHCl_3$	5·038	− 5·2	− 7·2	− 8·0	− 9·9	− 27	—
Et_2O	4·778	− 23·1	− 29·7	− 31·7	− 37·5	− 82	—
MeOH	4·752	− 30·8	− 38·7	− 42·2	− 49·6	− 107	—
EtOH	4·994	− 35·5	− 45·4	− 48·3	− 56·3	− 124	—
Corresponding l-*ester.*							
EtOH	4·994	+ 34·0	+ 44·7	+ 47·9	+ 55·8	+ 120	—
(b) d-*β-Naphthylmethylcarbinol.*							
EtOH	5·068	+ 34·1	+ 41·3	+ 44·0	+ 49·8	+ 84	1·68
C_6H_6	4·892	35·9	44·3	46·3	52·65	88·8	1·70
Et_2O	4·940	43·7	52·9	55·9	62·8	108	1·72
$CHCl_3$	4·834	45·0	55·8	58·0	66·3	117	1·76
CS_2	4·685	52·6	66·2	69·8	79·2	144	1·82
C_5H_5N	4·790	66·6	82·0	87·0	98·6	175	1·77
Corresponding l-*carbinol.*							
EtOH	4·920	− 34·8	− 41·9	− 44·1	− 49·7	− 85	1·71

TABLE II.

Comparison of the Properties of α- and β-Naphthylmethylcarbinols and their Derivatives.

			α-.	β-.
dl-Carbinol	M. p.	—	66°	71—72°
l- ,, ...	M. p.	—	47	71—72
l- ,, ...	$[\alpha]_{5461}$	in EtOH	− 89·0°	− 49·8°
,, ...	,,	in $CHCl_3$	− 78·5	− 66·3
l-Acetate	$\alpha^{19°}_{5461}$	(*l*, 1·0)	− 42·7	− 180·9
dl-Hydrogen phthalate	M. p.	—	131—132°	125°
l- ,, ,, ...	M. p.	—	(oil)	101—102
l- ,, ,, ...	$[\alpha]_{5461}$	in EtOH	+ 84·8°	+ 55·8°
l- ,, ,, ...	,,	in $CHCl_3$	+ 53·5	+ 9·3

Replacement Reactions of l-β-*Naphthylmethylcarbinyl Hydrogen Phthalate.*—(a) *With acetic acid.* By the action of glacial acetic acid containing a small proportion of sodium acetate, the hydrogen phthalate is slowly converted into the acetate which, although its rotatory power is only about 6% of that of the optically pure ester, is apparently produced without inversion of configuration. The *l*-hydrogen phthalate undergoes extensive racemisation, particularly when the period of reaction is prolonged.

(b) *With formic acid.* Anhydrous formic acid converts the *l*-hydrogen phthalate rapidly and completely into the *dl*-formate. The readiness with which this ester is thus produced is in marked contrast to the sluggishness with which β-naphthylmethylcarbinol is esterified by anhydrous formic acid.

The significance of these reactions will be discussed in a future communication.

EXPERIMENTAL.

dl-β-Naphthylmethylcarbinol was obtained according to Lund's procedure (*Ber.*, 1937, **70**, 1520) by reduction of technical β-naphthyl methyl ketone (m. p. 54—55°; 170 g.) by heating it with a solution of aluminium *iso*propoxide (from 20 g. of aluminium) in *iso*propyl alcohol (600 c.c.) for several hours. The acetone produced during the reaction was allowed to distil slowly, and when the reaction appeared complete, the excess of *iso*propyl alcohol was removed by distillation. Treatment of the residue with cold dilute acid liberated the carbinol, which, after crystallisation from aqueous alcohol, had m. p. 59—62° (170 g.). It separated from ether–light petroleum in spherical masses of soft, fine needles, m. p. 71—72° (Lund, *loc. cit.*, gives m. p. 72°).

dl-β-*Naphthylmethylcarbinyl Hydrogen Phthalate.*—A mixture of the carbinol (115 g.), phthalic anhydride (95 g.), and pyridine (55 g.) was heated on the steam-bath for several hours; the homogeneous product was cooled, and decomposed with dilute hydrochloric acid, and the resulting acid *ester* crystallised from aqueous alcohol and subsequently from ether–light petroleum. It (158 g.) formed bulky masses of soft, fine needles, m. p. 125° (Found, by titration with N/10-NaOH; *M*, 325. $C_{20}H_{16}O_4$ requires *M*, 320).

