#### 2: 4-DIMETHYLTETRAHYDROQUINOLINES. 725

### LXXVII.— The Four Stereoisomeric Optically Active 2:4-Dimethyltetrahydroquinolines.

#### By JOHN THOMAS.

THE dialkyltetrahydroquinolines, in which the two alkyl radicles are attached to separate carbon atoms in the piperidine ring, contain two asymmetric carbon atoms in the molecule, and would hence be expected to exist in two pairs of enantiomorphously related optically active isomerides; the reduction product of a dialkylquinoline containing the two alkyl radicles in the pyridine ring should thus yield a mixture of four optically active substances. In general, the dialkyltetrahydroquinolines prepared by reducing the corresponding dialkylquinolines have been described as single substances, and it seemed therefore of interest to ascertain whether in any particular case the four isomerides referred to could be actually separated from the synthetic secondary base.

The investigation of 2:4-dimethyltetrahydroquinoline was undertaken for the purpose of resolving the problem indicated, and it is shown in the present paper that the synthetic base may be resolved into four optically active components; the separation was effected by

#### 726 THOMAS: THE FOUR STEREOISOMERIC OPTICALLY

crystallisation of the base with d- and l-a-bromocamphor- $\pi$ -sulphonic acids, as first employed by Pope and Harvey (Trans., 1901, **79**, 74). The synthetic 2:4-dimethyltetrahydroquinoline may thus be regarded as composed of two externally compensated bases, which may be conveniently distinguished as the 2:4-dimethyltetrahydroquinoline and the *iso*-2:4-dimethyltetrahydroquinoline; the distinction thus introduced is, of course, an arbitrary one.

#### 2:4-Dimethyl- and iso-2:4-Dimethyl-tetrahydroquinoline.

2:4-Dimethylquinoline is formed, as described by Beyer (J. pr. Chem., 1886, [ii], **33**, 401), by the interaction of paraldehyde, acetone, and aniline; several hundred grams were prepared and purified by means of the picrate, the base boiling at  $263-266^{\circ}$  being used for reduction. It was found that 2:4-dimethylquinoline is not reduced by tin and hydrochloric acid, as are the monomethyl-quinolines, but as Ferratini (Gazzetta, 1893, **23**, ii, 117) states that the base can be reduced by sodium and alcohol, without giving details, the following method of reduction was employed with success.

2:4-Dimethylquinoline (50 grams) is dissolved in absolute alcohol (500 grams) in a large flask, and sodium (75 grams) added in small portions; during the latter stages of the reaction the flask is heated to  $150^{\circ}$  on an oil-bath for about two hours. After solution of the sodium, water and hydrochloric acid are added, the alcohol distilled off, and excess of potassium hydroxide added; the separated base is extracted with benzene, and the benzene extract fractionally distilled after drying with potassium hydroxide. 2:4-Dimethyltetrahydroquinoline (45 grams) is thus obtained as a colourless oil boiling at  $250-254^{\circ}$ .

# $\begin{array}{c} \textit{Benzoyl-2:4-dimethyltetrahydroquinoline,} \\ C_{6}H_{4} < \begin{array}{c} CHM_{\theta} \cdot CH_{2} \\ NBz - CHM_{\theta} \end{array}$

The benzoyl derivative, prepared by the Schotten-Baumann reaction, crystallises from dilute alcohol in thin, colourless plates, melting at 115—116°; it is very soluble in alcohol or benzene, but less so in acetone, chloroform, or ethyl acetate:

0.2450 gave 0.7325 CO<sub>2</sub> and 0.1595  $H_2O$ . C=81.5; H=7.23.

 $C_{18}H_{19}ON$  requires C = 81.5; H = 7.17 per cent.

As the fractional crystallisation of the benzoyl derivative gave no immediate indication of a separation, the resolution of the mixed base with the optically active acid was attempted.

