THE RELATIONSHIP BETWEEN REFRACTIVE INDEX AND OPTICAL ROTATORY POWER WITH NON-POLAR SOLUTES AND SOLVENTS.

And

OPTICAL ACTIVITY INDUCED BY LARGE ELECTROSTATIC FIELDS.

By

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CONTENTS.

PART I.

THE RELATIONSHIP BETWEEN REFRACTIVE INDEX AND OPTICAL ROTATORY POWER WITH NON-POLAR SOLUTES AND SOLVENTS.

PART II.

OPTICAL ACTIVITY INDUCED BY LARGE ELECTROSTATIC FIELDS:

CONTENTS.

(contd.)

INTRODUCTION.

During the last thirty years detailed investigations have been carried out concerning the effect of molecular constitution, wavelength of the light, temperature and nature of the solvent, on the rotatory power of a large number of organic compounds. Interest has also been given to the work by theories put forward by chemists and physicists from purely theoretical considerations, the value of which can only be determined by experiment. A number of such theories refer to the relationship between the rotatory power and the structure and properties of the active molecule itself. Since the work described in this thesis is concerned only with the solvent effect, these theories will not be discussed in detail but merely summarised.

In 1890, Crum Brown put forward a hypothesis that the magnitude of the rotation is a function of the radicals attached to the assymetric carbon atom and concluded from experimental results that the function increased with the size of the radicals, but he was unable to suggest any quantitative relationship.

Betti (Gazz. Chim. Ital., 1923, <u>53</u>, 424) next found an experimental relationship between the dissociation constants of substituted benzoic acids and the magnitude of the rotation given by the aldehydes of the corresponding acids when condensed with d- β-naphthol-benzylamine. Thus, for para-substituted derivatives,

$$[M]_D^{20} \text{ --- } NO_2 < Cl < H < CH_3 < (OH, OCH_3) < N(CH_3)_2$$

$$k \text{ --- } NO_2 > Cl > H > CH_3 > (OCH_3, OH) > N(CH_3)_2$$

From these results it can be concluded that the effect of substituents on the optical activity of a compound is related to the electro-chemical changes in the molecule.

The work of Rutherford, Kossel, Lewis and Langmuir on the electronic conception of valency led to consideration of the various ways in which electrons can be distributed in compounds, and to the ideas of electro-valency, covalency and co-ordinate links. Since the electrons binding two adjoining atoms in a molecule are not always shared equally it was realised that these atoms may be positively or negatively charged with respect to each other, forming, in effect, a small electro-magnet. Such a group is called "polar". It thus appears that Betti's results were due to a polar effect of this kind. More accurate views on the polarity of groups were possible after Debye's method of determining dipole moments had been applied to a large number of compounds, the final distinction between electropositive and electronegative substituents being made with the aid of J. J. Thomson's vectorial rule.

These ideas were applied to the case of optically active compounds by Rule and co-workers (J.C.S., 1930, 1887), who examined the effect of polar substituents, X, when inserted into the optically active ℓ-menthyl acetate, giving optically active compounds of the type $X\cdot CH2\cdot COOC_{10}H_{19}$, in which case the introduction of a negative constituent can be considered as creating a positive field in the part of the molecule containing the menthyl radical, owing to the shift of electrons towards the substituent, e.g., $\underleftarrow{Cl\cdot CH_2\cdot COO\text{--}\ H}$. This change, which increased the degree of ionisation of the acid, results also in an increase in negative rotatory power. The introduction of a positive group such as NH_2 has the opposite effects of suppressing ionisation of the acid and diminishing the rotation. In this manner a good agreement was obtained between the changes in the dipole moment of the group, the dissociation constant of the acid and the molecular rotation of the ester.

On examining the rotatory power of any substance in solution one is immediately impressed by the fact that the magnitude varies considerably in different solvents, this fact being first noted by Biot in 1815. Little systematic work, however, seemed to have been done on the subject until Patterson (J.C.S., 1901, 158) put forward the suggestion that solvent influence was related to the "internal pressure" of the solvent which caused variation in the solution volume of the dissolved substance in the various solvents. In later years Dawson (J.C.S., 1920, 1041) suggested that the change in rotatory power in different solvents was brought about by the varying ability of the solute to form compounds with the solvent, although no evidence for compound formation was noted by later investigators. In 1926, Rule and Mitchell investigated the effect of solvents on the rotatory power of β-octyl esters of certain monosubstituted acetic acids (J.C.S., 1926, 3202) and found no general regularities. It was noted, however, that certain closely related groups of solvents, such as monosubstituted benzenes of type C_6H_5X, showed variations in optical rotation which gave a series for X thus:-

$$CH_3 > H > OEt > Br > I$$

This series, it was noted, is of the nature of a polar series, and is almost exactly the reverse of that given by the same groups when these are substituted in the optically active molecule itself, the arrangement for which is

$$I > Br > Cl > OMe > CH_3 > H$$

From this, the view was advanced that substituent groups, whether present in the optically active molecule or in the solvent, tend to produce changes in rotatory power, the magnitude of which depends upon the dipole moment of the substituent.

The first systematic attempt to establish a relationship between polarity of solvent and optical rotatory power was made two years later by Rule and McLean (J.C.S., 1931, 674). *l*-Menthyl methyl naphthalate was chosen as the active solute on account of its great sensitivity to change in solvent. The solvents used were derivatives of the hydrocarbons methane, ethane, benzene and naphthalene. As an illustration of the results obtained, the benzene series is most suitable and the results are given in Table I.

TABLE 1.

l-Menthyl methyl naphthalate in solution.

