31. *Studies in Solvent Action. Part XIII. Optical Rotatory Power and the Refractive Index of the Medium.*

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All the optically active solutes previously discussed in these communications have been polar in type, and under suitable conditions their molecules readily enter into association with one another or with those of an added solvent. Although numerous active compounds of low polarity are available in the unsaturated hydrocarbons of the terpene group, very few examples of non-polar saturated hydrocarbons have yet been isolated in the optically pure state. The latter class is of particular interest from the standpoint of solvent influence, since it is to be expected that the rotatory powers of their solutions will be largely independent of the polar nature of the solvent medium. This conclusion has now been tested in the case of *d*-pinane, which may be prepared by the catalytic hydrogenation of *d*-pinene under high pressure. At the same time the properties of the unsaturated hydrocarbons *d*-pinene and *d*-limonene have also been investigated.

d-*Pinane.**—The molecular rotatory powers found for *d*-pinane are tabulated in order of ascending magnitudes in Table I; they include observations for the hydrocarbon in the homogeneous state and in solution in 35 solvents of widely different types ranging from derivatives of methane, benzene, and naphthalene to pyridine and quinoline. As the work progressed, it became evident that the changes in optical rotation were in fact mainly dependent upon the refractive index of the medium, and in order to make a more quantitative test of this relationship the determinations were repeated with 26 selected solvents, the refractive indices of the solutions being also measured, since it is this property and not the refractive power of the pure solvent which is of theoretical significance. For the dilute solutions employed, however, the resulting corrections in the values of $n_D^{20°}$ were only of the order of ± 0·002 in average cases, with a maximum of ± 0·008 for liquids of very high or very low refractive indices. The maximum probable errors in the determinations of the molecular rotatory power are estimated to be ± 0·4° in solutions of lower and ± 0·3° in those of higher optical activity.

Influence of the Refractive Index.—The data recorded in the table show a well-marked tendency for the rotatory powers to rise as the refractive index of the solution increases, although the agreement is interrupted by many minor displacements, most of which are too large to be attributable to experimental error. One of the non-polar solvents employed, carbon tetrachloride, has a refractive index of practically the same value as *d*-pinane itself, and correspondingly it is found that dilution with this medium has no appreciable influence upon the molecular rotation of the active compound. On the other hand, the absence of any pronounced polar effect is shown in the impartial distribution throughout the table of solvents of zero and of extremely high dipole moments.

In the theoretical treatment of optical activity, the refractive index of the solvent medium has long been regarded as one of the fundamental factors governing the magnitude

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* A preliminary note on the results obtained with *d*-pinane has been published in *Nature*, 1934, **133**, 910.

TABLE I.

Rotatory Powers of d-*Pinane in Solution.*

Solvent.	$n_D^{20°}$.	μ.	$[M]_D^{20°}$.	Solvent.	$n_D^{20°}$.	μ.	$[M]_D^{20°}$.
*Acetonitrile	1·3441	3·21	25·8	Benzene	1·4992	0	32·9
Methyl alcohol	1·3266	1·68	26·4	Acetophenone	1·5310	2·97	33·2
*Acetic acid	1·3718	1·73	26·9	Benzaldehyde	1·5431	2·75	33·2
Nitromethane	1·3864	3·05	27·3	Toluene	1·4930	0·4	33·7
Pentane	1·3640	0	27·4	Anisole	1·5141	1·25	34·5
*Acetaldehyde	1·3316	2·72	27·7	Chlorobenzene	1·5229	1·56	34·7
Hexane	1·3835	0	27·8	*o*-Dichlorobenzene	1·5466	2·24	34·7
Acetone	1·3653	2·76	28·9	*α-Chloronaphthalene	1·6332	1·59	34·9
*Methylene chloride	1·4245	1·51	29·0	Bromobenzene	1·5580	1·56	35·1
Chloroform	1·4489	1·05	30·2	*α-Bromonaphthalene	1·6558	1·58	35·1
Benzonitrile	1·5255	3·85	30·8	Ethylene dibromide	1·6303	1·0	35·3
Methylene bromide	1·5385	1·89	31·4	Iodobenzene	1·6162	1·25	35·6
(Homogeneous)	1·4630	0	31·5	*α-Naphthyl methyl ether	1·6201	1·3	35·6
Carbon tetrachloride	1·4616	0	31·6	Aniline	1·5842	1·60	36·4
*Pyridine	1·5088	2·11	32·3	Methylene iodide	1·7341	1·10	36·6
Mesitylene	1·4944	0	32·5	*Quinoline	1·6246	2·11	38·6
Nitrobenzene	1·5468	3·90	32·5	Carbon disulphide	1·6246	0	38·7
Methyl iodide	1·5291	1·35	32·6	*α-Iodonaphthalene	1·7054	1·43	39·7