#### ACTIVE 2: 4-DIMETHYLTETRAHYDROQUINOLINES.

#### d-2:4-Dimethyltetrahydroquinoline d-a-Bromocamphor-n-sulphonate, C<sub>11</sub>H<sub>15</sub>N,C<sub>10</sub>H<sub>14</sub>OBr·SO<sub>3</sub>H.

2:4-Dimethyltetrahydroquinoline and d-a-bromocamphor- $\pi$ -sulphonic acid, in molecular proportion, were boiled together in dilute alcoholic solution until all had dissolved; a viscid oil separated on cooling, and this gradually crystallised during several days in the The semicrystalline mass was pressed on the vacuum desiccator. filter and freed from oil by repeated crystallisation from hot dilute alcohol; after seven crystallisations the specific rotatory power in dilute aqueous solution attained the constant value of  $[\alpha]_{\rm p} + 84.4^{\circ}$ . The salt crystallises in voluminous, white needles, and melts at 126°, previously softening at 119°. It is extremely soluble in alcohol, readily so in acetic acid, benzene, chloroform, or acetone, and only moderately so in water or ethyl acetate:

0.2008 gave 0.3906 CO<sub>2</sub> and 0.1154 H<sub>2</sub>O. C=53.1; H=6.33.

 $C_{21}H_{30}O_4NBrS$  requires C=53.4; H=6.35 per cent.

As the rotation constants vary considerably with the solvent in the cases of this and other substances described in the present paper, a considerable number of determinations were made, all at 18°.

	Weight in	. in		
Solvent.	in 25 c.c.	$a_{\rm D}$ III 2-dcm. tube.	[a].	<b>[M]</b>
Water	0.1040	$+0.72^{\circ}$	+ 86.2	+ 407°
	0.2052	1.395	84.9	401
	0 3090	2.10	85.0	401
	0.4100	2.84	86.5	408
Benzene	0.1200	0.85	68 3	822
	0.3000	1.62	67.8	320
Chloroform	0.1570	1.02	83.6	395
	0.2940	1.99	84.6	399
Acetone	0.1488	1.08	90.7	428
	0.5860	2.12	90.2	426
Ethyl alcohol	0.1600	1.27	99.2	468
-	0.3382	2.67	98.7	466
Ethyl acetate	0.1292	1.23	96.4	456
-	0.3145	2.42	97·3	459
Acetic acid	0.1367	1 · <b>1</b> 8	107.6	508
	0.2582	2.73	105.8	500

Disregarding the first determination in aqueous solution as not possessed of much accuracy owing to the dilution of the solution, the molecular rotatory power of the salt in dilute aqueous solution may be taken as  $[M]_{D} + 401^{\circ}$ ; allowing the value  $[M]_{D} + 279^{\circ}$  for the acidic ion (Pope and Read, Trans., 1910, 97, 2201), the molecular rotatory power of the basic ion is calculated as  $[M]_{n} + 122^{\circ}$ . It is shown below that the molecular rotatory power of the basic ion, as calculated from observations made with the hydrochloride, is greater than  $[M]_{D} + 160^{\circ}$ ; another instance is thus added to those recorded by Pope and Read (this vol., p. 775) of the abnormal molecular rotatory powers of salts of the type dBdA in aqueous solution.

#### d-2: 4-Dimethyltetrahydroquinoline, $C_6H_4 < CHMe \cdot CH_2$ NH - CHMe.

On distilling the salt just described with barium hydroxide in a current of steam, extracting the oil from the distillate with benzene, drying the benzene solution with potassium hydroxide, and subjecting it to fractional distillation, d-2:4-dimethyltetrahydroquinoline is obtained as a colourless oil boiling at 251—254°. The base is miscible with organic solvents, is practically insoluble in water, and gradually darkens in colour on exposure to the air; on cooling in boiling liquid air it solidifies to a hard, resinous mass. The following determinations of rotatory power were made:

- The observed rotation in a 2.4-dcm. tube at 20° is  $\alpha + 14.49^{\circ}$ , and the density at 20°/4° is 1.0009, whence  $[\alpha]_{D} + 60.13^{\circ}$  and  $[M]_{D} + 97.1^{\circ}$ .
- 0.2945 gram, made up to 20 c.c. with alcohol at 18°, gave  $\alpha_{\rm D} + 1.68^{\circ}$  in a 2-dcm. tube, whence  $[\alpha]_{\rm D} + 57.0^{\circ}$  and  $[M]_{\rm D} + 91.8^{\circ}$ .
- 0.7350 gram, made up to 20 c.c. with alcohol at 18°, gave  $\alpha_D + 3.31^\circ$  in a 2-dcm. tube, whence  $[\alpha]_D + 56.7^\circ$  and  $[M]_D + 91.3^\circ$ .

#### d-2: 4-Dimethyltetrahydroquinoline Hydrochloride, $C_{11}H_{15}N$ , HCl.

The hydrochloride separates in radiate groups of long, colourless prisms on cooling a hot solution of the base in concentrated hydrochloric acid; after washing with hydrochloric acid and crystallisation from hot water, the salt melts at 226°. It is readily soluble in warm alcohol, sparingly so in acetone, and practically insoluble in benzene or chloroform:

0.1510 gave 0.3680 CO<sub>2</sub> and 0.1117  $H_2O$ . C=66.5; H=8.21.

 $C_{11}H_{15}N$ , HCl requires C=66.8; H=8.10 per cent.

The following determinations of the rotation constants were made:

- 0.1155 gram, made up to 25 c.c. with water at 18°, gave  $a_D + 0.79^\circ$  in a 2-dcm. tube, whence  $[a]_D + 84.4^\circ$  and  $[M]_D + 167^\circ$ .
- 0.2270 gram, made up to 25 c.c. with water at 18°, gave  $a_{\rm D} + 1.51^{\circ}$  in a 2-dcm. tube, whence  $[a]_{\rm D} + 83.1^{\circ}$  and  $[M]_{\rm D} + 164.5^{\circ}$ .

0.1072 gram, made up to 25.4 c.c. with alcohol at 19°, gave  $a_{\rm p} + 0.775^{\circ}$  in a 2-dcm. tube, whence  $[a]_{\rm p} + 91.4^{\circ}$  and  $[M]_{p} + 181^{\circ}$ .

#### Benzoyl-d-2: 4-dimethyltetrahydroquinoline.

The benzoyl derivative is prepared by the action of benzoyl chloride and sodium hydroxide on the bromocamphorsulphonate, and, after crystallisation from dilute alcohol, is obtained in colourless, crystalline plates, which melt at 98-99°; it is readily soluble in benzene or alcohol, moderately so in acetone, ethyl acetate, or acetic acid, and very sparingly soluble in light petroleum :

0.2003 gave 0.5790 CO<sub>2</sub> and 0.1305  $H_2O$ . C=81.2; H=7.15.

 $C_{18}H_{19}ON$  requires C=81.5; H=7.17 per cent.

The rotation constants were determined at 18° as follows:

	Weight in	•		
Solvent	grams	$a_{\rm D}$ III 9 dam tube	[0]	EMO
DOIVENU.	m 25 c.c.	Z-ucm. tube.	[w]D.	[m]D.
Benzene	0.1696	-4·24°	$-312.5^{\circ}$	- 828°
	0.3028	7.60	313.7	831
Ethyl alcohol	0.1254	3.81	379 7	1006
•	0.2811	8.52	378.9	1004
Acetone	0.1045	3.13	374.5	992
	0.2902	8.76	377.0	999
Chloroform	0.1064	3.18	373.6	990
	0.2056	6.22	378.1	1002
Ethyl acetate	0.0980	3.12	397 • 7	1054
-	0.1919	6.03	392.8	1041
Acetic acid	0.1237	4.14	418.2	1109
	0.2118	6.88	420.6	1114
	(in 25.9 c.c.)			

The introduction of the benzoyl radicle has converted the dextrobase into a highly lævorotatory substance; the same kind of change of sign of the rotation constants is observed on benzoylating tetrahydroquinaldine (Pope and Peachey, Trans., 1899, 75, 1066), tetrahydro-p-toluquinaldine (Pope and Rich, Trans., 1899, 75, 1093), and bornylamine (Forster, Trans., 1898, 73, 386).