Solvent		$[M]^{20}_{5461}$	$\mu \times 10^{18}$ e.s.u. (of solvent)
Benzonitrile	$C_6H_5 \cdot CN$	-372°	3·85
Nitrobenzene	$C_6H_5 \cdot NO_2$	-423	3·98
Benzaldehyde	$C_6H_5 \cdot CHO$	-432	2·75
o-Dichlorobenzene	$C_6H_4 \cdot Cl_2$	-433	2·24
Chlorobenzene	$C_6H_5 \cdot Cl$	-463	1·52
Iodobenzene	$C_6H_5 \cdot I$	-465	1·50
Bromobenzene	$C_6H_5 \cdot Br$	-466	1·50
Anisole	$C_6H_5 \cdot OCH_3$	-466	1·25
Benzene	C_6H_6	-543	·0
Toluene	$C_6H_5 \cdot CH_3$	-546	0·4
Mesitylene	$s\text{-}C_6H_3(CH_3)_3$	-583	0
Cyclohexane	C_6H_{12}	-688°	0

The results from the other series were very similar.

From the above table it is immediately apparent that the polarity of the solvent, as shown by its dipole moment, and the magnitude of the optical rotatory power, are closely related. In this case the optical rotatory power increases with decreasing dipole moment of the solvent although it should be noted that it does not reach a constant value in solvents of zero dipole moment. With some optically active compounds, such as octyl bromide (Rule and co-workers, J.C.S., 1933, 379), the lowest values are given in non-polar solvents, while the maximum rotations are given by highly polar solvents. Evidence of the same relationship was also given by use of ℓ-menthyl picryl ether (Rule and Tod., J.C.S., 1931, 1929), sec.-β-octyl alcohols, ℓ-menthone, d-bromocamphor and other compounds (Miss Barnett, Thesis, Edin., 1932). Rule and McLean (Thesis, Edin., 1931) suggest that the observed effects are due to solvent dipoles exerting an influence on the intennal field of the active molecule either by deformation or by dipole association.

On the assumption that polar solvents and solutes lead to dipole association it is reasonable to assume that changes in the concentration of an active compound in solution in a non-polar solvent will lead to changes in the optical rotatory power due to consequent variations in the degree of solute-solute association. This assumption was successfully used by Rule and co-workers (J.C.S., 1933, 1217) to explain the anomalous rotatory powers obtained with nitro-octane and d-ethyl tartrate, and also accounts for the direction of the optical changes observed for many compounds as the concentration is increased. Rule and co-workers in investigating this aspect of the problem classified optically active solutes into four main divisions according to the substituent groups present and their reaction towards the solvent (Rule, Smith and Harrower, loc. cit.).

1. Non-polar solutes. These are nearly all saturated hydrocarbons and had not as yet been investigated. From the results of the above experiments it would be expected that changes in the internal field of the molecule would be very small. It was thus concluded that change in solvent would have very little effect on the optical rotatory power. This point was investigated later by Rule and Chambers (J.C.S., Jan. 1937) in the case of d-pinene when the above expectations were not realised, as will be illustrated later.

2. Weakly-polar solutes, which include the majority of of unsaturated hydrocarbons, ethers, alcohols, etc. These do not form definite association complexes in themselves but polarisation results show a slight tendency to orientation. In dilute solutions in non-polar solvents this effect is very slight but increases as the polarity of the solvent increases , so that with strongly-polar solvents solute-solvent association may become quite considerable. In dilute solutions one would therefore expect a close relationship between μ of solvent of $[M]$ of the solution.

3. Strongly polar solutes, such as nitro-, cyano- and ketonic compounds. These are in a state of association

in the homogeneous state, so that the change in rotation of these compounds, when in solution in a solvent, will depend on the ability of that solvent to break up the complexes. Owing to the fact that polar solvents will tend to form solute-solvent complexes with the molecules of the active compound no regularity can be expected with this class of solute.

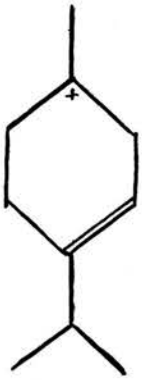
4. Solutes which undergo electronic rearrangment with the solvents such as stable compound formation, co-ordination, ionisation, etc. As examples of this we have carboxy-acids in basic solvents; etc. In such a case there will be no simple relationship between the magnitude of the optical rotation and the dipole moment.

It is interesting to note here that only solutes of type 1 and 2 can be of any practical value in finding an exact relationship between the magnitude of the optical rotatory power and the properties of the solvent and, indeed, it is by further investigation of type 2, and more especially of type 1, that the relationship has been further elucidated by Rule and Chambers, loc. cit.).

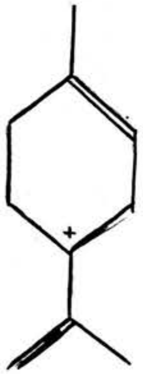
Additional proof that the changes in rotation in polar solvents are due to dipole association is given by the fact that the rotation in a polar solvent approaches that for a non-polar solvent as the temperature is raised. This is exactly as would be predicted, since the thermal agitation of the molecules must increase as the temperature rises, and this will impose strains on the association complexes tending to disrupt them. That such is the case has been illustrated by Rule and Cunningham (J.C.S., 1935, 1038) in the case of dimethylene tartrate, and by Rule and Crawford (J.C.S., 1937, 138) with l-benzoin and its methyl ether.

SOLVENT EFFECT WITH WEAKLY-POLAR And NON-POLAR SOLUTES.