* For these solvents the values of $n_D^{20°}$ are those given for the pure compounds in " Critical Constants "; otherwise the values are those observed for the corresponding solutions of *d*-pinane. In general, $l = 2$ and $c = 3·3$ (approx.), but lower concentrations were necessary with nitromethane ($c = 1·97$; $\alpha_D = 0·78°$) and acetonitrile ($c = 2·55$; $\alpha_D = 0·97°$). For methylene iodide, $l = 1$, $\alpha_D = 0·73°$. The remaining values of α_D lay between 1·49° and 2·63°.

of the rotatory power, but the relationship has never been established satisfactorily on an experimental basis. As is clear from the evidence adduced in earlier papers of this series, one reason for this failure lies in the remarkably large optical variations arising from changes in the state of association of the active compound in solution.

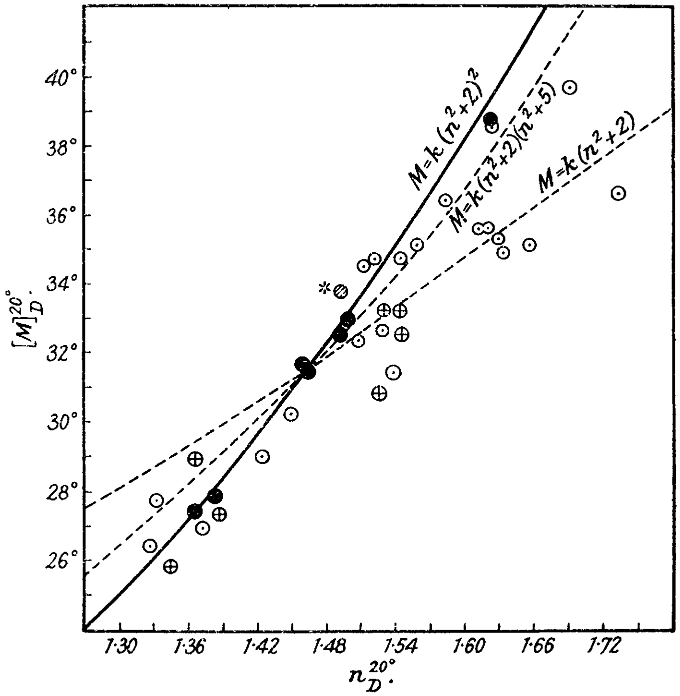
Mathematical expressions for the rotatory power which involve the refractive index of the medium have been derived on theoretical grounds by several workers. Thus Born in 1915 proposed a formula which for the limited purposes of this discussion may be simplified to $M = k_1(n^2 + 2)^2$. This was later modified by Gans, and more recently by Born himself (*Proc. Roy. Soc.*, 1935, **150**, *A*, 84) to $M = k_2(n^2 + 2)$. The theory of de Mallemann (*Rev. gén. Sci.*, 1927, **38**, 453) expresses a relationship with $(n^2 + 2)^2$, and that of Boys (*Proc. Roy. Soc.*, 1934, **144**, *A*, 681) may be reduced to $M = k_3(n^2 + 2)\ (n^2 + 5)$. An examination of the rotatory power of the weakly polar *d*-limonene in solution in six solvents has been made by Wolf and Volkmann (*Z. physikal. Chem.*, 1929, *B*, **3**, 139), who claim that the results confirm the modified formula of Born in which M is related to $(n^2 + 2)$; a more extended investigation of the compound, however, affords no support to this conclusion (see p. **151**).