#### 1-iso-2: 4-Dimethyltetrahydroquinoline d-a-Bromocamphor- $\pi$ -sulphonate, C<sub>11</sub>H<sub>15</sub>N,C<sub>10</sub>H<sub>14</sub>OBr·SO<sub>3</sub>H.

On concentrating the mother liquors remaining after the separation of d-2:4-dimethyltetrahydroquinoline d-a-bromocamphor- $\pi$ sulphonate, an oily residue is obtained, which slowly becomes partly crystalline; the crystalline material is separated as far as possible from the residual oil, and fractionally crystallised from very dilute alcohol. The two salts just named above are then obtained in crystalline form; l-isodimethyltetrahydroquinoline d-a-bromocamphor-m-sulphonate is distinguished from the isomeride in that it

#### 730 THOMAS: THE FOUR STEREOISOMERIC OPTICALLY

forms small, colourless, cube-shaped crystals, melting at 176-178°, and is more soluble in dilute alcohol:

0.2045 gave 0.3990 CO<sub>2</sub> and 0.1182 H<sub>2</sub>O. C=53.2; H=6.38. C<sub>21</sub>H<sub>20</sub>O<sub>4</sub>NBrS requires C=53.4; H=6.35 per cent.

It is difficult to purify this salt, and only a small quantity was obtained in a pure condition; the following determination of rotatory power was made on a specimen of which the rotation constants remained unchanged by further crystallisation:

0.2585 gram, made up to 25 c.c. with water at 18°, gave  $\alpha_{\rm D} + 1.44^{\circ}$  in a 2-dcm. tube, whence  $[\alpha]_{\rm D} + 55.7^{\circ}$  and  $[M]_{\rm D} + 263^{\circ}$ .

These values agree fairly with those obtained with the enantiomorphously related salt, which, as is shown below, is more easily prepared.

1-iso-2: 4-Dimethyltetrahydroquinoline,  $C_{11}H_{15}N$ .

On distillation with barium hydroxide in a current of steam, the above salt yields l-iso-2:4-dimethyltetrahydroquinoline, which is purified in the same way as the isomeride previously described; the base is a nearly colourless oil boiling at 243—244°, and slowly darkens in the air. The following determinations of rotatory power were made:

- The base exhibits the rotatory power of  $a_D 4.35^\circ$  in a 2.4-dcm tube at 15°, and its density at  $15^\circ/4^\circ$  is 1.0063, whence  $[\alpha]_D 18.03^\circ$  and  $[M]_D 29.05^\circ$ .
- 0.1903 gram, made up to 20 c.c. at 18° with alcohol, gave  $\alpha_{\rm D} 0.335^{\circ}$  in a 2-dcm. tube, whence  $[\alpha]_{\rm D} 17.6^{\circ}$  and  $[M]_{\rm D} 28.2^{\circ}$ .
- 0.6371 gram, made up to 25 c.c. with alcohol at 18°, gave  $\alpha_{\rm D} 0.91^{\circ}$  in a 2-dcm. tube, whence  $[\alpha]_{\rm D} 17.9^{\circ}$  and  $[M]_{\rm D} 28.8^{\circ}$ .

#### 1-iso-2:4-Dimethyltetrahydroquinoline Hydrochloride, C<sub>11</sub>H<sub>15</sub>N,HCl.

This salt and the other optically active hydrochlorides now described are conveniently prepared by dissolving the base in a little concentrated hydrochloric acid, dissolving the product in alcohol, and gradually adding ether; under this treatment *l-iso-2*:4dimethyltetrahydroquinoline yields the hydrochloride as a crystalline, white powder, melting at 178—180°: 0.1135 gave 0.2774 CO<sub>2</sub> and 0.0825 H<sub>2</sub>O. C=66.6; H=8.09. C<sub>11</sub>H<sub>15</sub>N,HCl requires C=66.8; H=8.10 per cent.