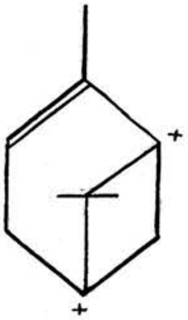
The logical result of the experiments just described was an examination of the effect of solvents on weakly-polar solutes and non-polar solutes, such as hydrocarbons of the terpene class. This was carried out by Rule and Chambers (J.C.S., Jan., 1937). In this work the effect on the optical rotatory power of d-p- $\Delta^{(3)}$-menthene, d-limonene and d-pinene, of a wide range of solvents was examined. These solutes were chosen as they are all highly active and very weakly-polar. Whilst menthene and limonene have only one asymmetric carbon atom, pinene has two.



d-p-$\Delta^{(3)}$ Menthene



d- Limonene



d-Pinene

Limonene differs from menthene and pinene in that it has two double bonds.

In each case the solvents were broken up into two groups, namely aliphatic and aromatic, and the concentration of solute only varied within narrow limits from 2·378 to 3·372, thus ensuring directly comparable results. The results for menthene can best be illustrated by a table (Table 2) in which the dipole moments of the solvents are taken from Sidgwick (Trans. Faraday Soc., 1934, 30). In view of later discoveries the refractive index of the solvent is also given.

TABLE 2.

d-Menthene in Solution.

Solvent		n_D (solvent)	$[M]_D^{20}$	$\mu \times 10^{18}$ e.s.u. (solvent)
Acetaldehyde	$CH_3\cdot CHO$	1·3316	145·8°	2·68
Nitromethane	$CH_3\cdot NO_2$	1·3815	148·5	3·03
Acetone	$(CH_3)_2\cdot CO$	1·3592	149·2	3·16
Acetonitrile	$CH_3\cdot CN$	1·3441	150·6	3·16
Acetic Acid	$CH_3\cdot COOH$	1·3718	152·0	1·73
Methyl Alcohol	$CH_3\cdot OH$	1·3284	152·0	1·66
Carbon Disulphide	CS_2	1·6276	152·3	0
Hexane	C_6H_{14}	1·3754	152·5	0
Carbon Tetrachloride	CCl_4	1·4607	153·2	0
(homogeneous)		1·4542	155·5	(small)
Chloroform	$CHCl_3$	1·4459	156·1	1·18
Methylene Chloride	CH_2Cl_2	1·4245	158·4	1·55
Methyl Iodide	CH_3I	1·5297	163·7	1·08

The general conclusions from the above were:

(1) the rotation tends to rise with decreasing polarity of the solvent, except in the case of $CHCl_3$, CH_2Cl_2 and CH_3I, all of which, however, have higher refractive indices than the average;

(2) the rotation tends to increase with rising refractive index although this is only very approximate, with many exceptions, notably CS_2. That such is the case explains, to a certain extent, the exceptionally high rotations given by $CHCl_3$, CH_2Cl_2 and CH_3I.

The aromatic solvents gave a similar series in which high polarity of the solvent was again associated with low rotation. In this case, however, there is no relationship between the magnitude of the rotation and the refractive index of the solvent, nor are the rotation values for the aromatic series any greater, on the average, than those for the aliphatic solvents although the refractive indices are much higher. It may be noted that the rotation does not increase or decrease regularly with increase in refractive index. This apparent absence of any refractive index effect is interesting since purely theoretical considerations assume that, in most cases, such a relationship should be given of the type

$$[M]^{20}_{\lambda} = k\left\{f(n^{20}_{\lambda})\right\},$$

where k is a constant for each particular substance.

If, therefore, this theoretical relationship is valid it ought to become evident in the case of solutes of zero or low polarity when dissolved in non-polar solvents, under which conditions purely polar influences should be a minimum.

d-LIMONENE.

The effect of solvents on the optical rotatory power of d-limonene was studied under exactly similar conditions. Since limonene has two double bonds it might be expected to show a greater indication of a polar effect and less of a refractive index effect than menthene. That such is not the case, however, is seen from the following tables of results taken from Chambers' thesis:-

TABLE 3.

d-Limonene in Solution.

(a)

Solvent (aliphatic)		n_D^{20} (solvent)	$[M]_D^{20}$	$\mu \times 10^{18}$ e.s.u. (solvent)
Methyl Alcohol	CH_3OH	1·3284	149·5°	1·66
Acetonitrile	CH_3CN	1·3441	150·8	3·16
Carbon Tetrachloride	CCl_4	1·4607	154·4	0
Acetone	$(CH_3)_2CO$	1·35 92	154·5	2·76
Acetaldehyde	$CH_3{\cdot}CHO$	1·3316	156·6	2·68
Chloroform	$CHCl_3$	1·4459	156·8	1·18
Hexane	C_6H_{14}	1·3754	157·3	0
Methylene Chloride	CH_2Cl_2	1·4245	158·0	1·55
Acetic Acid	$CH_3{\cdot}COOH$	1·3718	158·7	1·73
Nitromethane	$CH_3{\cdot}NO_2$	1·3815	159·3	3·03
Methyl Iodide	CH_3I	1·5297	166·8	1·08
Carbon Disulphide	CS_2	1·6276	166·6	0
(homogeneous)		1·4713	168·9	0·5

TABLE 3. (cont.)