In the case of *d*-pinane it is evident from the sequence of refractive indices in Table I that the connexion between M and n is not entirely regular. Nevertheless, it is of interest to discover how far the experimental data are in agreement with any of the above expressions. By making use of the values of $[M]_D^{20°}$ and $n_D^{20°}$ for *d*-pinane in the homogeneous state, both of which are readily determined with accuracy, the above constants k_1, k_2, and k_3 have been calculated to be 1·837, 7·605, and 1·065 respectively. From these constants the rotatory power of any given solution may be evaluated solely from a knowledge of its refractive index. In this manner the maximum variation in $[M]_D$ for *d*-pinane in the solvents under investigation should theoretically be 20·0° from k_1, 9·4° from k_2, and 15·6° from k_3. The experimentally observed range lies between these limits, *viz.*, 13·9°.

The results are best illustrated in the form of a diagram (Fig. 1) in which rotatory powers are plotted against refractive indices; curves are also reproduced for the theoretical rotations corresponding to the three expressions under discussion. It will be seen that the curve for $M = k_2(n^2 + 2)$ passes evenly among points representing solutions of a higher refractive index than that of pinane, but lies above all those of a lower refractive power. Apart from any other consideration, this peculiarity throws some doubt upon the validity of the

$(n^2 + 2)$ relationship.* More conclusive evidence is found in the properties of the *non-polar solutions.* On general grounds it is to be expected that a solution of a saturated hydrocarbon in a non-polar solvent will conform more closely to the theoretical than one containing a solute or solvent which is polar in type. Reference to the diagram shows that every point representing a solution in a non-polar medium lies on or very close to a smooth curve which also passes through the point for the non-polar *d*-pinane in the homogeneous state. *This curve is identical with that for the expression* $M = k_1(n^2 + 2)^2$, which therefore portrays most accurately the behaviour of such solutions. The relationship of Boys is indicated in the diagram by a curve making a small angle with the above.

FIG. 1.



The rotatory power of homogeneous d*-pinane is indicated by the meeting point of the three curves ; other points refer to solutions listed in Table I. Non-polar media are shown in black (toluene,* $\mu = 0{\cdot}4$, *is marked by an asterisk) and strongly polar media of* $\mu > 3$ *by crosses.*

From this point of view and the arrangement of the refractive indices in the second column of the table it appears that abnormally low rotatory powers are given with naphthalene derivatives, dibromo- and di-iodo-compounds, and all strongly polar liquids having $\mu > 3$. The pinane employed had been carefully purified, and the divergences observed in strongly polar liquids cannot be explained on the assumption that it contained a trace of *d*-pinene, because the rotatory power of the latter compound is raised and not diminished on dilution with strongly polar solvents (see p. 150). A saturated hydrocarbon, however, contains a number of extremely weak dipoles,† which while mutually cancelling one another in their behaviour towards a uniform electric field, may nevertheless react normally towards the localised charge of a dipole in a neighbouring molecule and so give rise to a minor influence of the type under discussion. Further evidence in support of this suggestion is provided by the manner in which the rotatory powers are affected by an increase in tempera-

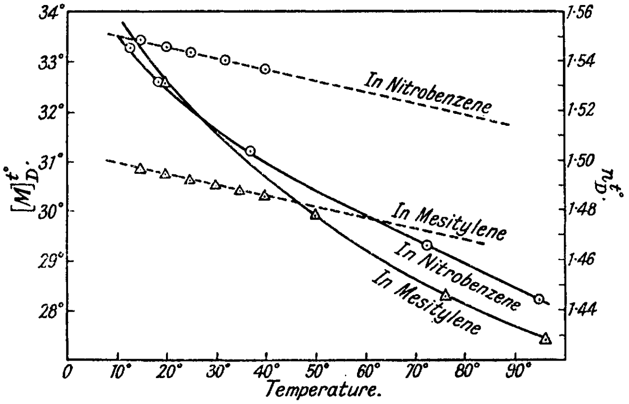
* These conclusions have been communicated to Prof. Born, who informs the authors that, according to J. M. J. Kooy (" Theorie der optische activiteit," Inaug. Diss., Leiden), a factor has been omitted from his calculations as published in 1935, the introduction of which leads to the corrected form $M = k(n^2 + 2)^2$.