The following determination of rotatory power was made:

0.3010 gram, made up to 20 c.c. with water at 18°, gave  $\alpha_{\rm p} - 0.18^\circ$ , whence  $[\alpha]_{\rm p} - 5.1^\circ$  and  $[M]_{\rm p} - 10.1^\circ$ .

On heating the solution for two hours on the water-bath it darkened in colour, but did not change in rotatory power.

#### $Benzoyl-1-iso-2: 4-dimethyltetrahydroquinoline, \ \mathbf{C_{11}H_{14}N} \cdot \mathbf{CO} \cdot \mathbf{C_6H_8}.$

The benzoyl derivative is obtained in theoretical yield by the Schotten-Baumann reaction, and is purified by recrystallisation from alcohol; it forms small, colourless, cube-shaped crystals, melting at 90°. The compound is very soluble in alcohol, ethyl acetate, acetone, or benzene, and sparingly so in light petroleum:

0.2210 gave 0.6540 CO<sub>2</sub> and 0.1465  $H_2O$ . C=80.8; H=7.32.

 $C_{18}H_{19}ON$  requires C=81.5; H=7.17 per cent.

The examination of a number of alcoholic solutions of the substance showed it to be optically inactive in alcohol; this behaviour is not, however, due to optical inversion, because on hydrolysis by boiling with concentrated hydrochloric acid the optically active base was recovered.

#### 1-2: 4-Dimethyltetrahydroquinoline 1-a-Bromocamphor- $\pi$ -sulphonate.

After the separation of as large a proportion as possible of the two optically active bases above described, the mixture of bases contained in the mother liquors is separated with barium hydroxide in the usual manner; a strongly lævorotatory base, exhibiting the value  $a_{\rm p} - 12^{\circ}$  to  $-13^{\circ}$  in a 1-dcm. tube, results, and this is then dissolved in boiling dilute alcohol, with the addition of the corresponding quantity of l-a-bromocamphor- $\pi$ -sulphonic acid. On cooling, an oil separates, which can only be caused to crystallise with great difficulty and after long keeping; the crystalline deposit is fractionally crystallised from alcohol, as in the case of the previously described salts, and is thus resolved into two pure substances, which prove to be enantiomorphously related to the *d*-bromocamphorsulphonates dealt with above. l-2:4-Dimethyltetrahydroquinoline l-a-bromocamphor- $\pi$ -sulphonate resembles its enantiomorphously related isomeride in general properties; its rotation constants were determined as follows:

#### 732 THOMAS: THE FOUR STEREOISOMERIC OPTICALLY

	Weight in grams	a <sub>D</sub> in 2-dcm. tube		
Solvent.	in 25 c.c.	at 18°.	[ <b>a]</b> <sub>D</sub> .	[M] <sub>D</sub> .
Water	0.1125	– 0 <b>·</b> 77°	– 85•5°	- 404°
	0.2135	1.48	86.1	407
	0.3825 (in 20 c.c	c.) <b>3·</b> 27	84.7	400
Benzene	0.1042	0.57	68.4	323
	0.2180	1.19	68.2	322
Chloroform	0.1055	0.692	82.4	389
	0.2154	1.43	82.9	391
Ethyl alcohol	0.1165	0.912	98.1	462
-	0.2118	1.62	97.5	460
Acetic acid	0.1145	0.982	107.1	505
	0.2328	1.96	105.2	496
Ethyl acetate	0.2510	1.95	97.2	459
-	0.1148 (in 20 c.	c.) 1 <sup>.</sup> 09	95.8	452
Acetone	0.1525	0.92	91.1	430

Good agreement exists between these values and those obtained for the enantiomorphously related salt.