(b)

Solvent (aromatic)		n^{20}_D (solvent)	$[M]^{20}_D$	$\mu \times 10^{18}$ e.s.u. (solvent)
Cyclohexane	C_6H_{12}	1·4273	157·9°	0
Toluene	$C_6H_5\cdot CH_3$	1·4950	165·2°	0·37
Mesitylene	$s\text{-}C_6H_3(CH_3)_3$	1·4962	165·2°	0
Benzene	C_6H_6	1·5014	165·5°	0
Anisole	$C_6H_5OCH_3$	1·5164	167·3°	1·23
Benzonitrile	$C_6H_5\cdot CN$	1·5278	167·9°	3·94
(homogeneous)		1·4713	168·9°	0·5
Chlorobenzene	C_6H_5Cl	1·5250	169·2°	1·52
Acetophenone	$C_6H_5\cdot CO\cdot CH_3$	1·5332	169·5°	2·97
o-Dichlorobenzene	$C_6H_4Cl_2$	1·5490	170·5	2·24
Benzaldehyde	C_6H_5CHO	1·5463	170·8	2·75
Aniline	$C_6H_5\cdot NH_2$	1·5863	172·5	1·52
Iodobenzene	C_6H_5I	1·6180	174·3	1·25
Nitrobenzene	$C_6H_5\cdot NO_2$	1·5540	177·2	3·94

From these results it is obvious that there was no clear relationship between the dipole moment of the solvent and the optical rotatory power of the solution. It was noted, however, that solvents of high refractive index tended to give solutions of higher rotation than solvents of low refractive index, especially in the aromatic series. Exceptions to this conclusion are the strongly polar liquids, benzaldehyde and nitrobenzene, but for the other solvents there was almost an exact parallel between refractive index and optical rotatory power. It was concluded from this that, superimposed on the refractive index effect, was a polar effect, the former predominating.

d-PINENE.

TABLE 4.

d-Pinene in Solution.

Solvent		$[M]_D^{20°}$	μ (solvent)	$n_D^{20°}$ (solvent)
Carbon Disulphide	CS_2	55·6°	0	1·6276
Methyl Iodide	CH_3I	60·5	1·08	1·5297
Mesitylene	s-$C_6H_3(CH_3)_3$	62·3	0	1·4962
Benzene	C_6H_6	63·4	0	1·5014
Cyclohexane	C_6H_{12}	63·7	0	1·4273
(homogeneous)		64·3	small	1·4651
Anisole	$C_6H_5·OCH_3$	65·2	1·25	1·5164
Iodobenzene	C_6H_5I	65·6	1·25	1·6180
Toluene	$C_6H_5·CH_3$	65·7	0·4	1·4950
Chlorobenzene	$C_6H_5·Cl$	67·9	1·52	1·5250

TABLE 4. (cont.)

Solvent		$[M]_D^{20}$	μ (solvent)	n_D^{20} (solvent)
Hexane	C_6H_{14}	68·9°	0	1·3754
Carbon Tetrachloride	CCl4	69·4	0	1·4607
Aniline	$C_6H_5 \cdot NH_2$	70·7	1·52	1·5863
o-Dichlorobenzene	$C_6H_4Cl_2$	70·7	2·24	1·5490
Methyl Alcohol	$CH_3 \cdot OH$	71·1	1·66	1·3284
Acetophenone	$C_6H_5 \cdot CO \cdot CH_3$	71·8	2·97	1·5332
Acetone	$(CH_3)_2 \cdot CO$	72·1	2·76	1·3592
Benzonitrile	C_6H_5CN	73·4	3·85	1·5278
Benzaldehyde	$C_6H_5 \cdot CHO$	73·6	2·7	1·3316
Methylene Chloride	$CH_2 \cdot Cl_2$	75·3	1·55	1·4245
Chloroform	$CHCl_3$	75·9	1·18	1·4459
Nitromethane	$CH_3 \cdot NO_2$	76·0	3·03	1·3815
Acetonitrile	$CH_3 \cdot CN$	76·2	3·16	1·3441
Nitrobenzene	$C_6H_5 \cdot NO_2$	76·2	3·90	1·5504
Acetic Acid	$CH_3 \cdot COOH$	76·4	1·73	1·3718

It was noted from the above table for d-pinene that there was no regular effect of any kind traceable but some indication was found of both a refractive index effect and a polar effect such that increased polarity raised the rotation and increased refractive index lowered it, these two opposing effects being superimposed. This was well illustrated by the fact that carbon disulphide which is of zero dipole moment and the highest refractive index showed an exceptionally low value of optical rotatory power.

It was evident from the data referring to menthene, limonene, and pinene that there is no simple relationship between either the dipole moment of the solvent or its refractive index and the magnitude of the optical rotatory power. It was reasoned, however, that the above terpenes are unsaturated and therefore not entirely non-polar; solute-solvent complexes could thus be formed which might have a relatively large effect on the rotation even although the tendency of the hydrocarbon molecules towards self-association was small. The next step in attacking the problem seemed, therefore, to employ saturated, non-polar compounds of high optical activity. Unfortunately, such compounds are, in general, exceedingly difficult to procure in the optically pure state, although it is stated in the literature that pinane can be prepared in the pure state by catalytic hydrogenation of pinene, using platinum-black as a catalyst (cf. Lipp, Ber., 1923, 56, 2098). Pinane, being non-polar, was expected to exhibit more clearly any relationship which might exist between refractive index or polarity of solvent and the magnitude of the optical rotatory power (Rule and Chambers, loc. cit.).

d-PINANE.

The results given by Rule and Chambers are:-

TABLE 5.

d-Pinane in Solution.