† The CH– dipole has been estimated to be of the order $\mu = 0{\cdot}2$.

ture. It is possible that an additional cause of irregularity in the refractivity effect in Table I lies in other variations in the state of the optically active compounds in solution, such as those due to changes in the as yet little understood van der Waals forces, or to modifications in the spatial disposition of the active molecule.

Temperature and Concentration Changes.—A temperature generalisation for an optically active compound, whose solutions vary in rotatory power with the polarity of the solvent, has already been deduced theoretically and established by experiment. In a polar medium the degree of solute–solvent association diminishes as the temperature rises, and the corresponding temperature–rotation curve therefore tends to approach the normal curve for a solution in a non-polar liquid of the same refractive index (see foregoing paper). Although the rotatory power of *d*-pinane is not closely related to the polar properties of the solvent, a weak polar influence appears to be indicated by the low rotations found in liquids of $\mu > 3$. This is borne out by the form of the *T–R* diagrams (Fig. 2) for pinane when dissolved in mesitylene and nitrobenzene severally. At low temperatures nitrobenzene, despite its greater refractive index, yields a solution of slightly smaller rotatory power than the less refractive mesitylene; but as the temperature rises the curve for nitrobenzene crosses that for mesitylene and assumes a higher position in agreement with its refractive power. Determinations of the refractive indices of these two solutions over the temperature range 15—40° show that the values are represented by two almost parallel straight lines (Fig. 2) and afford no explanation of the form of the *T–R* curves. It may thus be concluded that the reversal in the positions of the two curves at low temperatures is due to a weak polar disturbance arising from association between the hydrocarbon and the strongly polar nitrobenzene, an effect which disappears at higher temperatures. Similar disturbances may be expected to be present in other cases where the solvent is polar in character.

FIG. 2.



Solutions of d-*pinane : continuous lines show rotatory powers ; broken lines, refractive indices.*

The typical changes in rotatory power which accompany a rise in the degree of solute–solute association are clearly shown when a polar compound such as *l*-benzoin or its methyl ether is examined at increasing concentrations in solution in a non-polar solvent. No effect of this kind is observed with *d*-pinane when dissolved in carbon disulphide, since the molecules of saturated hydrocarbons have little tendency to associate with one another. In this case the rotation–concentration diagram is found to be represented by a straight line, the slope of which corresponds to the variation in the refractive power of the solution. The linear relationship is in agreement with the fact that for two *non-polar* liquids the refractive index of the mixture is an additive property :

d-*Pinane in carbon disulphide* (t = 20°).

c	3·492 *	38·6	50·57	(Homog. pinane)
n_D	1·6246	1·5490	1·5241	1·4630
α_{5893}	1·96	9·99	12·62	19·54
$[M]_D$	38·7	35·7	34·5	31·5

* $l = 2$; in all other cases $l = 1$.

When various mixtures of carbon disulphide and the polar liquid methyl alcohol are employed as the solvent medium, with pinane added in a fixed concentration, the refractive index of the mixture is found to be less than that calculated from the proportions of the components present. Here also the variations in optical activity closely follow the changes in refractive power. The differences between the observed values and those calculated according to the three expressions discussed above are included in the table, from which it appears that a relationship involving the fourth power of the refractive index accords best with the experimental data for these solvents.

d-*Pinane* (c = ca. 3·35) *in mixtures of carbon disulphide and methanol.*

Solvent.	$n_D^{20°}$.	$[M]_D^{20°}$, obs.	($M_{obs.} - M_{calc.}$) using $(n^2 + 2)$.	$(n^2 + 2)^2$.	$(n^2 + 2)(n^2 + 5)$.
CS_2	1·6246	38·7°	+3·4	−0·85	+0·9
CS_2, 12·7 g. + CH_3·OH, 12·1 g. ...	1·4377	29·5	−1·4	−0·85	+0·75
CS_2, 6·36 g. + CH_3·OH, 8·0 g. ...	1·4162	28·8	−1·7	−0·7	+0·75
CH_3·OH	1·3266	26·4	−2·2	+0·4	−0·7