#### 1-2: 4-Dimethyltetrahydroquinoline.

This base closely resembles its *d*-isomeride, and exhibits the following rotation constants:

The rotation  $\alpha_{\rm D} - 13.75^{\circ}$  was observed in a 2.4-dcm. tube at 20°, and the density was determined at  $20^{\circ}/4^{\circ}$  as 1.00078, whence  $[\alpha]_{\rm D} - 57.24^{\circ}$  and  $[{\rm M}]_{\rm D} - 92.15^{\circ}$ .

0.2540 gram, made up to 20 c.c. with alcohol, gave  $a_{\rm D} - 1.43^{\circ}$  in a 2-dcm. tube at 18°, whence  $[\alpha]_{\rm D} - 56.2^{\circ}$  and  $[M]_{\rm D} - 90.6^{\circ}$ .

0.5250 gram, made up to 20 c.c. with alcohol, gave  $\alpha_{\rm D} - 2.94^{\circ}$  in a 2-dcm. tube at 18°, whence  $[\alpha]_{\rm D} - 56.0^{\circ}$  and  $[M]_{\rm D} - 90.2^{\circ}$ .

These values are a little lower than those obtained with the enantiomorphously related compound.

#### 1-2: 4-Dimethyltetrahydroquinoline Hydrochloride.

This salt forms a white, crystalline powder melting at 226°, and was obtained in larger quantity in a pure condition than was its isomeride, because the parent base formed the major proportion of the mixture from which it was separated. The following determinations of rotatory power thus possess considerable accuracy:

Solvent.	Weight in grams in 20 c.c.	$a_{\rm D}$ in 2-dcm. tube.	[a] <sub>b</sub> .	[M] <sub>p</sub> .
Water	0·1165 0·2245	- 0 <b>·95°</b> 1·44	-81.5° 80.8	- 161·2° 159·8
(i Alcohol	n 25·2 c.c.) 0·1082 0·2920	0 <b>·99</b> 2·18	91 ·4 93 ·2	180 <b>·5</b> 184·5

#### Benzoyl-1-2: 4-dimethyltetrahydroquinoline.

The benzoyl derivative crystallises in plates melting at 98-99°, and is highly dextrorotatory:

0.1895 gave 0.5578 CO<sub>2</sub> and 0.1224 H<sub>2</sub>O. C=80.7; H=7.20. C<sub>18</sub>H<sub>19</sub>ON requires C=81.5; H=7.17 per cent.

The values obtained for the rotation constants agree closely with those given above for the enantiomorphously related isomeride.

	Weight in	Volume	Tem- a	p in 2-dcm.		
Solvent.	grams.	in c.c.	perature.	tube.	[a] <sub>D</sub> .	[M] <sub>D</sub> .
Benzene	0.1214	25.0	19°	+3.02°	$+314.1^{\circ}$	+832.3
	0.0290	20.0	18	2.485	314.7	833.7
	0:2023	25.0	18	5.08	313.5	830.3
Ethyl alcohol	0.0712	20.0	18	2.71	377.6	1000.6
Acetic acid	0.0890	25.0	19	2.99	420.0	1113.0
Ethyl acetate	0.0455	20.2	19	1.81	401.7	1063.0

The externally compensated 2:4-dimethyltetrahydroquinoline obtained by mixing equal quantities of the two components does not crystallise on cooling in boiling liquid air; the corresponding *hydrochloride* forms a white, crystalline powder, melting at 220—222°. A mixture of the two optically active benzoyl derivatives in equal proportion yields the externally compensated benzoyl derivative described above.

## d-iso-2:4-Dimethyltetrahydroquinoline 1-a-Bromocamphor- $\pi$ -sulphonate.

The preparation of this salt has been already described above; the substance forms small, cube-shaped crystals, melting at 176-178°:

0.2175 gave 0.4240 CO<sub>2</sub> and 0.1246 H<sub>2</sub>O. C=53.2; H=6.38. C<sub>21</sub>H<sub>30</sub>O<sub>4</sub>NBrS requires C=53.4; H=6.33 per cent.