Solvent		n_D^{20} (solvent)	μ (solvent)	$[M]_D^{20}$
Acetonitrile	$CH_3 \cdot CN$	1·3441	3·21	25·8°
Methyl Alcohol	$CH_3 \cdot OH$	1·3266	1·68	26·4
Acetic Acid	$CH_3 \cdot COOH$	1·3718	1·73	26·9
Nitromethane	$CH_3 \cdot NO_2$	1·3864	3·05	27·3
Pentane	C_5H_{12}	1·3640	0	27·4
Acetaldehyde	$CH_3 \cdot CHO$	1·3316	2·72	27·7
Hexane	C_6H_{14}	1·3835	0	27·8
Acetone	$(CH_3)_2 \cdot CO$	1·3653	2·76	28·9
Methylene Chloride	CH_2Cl_2	1·4245	1·51	29·0
Chloroform	$CHCl_3$	1·4489	1·05	30·2
Benzonitrile	$C_6H_5 \cdot CN$	1·5255	3·85	30·8
Methylene Bromide	$CH_2 \cdot Br_2$	1·5385	1·89	31·4
(Homogeneous)		(1·4630)	(0)	(31·5)
Carbon Tetrachloride	CCl_4	1·4616	0	31·6
Pyridine	C_6H_5N	1·5088	2·11	32·3
Mesitylene	$s\text{-}C_6H_3(CH_3)_3$	1·4944	0	32·5
Nitrobenzene	$C_6H_5 \cdot NO_2$	1·5468	3·90	32·5
Methyl Iodide	$CH_3 \cdot I$	1·5291	1·35	32·6

TABLE 5. (cont.)

Solvent		n_D^{20} (solvent)	μ (solvent)	$[M]_D^{20}$
Benzene	C_6H_6	1·4992	0	32·9°
Acetophenone	$C_6H_5 \cdot CO \cdot CH_3$	1·5310	2·97	33·2
Benzaldehyde	$C_6H_5 \cdot CHO$	1·5430	2·75	33·2
Toluene	$C_6H_5 \cdot CH_3$	1·4930	0·4	33·7
Anisole	$C_6H_5 \cdot OCH_3$	1·5141	1·25	32·9
Chlorobenzene	C_6H_5Cl	1·5229	1·56	33·2
o-Dichlorobenzene	$C_6H_4 \cdot Cl_2$	1·5466	2·24	33·2
α-Chloronaphthalene	$C_{10}H_7 \cdot Cl$	1·6332	1·59	34·5
Bromobenzene	$C_6H_5 \cdot Br$	1·5580	1·56	34·7
α-Bromonaphthalene	$C_{10}H_7Br$	1·6558	1·58	34·9
Ethylene Dibromide	$C_2H_4Cl_2$	1·6303	1·0	35·1
Iodobenzene	$C_6H_5 \cdot I$	1·6162	1·25	35·3
α-Naphthyl methyl ether	$C_{10}H_7 \cdot OCH_3$	1·6201	1·3	35·6
Aniline	$C_6H_5 \cdot NH_2$	1·5842	1·60	36·4
Methylene Iodide	$CH_2 \cdot I_2$	1·7341	1·10	36·6
Quinoline	C_9H_7N	1·6246	2·11	38·6
Carbon Disulphide	CS_2	1·6246	0	38·7
α-Iodonaphthalene	$C_{10}H_7I$	1·7054	1·43	39·7

From these results it was concluded that the polar effect was almost completely eliminated, since solvents of high polarity did not have any fixed position in the table. It was observed that the rotation increased roughly with increase in refractive index and that if non-polar solvents alone were considered there was an almost quantitative relationship between refractive index and the optical rotatory power. This was of particular interest, since such a relationship had been predicted from purely theoretical considerations. No such relationship had previously been confirmed by experimental results but this is perhaps not surprising, since very small changes in molecular association are known to be capable of producing large changes in rotation.

Since the results for d-pinane in non-polar media showed such a close connection between refractive index and optical rotatory power it was decided to see how far the relationship agreed quantitatively with the most important theories of optical activity, such as those of Born, Ganz and Boys.

Born (Physik. Z., 1915, 16, 251) and (Ann. Physik., 1918, 55, 177), by considering a conception of resonators coupled in pairs, derived a complicated formula for the rotatory power which was a function of the refractive index and the characteristic frequencies, etc. of the active molecule. For a given molecule in solution, however, the only variable for the function is the refractive index of the solution, and for any given wavelength the formula then reduces to the following:-

$$[M]_{\lambda}^{T} = k(n_{\lambda}^{T\,2} + 2)^{2}$$

This relationship was later modified by Ganz (Z.Physik., 1923, 17, 353 ; Ann. Physik., 1926, 79, 548), to the form

$$[M]_{\lambda}^{T} = k(n_{\lambda}^{T\,2} + 2)$$

which was later confirmed by Born himself (Proc. Roy. Soc., 1935, 150, A, 84). See, however, p. 56 of Discussion.

The third theory is due to S. F. Boys (Proc. Roy. Soc., 1934, 144, A, 861) who considered that each atom in a molecule becomes an oscillating electric doublet under the influence of a light wave. In simple cases the velocities of the d- and -circularly polarised light, which are the constituents of plane polarised light, can be calculated. The rotation is given by the difference of these two functions. From this Boys derived the following formula:

$$[\alpha]_{\lambda} = \frac{72900(n^{2}+2)(n^{2}+5)\cdot \sum R_{A}R_{B}R_{C}R_{D}\cdot I}{32\,\pi^{2}\,\lambda^{2}\,MN^{3}}$$

where n = refractive index of the medium,

R_A, etc. = total refractivities of each group on the asymmetric C. atom,

N = Avogadro's number,

I = a factor involving interatomic distances.