d-*Pinene.*—Unsaturated hydrocarbons, as a rule, possess exceedingly small dipole moments, but in consequence of this measurable polarity it is to be expected that in favourable cases their rotatory powers in solution will show some relation to the polar properties of the solvent. Table II contains the molecular rotations observed for *d*-pinene in the homogeneous state and for solutions in 24 solvents, the arrangement again being in ascending values of [*M*]. Clear evidence is provided in these figures of a polar as well as a refractive effect, neither of which predominates so greatly as to be free from irregularity. Thus all the lower rotations between 55° and 70° refer to solvents of zero or small dipole moment. Homogeneous *d*-pinene also falls into its proper place in this group. On the other hand, all rotations above 70° are found for solvents of medium or high polarity, chloroform being the sole exception. Superimposed upon this influence there is possibly a less definite tendency for compounds of high refractive index to form solutions of low rotatory power and *vice versa*, as appears to be shown in the order of the non-polar solvents among themselves, and in the high rotations given in the majority of media possessing small refractive indices. On this interpretation of the data carbon disulphide is an extreme example in which very high refractive index goes hand in hand with zero dipole moment, the two properties uniting to give an abnormally low activity. In acetonitrile and nitromethane the conditions are reversed, low refractive power and high polarity leading to highly active solutions. Other as yet unknown factors must also be in operation, as in the case of *d*-pinane.

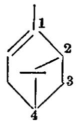
TABLE II.

d-*Pinene in Solution.*

Solvent.	$[M]_D^{20°}$.	μ.	$n_D^{20°}$.	Solvent.	$[M]_D^{20°}$.	μ.	$n_D^{20°}$.
Carbon disulphide	55·6°	0	1·6276	*o*-Dichlorobenzene	70·7°	2·24	1·5490
Methyl iodide	60·5	1·08	1·5297	Methanol	71·1	1·66	1·3284
Mesitylene	62·3	0	1·4962	Acetophenone	71·8	2·97	1·5332
Benzene	63·4	0	1·5014	Acetone.....................	72·1	2·76	1·3592
*cyclo*Hexane	63·7	0	1·4273	Benzonitrile	73·4	3·85	1·5278
(Homogeneous)............	64·3	(Small)	1·4651	Acetaldehyde	73·6	2·7	1·3316
Anisole	65·2	1·25	1·5164	Methylene chloride	75·3	1·55	1·4245
Iodobenzene	65·6	1·25	1·6180	Chloroform	75·9	1·18	1·4459
Toluene	65·7	0·4	1·4950	Nitromethane	76·0	3·03	1·3815
Chlorobenzene	67·9	1·52	1·5250	Acetonitrile	76·2	3·16	1·3441
Hexane	68·9	0	1·3754	Nitrobenzene	76·2	3·90	1·5504
Carbon tetrachloride ...	69·4	0	1·4607	Acetic acid	76·4	1·73	1·3718
Aniline	70·7	1·52	1·5863				

Concentration of pinene varied from 4·016 to 4·212, and observed values of α from 3·39° to 4·70° ($l = 2$) (homogeneous pinene, $\alpha_D^{20°} = 20·48°$, $l = 0·5$). The refractive indices quoted are those of the pure solvents.

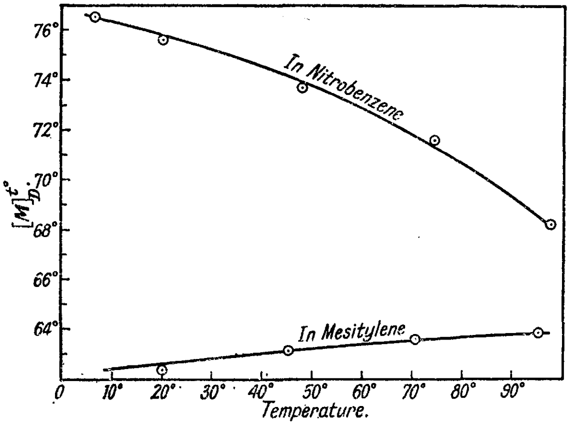
Pinene therefore differs from the great majority of the optically active compounds already examined in exhibiting a rotatory power which is *raised* in solvents of strong polarity. A tentative explanation of this peculiarity may be sought in the nature of the two centres of asymmetry in the pinene molecule and in their relative distances from the double bond. If, for example, the rotatory power is made up of a strong dextro-contribution from atom 4 and a weak lævo-contribution from atom 2, then the influence of a strongly polar solvent as transmitted through the double bond would act chiefly on the nearer asymmetric atom 2, probably depressing its characteristic lævo-contribution and resulting in an increased molecular dextrorotation.