The molecular rotatory power of the basic ion was determined by the following polarimetric measurements made in water solution at 18°; the weights of substance given were made up to 25 c.c.:

Weight in grams.	α <sub>▷</sub> in 2-dcm. tube.	[α] <sub>D</sub> .	[M] <sub>₽</sub> .
0.3215	-1·42°	- 55·2°	$-261^{\circ}$
0.3323	1.47	54.8	259
0.2212	0.975	55.4	262
0.1140	0.21	55.5	262

#### d-iso-2: 4-Dimethyltetrahydroquinoline.

This base was obtained as a pale yellow oil, which boils at 244—246°. In a 2.4-dcm. tube at 15° it exhibited the rotatory power  $a_{\rm D} + 4.40^{\circ}$ , and the density, determined at 15°/4°, was found to be 1.0044, whence  $[\alpha]_{\rm D} + 18.23^{\circ}$  and  $[{\rm M}]_{\rm D} + 29.52^{\circ}$ .

- 0.5254 gram, made up to 25 c.c. with alcohol at 18°, gave  $\alpha_D + 0.975^\circ$  in a 2-dcm. tube, whence  $[\alpha]_D + 18.5^\circ$  and  $[M]_D + 29.7^\circ$ .
- 0.6920 gram, made up to 25 c.c. with alcohol at 17°, gave  $\alpha_D + 1.025^\circ$  in a 2-dcm. tube, whence  $[\alpha]_D + 18.5^\circ$  and  $[M]_D + 29.7^\circ$ .

#### 7342: 4-DIMETHYLTETRAHYDROQUINOLINES.

These values show a close agreement with those given for the enantiomorphously related base.

#### d-iso-2:4-Dimethyltetrahydroquinoline Hydrochloride.

This salt forms a colourless, crystalline powder, melting at 178-180°; during its purification, and also in that of the enantiomorphously related isomeride, some evidence was obtained of the presence of an externally compensated hydrochloride, so that it is possible that the separation of the two iso-bases by means of the corresponding bromocamphorsulphonates is not quite perfect:

0.1505 gave 0.3677 CO<sub>2</sub> and 0.1100  $H_2O$ . C=66.3; H=6.15.

 $C_{11}H_{16}N$ , HCl requires C=66.8; H=8.10 per cent.

0.2170 gram, made up to 20 c.c. with water at 18°, gave  $a_{\rm D} + 0.68^{\circ}$  in a 2-dcm. tube, whence  $[a]_{\rm D} + 5.1^{\circ}$ and  $[M]_{\rm p} + 10.1^{\circ}$ .

A mixture of d- and l-iso-2:4-dimethyltetrahydroquinoline in equal proportions boiled at 246°, and did not crystallise when cooled in boiling liquid air.

In order to ascertain the proportion in which the two externally compensated bases are present in the reduction product of 2:4-dimethylquinoline, 48 grams of the tetrahydrodimethylquinoline were dissolved in dilute alcohol with the requisite amount of d-bromocamphorsulphonic acid, and the resolution effected as described above; each crystalline product was carefully fractionated, and its rotatory power determined. Whilst 141 grams of the mixture of four salts should have been obtained, the following quantities were actually separated in a fair state of purity:

23.6 grams of *d*-base, *d*-acid giving  $[a]_{p} + 86.2^{\circ}$  in water.

of *l*-base, *l*-acid giving  $[a]_{\rm p} - 86.5^{\circ}$  in water. 23.0,,

of *l-iso*-base, *d*-acid giving  $[a]_{\rm p} + 55.4^{\circ}$  in water. 21.1••

of *d*-iso-base, *l*-acid giving  $[\alpha]_{D} - 54.8^{\circ}$  in water. 21.6,,

The total quantity of salt separated was thus 89 grams in place of the 141 grams originally present; the balance of the material was oily, and could not be extracted in the form of pure salts. So far as these results can be interpreted, it would appear that the two externally compensated bases are produced in approximately equal quantities during the reduction of 2:4-dimethylquinoline.

The author desires to express his thanks to Professor Pope for suggesting and supervising the work now described.

THE CHEMICAL LABORATORY. THE UNIVERSITY, CAMBRIDGE.