Since it is impossible to calculate I in practice, Boys derived an expression which could be determined when the groups attached to the asymmetric carbon atom are small. This was given as follows:-

$$[\alpha]_\lambda = \frac{C(n^2+2)(n^2+5)\cdot R_A R_B R_C R_D (1+F)(a-b)(a-c)(a-d)(b-c)(b-d)(c-d)}{\lambda^2 M (a+b+c+d)^4}$$

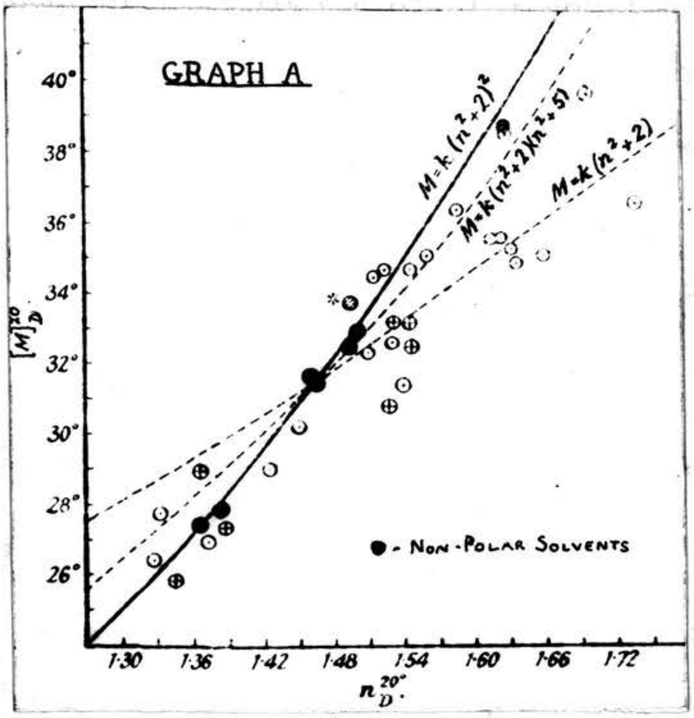
where C = a constant,
a, b, c and d = effective radii of the groups,
$F = f(\Delta a) + f(\Delta b) + f(\Delta c) + f(\Delta d)$

This formula can be reduced to

$$[M]^T_\lambda = k({n^T_\lambda}^2 + 2)({n^T_\lambda}^2 + 5)$$

for non-polar solute and solvent. In the case of polar solutes and solvents, association can be assumed to influence the refractivities or the effective radii of the attached groups. It is of interest to note that Boys suggested that the effect of polar solvents would go hand in hand with their dielectric constants, which had already been shown by Rule to be the case for many substances.

To test these relationships in the case of d-pinane a graph of $[M]$ against $\underline{n}$ was drawn and points plotted for each solvent (Rule and Chambers, loc. cit.). Using the relationship $[M] = k_1(n^2 + 2)$, k_1 can be calculated from the values of $[M]$ and $\underline{n}$ for homogeneous pinane and thus $[M]$ can be calculated for


GRAPH A
$M=k(n^2+2)^2$
$M=k(n^2+2)(n^2+5)$
$M=k(n^2+2)$
● - NON-POLAR SOLVENTS
$[M]^{20}_D$
40°
38°
36°
34°
32°
30°
28°
26°
1·30
1·36
1·42
1·48
1·54
1·60
1·66
1·72
$n^{20°}_D$

known values of n. This relationship was plotted on a graph (Graph A), and also the curves for $[M] = k_2(n^2 + 2)^2$ and $[M] = k_3(n^2 + 2)(n^2 + 5)$, as shown on the opposite page.

It was noted from the graph that all solvents of lower refractive index than pinane fell below the $(n^2 + 2)$ line, while nearly all of refractive index higher than pinane fell above it. This fact alone proves that this relationship does not hold for d-pinane. Further, the lines representing $[M] = k(n^2 + 2)^2$ and $[M] = k(n^2 + 2)(n^2 + 5)$ have many points on or near them, whilst the line corresponding to $[M] = k(n^2 + 2)^2$ includes all points for pinane in non-polar solvents.

It was concluded, therefore, that, for non-polar solutes and solvents, a relationship probably exists between refractive index and optical rotatory power represented by the equation

$$[M]_\lambda = k(n_\lambda^2 + 2)^2 .$$

In view of these regularities it was considered of importance to prepare other optically-active saturated hydrocarbons, in order to examine their properties when dissolved in a wider range of non-polar solvents than was used in the above case. The results of such work are described in the following part of this thesis, and include an account of a re-investigation of d-pinane in non-polar media.

EXPERIMENTAL.

Purification of Solvents:

(1) Acetone. Hopkin and Williams' "Analar" acetone which contained about 1% of water was dried over calcium chloride for 3 days at 30°C. and distilled. The middle fraction was taken which had b.p. 56·6°/760 mm.

(2) Hexane. Hexane, specially purified for spectroscopy, was used without any further purification.

(3) n-Heptane. Light's product which is quoted 100% pure was used without further purification.

(4) Cyclohexane. B.D.H. cyclohexane, specially purified for spectroscopy, was used without further purification.

(5) Carbon Tetrachloride. B.D.H. carbon tetrachloride, R.I., highly purified for refractive index determination of minerals, was used without further purification.

(6) Toluene. B.D.H. toluene, R.I., was used without further purification.

(7) **Mesitylene.** Light's pure mesitylene was used without further purification.

(8) **p-Xylene.** B.D.H. p-xylene was used without further purification.

(9) **Benzene.** B.D.H. "extra pure" benzene was used without further purification.

(10) **Decahydronaphthalene.** Light's product was refluxed for 3 hours over sodium and fractionated. The middle fraction was used. This had b.p. 187-189°/760 mm.

(11) **1-Methyl-Naphthalene.** The B.D.H. product was refluxed for 3 hours with sodium and fractionated, the middle fraction being used. This had b.p. 240·8 - 241·1%/760 mm.