The analysis of the experimental data being assumed to be correct, the refractive influence is also unusual, as the highest rotatory powers are given in solvents of low refractive index. Such a relationship is contrary to the requirements of current theories of optical activity, but the results of the present investigation show that these can only be expected to apply to non-polar optically active compounds in a non-polar medium. Another exception of this kind has already been found in the case of *d*-bromo-octane in aliphatic solvents (J., 1933, 377).

Concentration and Temperature Changes.—In view of the low polarity of unsaturated hydrocarbons, it is not unexpected to find that the variations in the rotatory power of *d*-pinene with change of concentration in a *non-polar* solvent depend chiefly upon the refractive index of the mixture. This can be deduced directly from Table II. When *d*-pinene ($n_D^{20°}$ = 1·4651) is diluted with a solvent of higher refractive power, such as carbon disulphide, mesitylene, or benzene, the optical rotation is diminished; and when the diluting medium has a lower refractive power, as with hexane or carbon tetrachloride, the rotation is raised. For the last solvent the value of *n* is not appreciably less than that of pinene itself, and the magnitude of the optical change on dilution may be due in part to other causes, such as the presence in the molecule of four polar CCl groups. Probably the small inversion in the relative positions of the *cyclo*hexane solution and homogeneous pinene in the table is to be attributed to a minor disturbance in the refractive influence arising from the weakly polar character of pinene, leading to a somewhat higher rotation for the homogeneous compound than for a solution in a saturated hydrocarbon of approximately the same refractive index. When rotatory powers are plotted against concentrations in these non-polar solvents, smooth curves are obtained in place of the straight-line relationship found with pinane. This difference emphasises the polar character of pinene.

FIG. 3.



Temperature–rotation diagram for d-*pinene.*

The existence of optical effects due to the polarity as well as the refractive index of the medium may also be traced in the temperature–rotation curves over the range 20—90° for solutions of *d*-pinene in mesitylene and nitrobenzene (Fig. 3). In the former solvent the rotatory power increases slightly with rise of temperature, whereas in the latter it decreases rapidly. It is obvious that the two curves will cross at a still higher temperature and so reverse the order of the rotatory powers. The conclusions deduced from the data in Table II being borne in mind, it appears that at lower temperatures the chief factor governing the position and form of the nitrobenzene curve in Fig. 3 is the strong polarity of the solvent. This results in association between solute and solvent, which in the case of *d*-pinene leads to a higher optical rotation. With rise of temperature the degree of association diminishes and the refractive power of the solvent then tends to assume a leading rôle. Since the optical rotation of pinene is lowered in solvents of high refractive index, the *T–R* curve for nitrobenzene falls towards the mesitylene curve, eventually crossing it to take up a lower position.

d-*Limonene.*—The rotatory powers of limonene in solution are given in Table III, from which it is seen that the optical rotation is controlled mainly by the refractive index of the medium in such a manner that high refractive power corresponds to high molecular rotation. This relationship is not without a considerable degree of irregularity, even when the comparison is limited to solutions in non-polar media. Not only does carbon tetrachloride yield a solution of much lower activity than was to have been expected from the value of *n*, but hexane and *cyclo*hexane, although differing appreciably in refractive power, yield solutions of practically identical molecular rotations. *d*-Limonene in the homogeneous condition possesses a refractive index of intermediate magnitude, but its rotatory power in this state is greater than that found for any of its solutions in non-polar solvents, not even excepting the very highly refractive carbon disulphide. For these reasons *d*-limonene cannot be regarded as a suitable compound for testing the relationship existing between *M* and *n*, and little weight can therefore be attached to the work of Wolf and Volkmann (*loc. cit.*) in this connexion.