d-β-*Naphthylmethylcarbinyl Hydrogen Phthalate.*—Cinchonidine (145 g.) was dissolved in a hot solution of the *dl*-acid ester (158 g.) in acetone (300 c.c.). The crystalline material (157 g.) which separated on cooling was filtered off and recrystallised from acetone (3 l.) twice, yielding the optically pure *cinchonidine* salt (100 g.) in fine needles, m. p. 167° (decomp.). By working up the mother-liquors a further 30 g. were obtained; $[\alpha]_{5893}$ — 41·0°, $[\alpha]_{5461}$ — 48·5°, $[\alpha]_{4358}$ — 90·0° (*l*, 2; *c*, 5·200) in chloroform solution (Found : N, 4·9. $C_{39}H_{38}O_5N_2$ requires N, 4·6%). Decomposition of this cinchonidine salt with dilute hydrochloric acid yielded d-β-*naphthylmethylcarbinyl hydrogen phthalate*, which separated readily from either aqueous alcohol or ether–light petroleum in fine, soft needles, m. p. 101—102°. Rotatory powers are recorded in Table I (Found, by titration with NaOH : *M*, 326. $C_{20}H_{16}O_4$ requires *M*, 320).

l-β-*Naphthylmethylcarbinyl Hydrogen Phthalate.*—Decomposition with dilute hydrochloric acid of the more soluble fractions of the cinchonidine salt yielded the *l* + *dl*-hydrogen phthalate, with $[\alpha]_{5893}$ + 31° in ethyl-alcoholic solution. When a solution of this ester (38 g.) and strychnine (38·5 g.) in hot methyl alcohol (150 c.c.) was cooled, it deposited a salt which, after three recrystallisations from methyl alcohol (2·5 l.), yielded *strychnine* l-β-*naphthylmethylcarbinyl phthalate* as rosettes of glistening needles, m. p. 200—202°; $[\alpha]_{5893}$ — 45·3°, $[\alpha]_{5461}$ — 57·0°, $[\alpha]_{4385}$ — 97·3° (*l*, 2; *c*, 5·034) in chloroform solution (Found : N, 4·7. $C_{36}H_{40}O_6N_2$ requires N, 4·7%). Decomposition of this strychnine salt with dilute ammonia yielded l-β-*naphthylmethylcarbinyl hydrogen phthalate*, fine needles, m. p. 101—102° from aqueous alcohol. Rotatory powers are in Table I (Found, by titration : *M*, 326).

The specific rotatory powers of the *d*- and the *l*-hydrogen phthalic ester obtained by decomposition of the alkaloidal salts were not altered by crystallisation of these esters from various solvents. On the other hand, a mixture of *d* + *dl*-hydrogen phthalic ester was separated by one crystallisation from ether–light petroleum into two fractions, $[\alpha]_{5893}$ + 2·0° and + 32·8°. This affords further evidence that optical purity has been reached in the fractional crystallisation of the cinchonidine and strychnine salts.

d-β-Naphthylmethylcarbinol, obtained by hydrolysis of the *d*-hydrogen phthalic ester in aqueous-alcoholic sodium hydroxide, separates from ether–light petroleum in nodules of soft, short needles, m. p. 71—72°. A mixture of approximately equal parts of this *d*-alcohol and the corresponding *dl*-alcohol softens and melts at 63—68°.

l-β-Naphthylmethylcarbinol, obtained similarly from the corresponding *l*-hydrogen phthalic ester, has m. p. 71—72°. Rotatory powers are recorded in Table I. Confirmation that optical purity has been reached is afforded by the observation that an incompletely resolved specimen of the *d* + *dl*-alcohol, with $[\alpha]_{5461}$ + 47·9° in ethyl-alcoholic solution, by recrystallisation from ether–light petroleum yielded the alcohol with a maximum rotatory power identical with that of the alcohol obtained by the hydrolysis of its hydrogen phthalic ester of maximum rotatory power.

d-β-Naphthylmethylcarbinyl formate (2 g.) was obtained when a solution of the *d*-alcohol (2 g.) and sodium formate (1·5 g.) in anhydrous formic acid (30 c.c.) was kept at 40° for 4 hours (at higher temperatures a resinous material is produced); small needles, from ether–light petroleum, m. p. 62—64°, $[\alpha]_{5893}$ + 10·5°; $[\alpha]_{5461}$ + 13·2° (*c*, 5·010; *l*, 2) in ethyl-alcoholic solution. The corresponding *dl*-formate, prepared similarly, had m. p. 54—55° either alone or when mixed with the *dl*-formate prepared by the action of formic acid on *dl*-β-naphthylmethylcarbinyl hydrogen phthalate.

