

**71.** *Solvent Effects with Optically Active Saturated Hydrocarbons.*

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The theoretical relationship assumed to exist between the optical activity of a compound and the refractive index of its solution is further tested in the cases of the saturated hydrocarbons *l*-dimenthyl, *l*-dibornyl, and *d*- and *l*-isocamphanes, when dissolved in non-polar diluents. In no case was the magnitude of the rotation found to be simply related to the refractive properties. The approximate relationship previously reported for *d*-pinane in non-polar solvents has been confirmed.

In a number of communications concerning the variation of rotatory power with change of solvent it has been shown that, for optically active compounds of polar type, the magnitude of the rotation is in the majority of cases related to the polar properties of the solvent medium (Rule and co-workers, J., 1931, 674, 2652; 1932, 1409, 2332; 1933, 376, 1217; 1935, 1038, 1041; 1937, 138). The dipole moment of a substance itself involves a complex relationship with its refractivity, but the connexion between rotatory power,  $M$ , and refractive index,  $n$ , of a solution is represented in most of the modern theories of optical activity as being a simple one:  $M$  is assumed to vary directly with  $n$ . For instance, Born (*Proc. Roy. Soc.*, 1935, A, 150, 84) proposed the expression  $M = k(n^2 + 2)$ , de Malleman (*Rev. gen. Sci.*, 1927, 38, 453) deduced a relationship with  $(n^2 + 2)^2$ , and Boys (*Proc. Roy. Soc.*, 1934, 144, 681) one with  $(n^2 + 2)(n^2 + 5)$ .

Until very recently the only available data bearing upon this problem referred to the

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weakly polar unsaturated hydrocarbons or to compounds of a more strongly polar type. In view of the disturbing influences undoubtedly exerted upon the rotation by the mutual interactions between polar groups in solvent and optically active molecules, an attempt was made (Rule and Chambers, J., 1937, 145) to reduce these effects to a minimum by determining the rotatory power of a saturated hydrocarbon, *d*-pinane, in the homogeneous state and also when dissolved in a variety of non-polar solvents. It was found that under these conditions the rotations were in close agreement with the expression  $M = k(n^2 + 2)^2$ .

In order to obtain further evidence, similar experiments were carried out upon the saturated, optically active hydrocarbons dimethyl, dibornyl, and *isocamphane*; but in none of these cases could any clear relationship between  $M$  and  $n$  be traced (see tables). The rotatory powers of *isocamphane* dissolved in non-polar solvents rise irregularly with the refractive indices of the mixtures, the rate of increase being appreciably greater than is represented by the theoretical expression  $M = k(n^2 + 2)^2$ , and considerably more than is indicated by the other two relationships mentioned above. For dibornyl, the values of  $M$  are very irregular and show little tendency to rise with  $n$ , whilst for dimethyl the change is in the reverse direction,  $M$  tending downwards as  $n$  rises. Repetition of the work of Rule and Chambers (*loc. cit.*) on pinane has confirmed the values already recorded and their approximate agreement with the expression  $M = k(n^2 + 2)^2$ , but in view of the additional results now published, this agreement must be regarded as fortuitous.