The dispersions of the hydrocarbons in question have been described in the literature and are not further discussed in this communication.

TABLE III.

Rotatory Powers of d-*Limonene in Solution.*

Solvent.	$[M]_D^{20°}$.	μ.	$n_D^{20°}$.	Solvent.	$[M]_D^{20°}$.	μ.	$n_D^{20°}$.
Methanol	149·5°	1·66	1·3284	Benzene	165·5°	0	1·5014
Acetonitrile	150·8	3·16	1·3441	Carbon disulphide	166·6	0	1·6276
Carbon tetrachloride	154·4	0	1·4607	Methyl iodide	166·8	1·08	1·5297
Acetone	154·5	2·76	1·3592	Anisole	167·3	1·23	1·5164
Acetaldehyde	156·6	2·68	1·3316	Benzonitrile	167·3	3·94	1·5278
Chloroform	156·8	1·18	1·4459	(Homogeneous)	168·9	(0·5)	1·4713
Hexane	157·3	0	1·3754	Chlorobenzene	169·2	1·52	1·5250
*cyclo*Hexane	157·9	0	1·4273	Acetophenone	169·5	2·97	1·5332
Methylene chloride	158·0	1·55	1·4245	*o*-Dichlorobenzene	170·5	2·24	1·5490
Nitromethane	158·3	3·03	1·3815	Benzaldehyde	170·8	2·75	1·5453
Acetic acid	158·7	1·73	1·3718	Aniline	172·5	1·52	1·5863
Toluene	165·2	0·37	1·4950	Iodobenzene	174·3	1·25	1·6180
Mesitylene	165·2	0	1·4962	Nitrobenzene	177·2	3·94	1·5504

EXPERIMENTAL.

d-*Pinane.*—Kahlbaum's *d*-α-pinene was purified by distillation in steam in presence of a trace of sodium carbonate and was then dried and twice fractionated under atmospheric pressure. The fraction of b. p. 154·5°/757 mm. was collected; $d_{4°}^{20°}$ 0·8667, $[\alpha]_D^{20°}$ + 47·3°.

The *d*-pinene was converted into *d*-pinane by catalytic hydrogenation under pressure (cf. Lipp, *Ber.*, 1923, **56**, 2098), the apparatus being of the type due to Adams and Voorhees ("Organic Syntheses," 1928, VIII, 10). Various preparations of platinum catalyst were tested, and the most complete absorption of hydrogen was obtained when platinum-black prepared by a modification of Loew's method (Houben–Weyl, 1928, II, 496) was used, the pinene being treated in absence of solvent under an initial pressure of 55 lb./sq. in. In this manner 97% of the theoretical quantity of hydrogen required for 23 g. of pinene was absorbed in six hours. Final purification was effected according to Lipp (*loc. cit.*), the fraction of b. p. 162—167°/758 mm. being collected and shaken with successive small quantities of a 1% solution of potassium permanganate in sodium carbonate until the colour persisted for 30 minutes. It was then distilled in steam and dried over sodium sulphate. After being distilled over sodium under diminished pressure it was redistilled and collected at 166—166·5°/762 mm. The resulting *d*-pinane had $d_{4°}^{20°}$ 0·8560, $[\alpha]_D^{20°}$ 22·83°, $n_D^{20°}$ 1·4630 (Lipp quotes $[\alpha]_D^{20°}$ 23·1° from a pinene of $[\alpha]_D^{20°}$ 47·5°).

d-*Limonene*.—The original sample of limonene (B.D.H.) had a low activity and was therefore converted into the tetrabromide (Godlewsky, *Chem.-Ztg.*, 1898, **22**, 827), and the latter purified by crystallisation, giving m. p. 104°, $[\alpha]_D^{20°}$ + 77·7° in chloroform (c = 7·666) (von Braun and Lemke, *Ber.*, 1923, **56**, 1562, record m. p. 104° and $[\alpha]_D^{20°}$ = + 74·5° in chloroform, c = 22·4). The tetrabromide was debrominated in ethereal solution by addition of magnesium (Braun and Lemke, *loc. cit.*). Finally, the *d*-limonene was purified by being boiled over sodium and subsequently fractionated; b. p. 60·5—61°/13 mm., $d_{4°}^{20°}$ 0·8403, $[\alpha]_D^{20°}$ 124·2° (Braun and Lemke record $[\alpha]_D^{20°}$ 126·8°).