(12) **Carbon Disulphide.** B.D.H. "A.R." carbon disulphide was dried over calcium chloride and fractionated, the middle fraction, b.p. 46·4°/760 mm., being used.

(13) **Nitrobenzene.** This was partly crystallised out by freezing. The solid was separated, melted and dried over P_2O_5 for several days, being finally distilled over lime. The middle fraction was taken, b.p. 210·6 - 210·8°/760 mm.

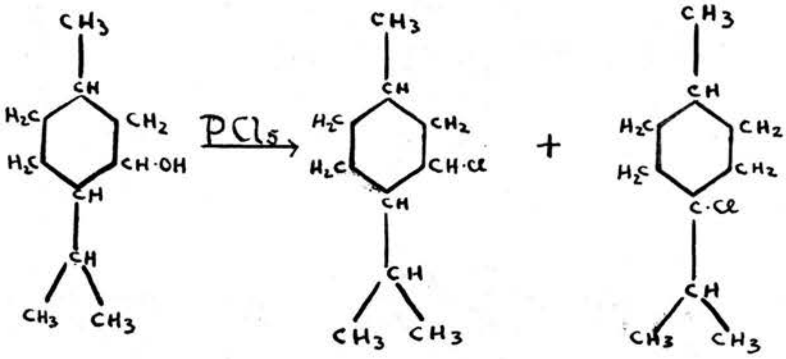
(14) Carbon Tetrabromide. B.D.H. carbon tetrabromide was used in solution in carbon tetrachloride.

(15) Alcohol. Absolute alcohol was boiled under reflux over lime for 12 hours and then fractionated, the middle fraction being taken. This had b.p. 78·3 - 78·5°/760 mm.

PREPARATION of *l*-DIMENTHYL.

(1) Preparation of *l*-Menthyl Chloride.

(Kursanoff, Ann., 1901, 318, 328).



150 gms. *l*-menthol

230 gms. P.Cl_5

The PCl_5 was placed in a round-bottomed flask and covered with low-boiling petrol ether, the whole being well cooled by being surrounded by an ice-salt mixture. The *l*-menthol, dissolved in petrol ether, was then slowly added. There was very vigorous reaction, HCl being rapidly evolved. When the reaction was completed the flask was vigorously shaken for a few minutes and the contents poured on to ice. This was left overnight to decompose the phosphorus oxychloride formed in the reaction. The petrol-ether layer was then separated and shaken vigorously with sodium carbonate solution until there was no further effervescence. It was then washed with water, separated, dried over $CaCl_2$ and distilled under reduced pressure. The fraction boiling from 105° - 115° at 30 mm. was collected.

Yield: 125 gm. (74% theory); α_D, +0·97° (ℓ = 1).

(2) <u>Preparation of "Stable" Menthyl Chloride</u>.

When the menthyl chloride is treated with aniline or alcoholic potassium hydroxide, part of it is acted upon with the elimination of hydrochloric acid to form menthene. The remainder, the so-called "stable" menthyl chloride, is unacted upon and can be recovered. It is thus assumed that the menthyl chloride is a mixture of two isomers.

120 gm.	menthyl chloride (from previous preparation)
300 gm.	methyl alcohol
40 gm.	KOH.

These were refluxed together for 60 hours or until no further precipitation of KCl was noticed. The mixture was then steam-distilled, when the menthene and the "stable" menthyl chloride came over and were separated, dried over calcium chloride and distilled under reduced pressure, using a fractionating column.

1st Fraction - B.p., 63 - 93°/20 mm. This proved to be largely menthene.

2nd Fraction - B.p., 93 - 100°/20 mm. This proved to be the "stable"

menthyl chloride, having
α_D, -47·9° ($\lambda = 1$), the value
quoted being -48°.
Yield, 40 gm.

(3) Preparation of l-Dimenthyl.

Method I.

It is claimed by Kursanoff that if this "stable" menthyl chloride is treated with sodium in ether, there is practically a quantitative yield of a solid dimenthyl of m.p. 105·5 - 106°, and $[\alpha]_D^{20}$, -51°18' (C = 20, in benzene).