l-β-*Naphthylmethylcarbinyl benzoate*, prepared by Einhorn's method, short needles, m. p. 62—64°, from ether–light petroleum, has $[\alpha]_{5893}$ — 53·4°, $[\alpha]_{5461}$ — 68·2° (*c*, 3·580; *l*, 2) in ethyl-alcoholic solution (Found : C, 82·2; H, 5·6. $C_{19}H_{16}O_2$ requires C, 82·6; H, 5·8%). The corresponding *dl*-compound has m. p. 51—52°.

d-β-*Naphthylmethylcarbinyl acetate* (3·5 g.) was prepared by the action of acetic anhydride (2·5 g.) and pyridine (1·8 g.) on the *d*-carbinol (3·5 g.), b. p. 172°/14 mm., $n_{D}^{19^\circ}$ 1·5745 (supercooled). It formed short needles, m. p. 34—35°, and separated from aqueous alcohol in glistening leaflets, m. p. 36—37°. In the homogeneous state it had α_{5893} + 74·65°, α_{5780} + 78·37°, α_{5461} + 90·44°, α_{4358} + 168·35° (*l*, 0·5; *t*, 19°); in ethyl-alcoholic solution (*c*, 5·344; *l*, 2) $[\alpha]_{5893}$ + 124·2°, $[\alpha]_{5780}$ + 130·5°, $[\alpha]_{5461}$ + 150·0°, $[\alpha]_{4358}$ + 271°; in glacial acetic acid (*c*, 3·408; *l*, 2) $[\alpha]_{5893}$ + 134·4°, $[\alpha]_{5780}$ + 142·1°, $[\alpha]_{5461}$ + 163·6°, $[\alpha]_{4358}$ + 296° (Found : C, 79·0; H, 6·6. $C_{14}H_{14}O_2$ requires C, 78·5; H, 6·5%). The *dl*-acetate, prepared similarly, had b. p. 172°/15 mm., $n_D^{19^\circ}$ 1·5753, but could not be induced to crystallise.

Action of Acetic Acid on l-β-*Naphthylmethylcarbinyl Hydrogen Phthalate at* 100°.—(i) The *l*-ester (10·5 g.) was heated with glacial acetic acid (56 g.) containing anhydrous sodium acetate (4 g.) on the steam-bath for about 40 hours. From the products of reaction there were recovered *l* + *dl*-β-naphthylmethylcarbinyl hydrogen phthalate (1·2 g.; $[\alpha]_{5461}$ + 8·9°, *c* 4·5, in alcoholic solution) and *l*-β-naphthylmethylcarbinyl acetate (4·5 g.), b.p. 171°/13 mm.; $n_D^{14^\circ}$ 1·5796; $\alpha_{5893}^{20^\circ}$ − 4·80°, $\alpha_{5461}^{20^\circ}$ − 5·86°, α_{4358}^{20} − 10·75° (*l*, 0·5) (activity = 6·5%, without inversion of configuration).

(ii) A mixture of the *l*-ester (2 g.; $[\alpha]_{5461}$ + 40° in alcohol), acetic acid (20 g.), and sodium acetate (0·5 g.) after being heated on the steam-bath for about 20 hours, yielded the *l* + *dl*-acetate (0·7 g.); $[\alpha]_{5461}$ − 8·8° (in ethyl alcohol). The recovered hydrogen phthalate (0·4 g.) had $[\alpha]_{5461}$ + 27° (*c*, 1·9) in ethyl alcohol.

Action of Formic Acid on l-β-*Naphthylmethylcarbinyl Hydrogen Phthalate.*—A solution of the *l*-ester (1·00 g.) in anhydrous formic acid (20 c.c.) deposited a crystalline crop of phthalic acid within 2 mins.; after 30 mins. this was filtered off. The filtrate was optically inactive; it was diluted with water, and the precipitated material crystallised from light petroleum—it proved to be dl-β-***naphthylmethylcarbinyl formate***, nodules of small needles, m. p. 55—56° (alone or mixed with an authentic specimen) (Found: C, 78·2; H, 5·9. $C_{13}H_{12}O_2$ requires C, 78·0; H, 6·0%). When heated with aqueous-alcoholic sodium hydroxide it yielded *dl*-β-naphthylmethylcarbinol, m. p. 71—72° alone or mixed with an authentic specimen.

Thanks are expressed to the Government Grants Committee of the Royal Society and to Imperial Chemical Industries Ltd. for grants.

BATTERSEA POLYTECHNIC, LONDON, S.W. 11. [*Received, March* 26*th*, 1940.]