Determinations of Rotatory Power.

Concentration changes (t = 20°).

d-Pinene in CS_2.

c	4·142 *	52·09	75·36	(Homog.)
α_{5893}	3·39°	11·57°	17·24°	20·48°

d-Pinene in C_6H_{14}.

c	4·038 *	20·03 †	50·06 †	70·10	(Homog.)
α_{5893}	4·08°	10·00°	24·22°	16·66°	20·48°

d-Limonene in C_6H_6.

c	2·050 *	8·128 *	42·18 *	(Homog.)
α_{5893}	4·99°	9·94°	51·95°	52·18°

* l = 2. † l = 1; in other cases l = 0·5.

Temperature changes (l = 1).

d-Pinane in nitrobenzene (c = 3·417 at 20°).

$n_D^{t°}$: 1·5490 at 15·0°; 1·5468 at 20·0°; 1·5440 at 25·0°; 1·5403 at 32·0°; 1·5372 at 40·0°.

t	13·1°	18·5°	36·7°	72·6°	95·2°
$d_{4°}^{t°}$	1·207	1·200	1·180	1·141	1·116
α_{5893}	0·83°	0·81°	0·76°	0·69°	0·65°

d-Pinane in mesitylene (c = 1·814 at 20°).

$n_D^{t°}$: 1·4969 at 15°; 1·4944 at 20·0°; 1·4923 at 25·0°; 1·4901 at 30°; 1·4877 at 35·0°; 1·4855 at 40·0°.

t	19·6°	50·5°	75·8°	96·4°
$d_{4°}^{t°}$	0·8665	0·8390	0·8168	0·7986
α_{5893}	0·44°	0·38°	0·35°	0·33°

d-Pinene in nitrobenzene (c = 4·068 at 20°).

t	9·1°	19·6°	48·1°	74·6°	98·1°
$d_{4°}^{t°}$	1·199	1·191	1·166	1·145	1·127
α_{5893}	1·15°	1·14°	1·08°	1·03°	0·98°

d-Pinene in mesitylene (c = 4·106 at 20°).

t	11·9°	20·4°	46·8°	70·5°	95·5°
$d_{4°}^{t°}$	0·8768	0·8699	0·8444	0·8295	0·8085
α_{5893}	1·91°	1·88°	1·85°	1·83°	1·79°

SUMMARY.

An examination has been made of the changes in the rotatory power of optically active saturated and unsaturated hydrocarbons arising from variations in solvent, concentration, and temperature.

1. For the saturated compound *d*-pinane the rotatory powers in *non-polar* solvents vary with the refractive index of the medium in agreement with Born's expression, $M = k(n^2 + 2)^2$. Solutions in the great majority of *polar* solvents have lower rotations than the calculated values. Concentration effects in the latter cases are governed chiefly by the alteration in refractive index, but a small depression in rotatory power due to the polarity of the solvent is revealed by the influence of a rise in temperature.

2. The rotatory power of the unsaturated hydrocarbon *d*-pinene appears to be raised in strongly polar solvents and lowered in those of high refractive index. The rotation of a solution in a non-polar medium does not show a linear relationship with the degree of concentration, pinene thus behaving as a polar compound. Temperature changes for polar solvents indicate a characteristic influence due to the polarity of the solute.

3. In the case of the unsaturated hydrocarbon *d*-limonene, the rotations tend to rise in

solvents of high refractive index, but the relationship is very irregular. Concentration changes in non-polar media show that limonene has the properties of a polar compound.

The authors record their indebtedness for the award of a Vans Dunlop Scholarship (A. R. C.) and a Carnegie Teaching Fellowship (H. G. R.), during the tenure of which this work was completed.

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[*Received, December 4th,* **1936**.]