#### Optical Rotatory Powers of Solutions.

1-Dimethyl.				1-Dibornyl.			
Non-polar solvents.	$[M]_D^{20^\circ}$ .	$n_D^{20^\circ}$ .	$c$ .	Non-polar solvents.	$[M]_D^{20^\circ}$ .	$n_D^{20^\circ}$ .	$c$ .
Mesitylene .....	-169.5°	1.49585	6.000	1-Methylnaphthalene	-63.6°	1.60773	5.968
<i>n</i> -Heptane .....	-169.3	1.39419	6.000	<i>p</i> -Xylene.....	-55.9	1.49614	6.060
Hexane .....	-168.6	1.38670	6.036	Toluene .....	-53.7	1.49405	6.128
<i>p</i> -Xylene.....	-167.3	1.49443	5.740	Benzene .....	-52.2	1.49973	6.056
1-Methylnaphthalene	-159.8	1.60591	6.036	Carbon tetrachloride...	-52.3	1.46320	5.984
Toluene .....	-155.6	1.49185	6.216	Carbon disulphide ...	-51.8	1.61858	6.032
Carbon tetrachloride...	-155.6	1.46111	5.968	<i>cyclo</i> Hexane .....	-51.7	1.43077	5.988
Carbon tetrabromide	-155.8	1.49251	6.012	<i>n</i> -Heptane .....	-51.6	1.39554	6.024
<i>cyclo</i> Hexane .....	-153.2	1.42937	5.980	Hexane .....	-51.2	1.38793	6.024
Decahydronaphthalene	-145.3	1.47614	5.992	Mesitylene .....	-51.0	1.49756	6.020
Benzene .....	-141.8	1.49824	5.800	Decahydronaphthalene	-50.9	1.47780	6.024
Carbon disulphide ...	-132.2	1.61581	6.020				
				Polar solvents.			
				Nitrobenzene .....	-56.0	1.54958	4.560
				Acetone .....	-53.5	1.36550	4.404
Polar solvents.				Polar solvents.			
Acetone .....	-189.7	1.36032	1.260				
Nitrobenzene .....	-137.9	1.55122	1.180				
d-isoCamphane.				1-isoCamphane.			
Non-polar solvents.				Non-polar solvents.			
1-Methylnaphthalene	+7.67	1.60365	6.696	1-Methylnaphthalene	-9.21	1.59393	12.144
Carbon disulphide ...	+6.87	1.61491	6.080	Carbon disulphide ...	-8.25	1.60047	12.704
Mesitylene .....	+6.86	1.49490	6.032	Mesitylene.....	-8.02	1.49285	12.048
<i>p</i> -Xylene.....	+6.56	1.49242	6.680	<i>p</i> -Xylene.....	-7.79	1.48956	12.664
Toluene .....	+6.37	1.49051	6.240	Toluene .....	-7.40	1.48820	12.308
Benzene .....	+6.32	1.49718	6.068	Benzene .....	-7.30	1.49347	13.244
Decahydronaphthalene	+6.10	1.47486	6.060	Decahydronaphthalene	-6.80	1.47418	12.184
Carbon tetrachloride...	+5.87	1.46012	6.300	Carbon tetrachloride...	-6.83	1.46021	12.128
<i>n</i> -Heptane .....	+5.44	1.39293	6.048	<i>cyclo</i> Hexane .....	-6.21	1.43017	12.064
<i>cyclo</i> Hexane .....	+5.42	1.42867	6.192	<i>n</i> -Heptane .....	-6.00	1.39797	12.212
Hexane .....	+5.38	1.38679	7.400	Hexane .....	-5.79	1.39138	12.433
				Polar solvents.			
				Acetophenone .....	-8.29	1.52297	12.400
				Bromobenzene .....	-8.19	1.54518	12.052
				Anisole .....	-7.95	1.50793	12.068
				Chlorobenzene .....	-7.71	1.51491	12.004
				Nitrobenzene .....	-7.55	1.53903	12.072
				Acetone .....	-5.56	1.37160	12.036

It was noted that the disparity between theory and experiment becomes increasingly greater on passing up the series, pinane (m. p. - 50°), *isocamphane* (m. p. 59°), dibornyl (m. p. 86°), and dimethyl (m. p. 106°), *i.e.*, with rise in m. p. of the hydrocarbon under examination. There remained, therefore, the possibility that the theoretical relationship

" might be realised experimentally with optically active non-polar compounds, which are liquids of low solidification point " (Pryde, Thesis, Edinburgh, 1938, p. 85), in which the intermolecular forces would presumably be much weaker than those operating in the case of a solid like dimethyl. The preparation of such a hydrocarbon, especially one of aliphatic type having a reasonably high rotatory power, is no simple task. Whilst it was still under consideration, a publication by Kenyon and Platt (J., 1939, 633) appeared bearing upon this point. The polarimetric data obtained by these investigators for *d*- $\gamma$ -methyl-*n*-heptane support the above conclusion that the relationship between *M* and *n* previously observed for *d*-pinane is entirely fortuitous and does not hold generally for saturated hydrocarbons in non-polar media. It is therefore not proposed to extend the scope of the present work.

#### EXPERIMENTAL.

*1-Dimethyl*.—*l*-Menthol was treated with phosphorus pentachloride, and the resulting mixture of chlorides heated with alcoholic potassium hydroxide for 60 hours. Steam-distillation, followed by fractionation, yielded the "stable" menthyl chloride (cf. Kursanoff, *Annalen*, 1901, 318, 328), b. p. 93—100°/20 mm.,  $\alpha_D - 47.9^\circ$  (*l* = 1). Treatment of this with sodium wire in ether under various conditions gave only a small amount (1—2%) of solid dimethyl, m. p. 105.5°,  $[\alpha]_D - 49.7^\circ$  (in benzene, *c* = 6), together with much menthane and menthene. Kursanoff (*loc. cit.*) records an almost quantitative yield of dimethyl, m. p. 106°,  $[\alpha]_D - 51.3^\circ$  in benzene.

The same compound,  $[\alpha]_D - 50.0^\circ$ , was also obtained in 2% yield by converting the "stable" chloride into menthylmagnesium chloride and adding it to an ethereal suspension of anhydrous cupric chloride (Sakellarios and Kyrimis, *Ber.*, 1924, 57, 326). Crystallisation from alcohol gave a dimethyl, m. p. 106°,  $[\alpha]_D^{20} - 51.0^\circ$  in benzene. The products contained no chlorine and were completely saturated (Found: C, 86.3; H, 13.8. Calc. for C<sub>20</sub>H<sub>38</sub>: C, 86.3; H, 13.7%).

*1-Hydrodicamphene (Dibornyl)*.—This was obtained from *d*-pinene hydrochloride,  $[\alpha]_D^{20} + 33.24^\circ$  (in benzene, *c* = 5), by the method of Sakellarios and Kyrimis (*loc. cit.*). It had m. p. 85.5—86°,  $[\alpha]_D^{20} - 19.4^\circ$  (in benzene, *c* = 6), and was completely saturated.

*d*-isoCamphane.—The hydrogenation of camphene,  $[\alpha]_D^{20} - 31.4^\circ$  (in benzene, *c* = 8), in the presence of platinum-black catalyst was completed within a few minutes. The resulting *d*-isocamphane was completely saturated, m. p. 55°,  $[\alpha]_D^{20} + 4.7^\circ$  (in benzene, *c* = 6). From a more highly active *d*-camphene (m. p. 41°,  $[\alpha]_D^{20} + 59.8^\circ$  in benzene), prepared according to Reychler (*Bull. Soc. chim.*, 1896, 15, 371), a slightly more active *l*-isocamphane was obtained, m. p. 59°,  $[\alpha]_D^{20} - 5.41^\circ$  (in benzene, *c* = 6).

*d*-Pinane.—This was prepared by hydrogenation of *d*-pinene ( $[\alpha]_D + 47.3^\circ$ ) as described by Rule and Chambers (*loc. cit.*). After purification by Lipp's method (*Ber.*, 1923, 56, 2098) by shaking with weak alkaline permanganate, the product still contained about 5% of unsaturated ethylenic hydrocarbon as shown by titration with bromine. The pinane was therefore treated with bromine until no further rapid absorption took place. It was then refluxed for 3 hours over sodium and distilled; b. p. 166.5°/760 mm.,  $[\alpha]_D^{20} + 22.1^\circ$ ,  $d_4^{20}$  0.8595,  $n_D^{20}$  1.46191. The optical data for this sample did not differ appreciably from those obtained by Rule and Chambers, using Lipp's method, and are not repeated here.