40 gm.	"stable" menthyl chloride
80 c.c.	absolute ether
10 gm.	sodium wire

The ether and the "stable" menthyl chloride were mixed in a flask fitted with a reflux condenser and the freshly prepared sodium wire was added. The flask was heated on a water-bath and allowed to reflux for 14 hours, when the sodium was noticed to crumble to a purple powder. The solid mass was then extracted with dry ether, the extract was filtered and the ether evaporated off on the steam-bath, when about 30 gm. of a liquid was left. When distilled, this liquid ought to have given practically no distillate below 200° if it consisted entirely of dimenthyl. It was found, however, that more than 75% came over at a temperature of 165-170°, after which the temperature of the distillate rose gradually to 310°, when it remained steady. About 5 c.c. of a thick liquid distilled over at this temperature. On cooling this liquid, 0·5 gm. of a colourless solid crystallised out and was removed by filtration. This was recrystallised from alcohol and was found to have m.p. 105-105·5° and $[\alpha]_D^{20} = -49{\cdot}7°$, which showed it to be the dimenthyl described by Kursanoff. It was thought at first that the reaction had not been completed in the 14 hours treatment, and the distillate, of b.p. 165-170°, was therefore diluted with twice its weight of absolute ether and refluxed for a further 14 hours with sodium wire. There was, however, no further reaction with the sodium so that this fraction could not have been unchanged menthyl chloride which has, in any case, b.p. 210°. Indeed, fusion with sodium showed no trace of chlorine. This liquid was found to have a rotation of α_D^{20} + 6·24° (ℓ= 1). It decolourised a small amount of bromine water so that there was present a small amount of unsaturated product. From its properties it can only be assumed to be a mixture of menthane and menthene. The formation of menthene could be explained by partial removal of HCl from the menthyl chloride by the sodium. At this stage the only explanation that could be advanced to account for the formation of menthane was the presence of moisture or alcohol in the ether. The preparation was therefore repeated, using ether which had been specially purified by shaking up several times with water to remove any alcohol, drying over phosphorus pentoxide for several days and repeated treatment with fresh sodium wire till effervescence ceased, and finally distilling it over sodium wire in a carefully dried apparatus. The result of this experiment was, however, exactly the same as before, the yield of solid dimenthyl being no greater, the bulk of the distillate again distilling at 165°. Since there was the possibility that water-vapour had entered the liquid while it was refluxing on the water-bath, the preparation was again repeated on an electrical heater, the top of the condenser being open to air through a phosphorus pentoxide drying tube. These changes, however, effected no improvement in the yield. The experiment was repeated using spectroscopically pure hexane in place of ether, but with the same yield of solid dimenthyl. Some doubt must, therefore, be cast on the statements made in the literature by Kursanoff, especially since some time after this work a reference was found to a paper by Carothers and co-workers (J.A.C.S., 1930, 5279) concerning the formation of paraffin hydrocarbons by the Wurtz synthesis using sodium and the halide dissolved in ether. The following is a quotation from this paper: "The first step in simple Wurtz reactions is the formation of the corresponding sodium alkyl, R-Na. This normally couples with the halide, forming the hydrocarbon R-R, but it may react in other ways and yield by-products. Sodium ethide reacts with diethyl ether

$$C_2H_5Na + (C_2H_5)_2O = C_2H_6 + C_2H_5ONa + C_2H_4$$

and one may expect the formation of considerable amounts of the hydrocarbon RH when the Wurtz reaction is carried out in that solvent." An example is quoted of decamethylene bromide which yielded 34% n-decane with such treatment. The large amount of menthane is therefore not entirely unexpected, the reaction being

$$R{\cdot}Cl + Na \longrightarrow R{\cdot}Na + NaCl$$

$$R{\cdot}Na + (C_2H_5)_2O \longrightarrow R{\cdot}H + C_2H_5ONa + C_2H_4$$

It might be expected that the following reaction also ought to take place:

$$R{\cdot}Cl + C_2H_5ONa \longrightarrow NaCl + R{\cdot}O{\cdot}C_2H_5$$

but menthyl ethyl ether was not apparently formed to any great extent although this might explain the gradual rise in boiling point from 160° to 310° when distilling the crude product, since the ether has b.p. 210°.

Method II.

While preparing dimenthyl in the above manner, hydrodicamphene was also being prepared by the method of Sakellarios and Kyrimis (Ber., 1924, 326). It was thought possible that this latter method might be applied with success in the case of dimenthyl. The method in question involves the treatment of pinene hydrochloride with magnesium turnings to give a Grignard reagent (see Prep. of hydrodicamphene, p. 39), which was poured on to a suspension of anhydrous cupric chloride in ether, when the following reaction takes place:-

$$2R{\cdot}MgCl + 2CuCl_2 \longrightarrow R{\cdot}R + 2MgCl_2 + Cu_2Cl_2$$

This reaction was carried out as follows, using menthyl chloride:

10 gm. "stable" menthyl chloride
20 c.c. absolute ether
3 gm. magnesium turnings
0·2 gm. ethyl bromide

The ethyl bromide in 2 c.c. of ether was poured on to the magnesium which was contained in a flask carrying a reflux condenser. The reaction was carried out in an atmosphere of nitrogen obtained by passing nitrogen gas through the apparatus. A reaction started and when this was most vigorous the mixture of the stable menthyl chloride was slowly added. The reaction between the menthyl chloride and the magnesium was slow and had to be completed by refluxing for several hours. When the change was completed the ether extract was poured on to a suspension of 8 gm. of anhydrous cupric chloride in ether. After standing for several hours it was refluxed for 1 hour and filtered. On evaporating off the ether, an oily liquid was obtained from which a small amount of solid separated out. This was filtered off and recrystallised, giving a product which was proved by melting-point and rotation to be the same solid as was obtained by the previous method. The yield, however, was no better, so that there is no advantage in using this method.

Yield, 0·2 gm. M.p., 104·5 - 105·5°.
$[\alpha]_D^{20°}$, -50·0° (in benzene, c = 6).

In order to obtain a sufficient amount of the solid dimenthyl, the experiment was repeated five times, using the first method, after which 2·8 gm. of crude dimenthyl were available. At this stage 120 gm. of menthyl chloride prepared by interaction of *l*-menthol and phosphorous pentachloride (without subsequent heating with alkali), was treated with sodium in ether and treated further in exactly the same manner as the "stable" menthyl chloride. In this preparation a yield of 1·3 gm. of solid dimenthyl was obtained, identical in properties with that obtained from the "stable" menthyl chloride. Since this is more than double the yield obtained from the same amount of *l*-menthol by the alcoholic alkali treatment it was decided to prepare a further supply of dimenthyl from untreated menthyl chloride. After one repetition of the above experiment, 4·5 gm. of crude solid dimenthyl were available. This was recrystallised from alcohol five times, after which there was no further change in rotation and the melting-point was sharp. In this way 3·5 gm. of pure solid dimenthyl were obtained; m.p., 105·8 - 106° ; $[\alpha]_D^{20°}$, -51·0° (in benzene, c= 6).

When tested with bromine in carbon tetrachloride it proved to be quite saturated and the hot copper wire test showed it to contain no halogen.

As a result of the unexpected polarimetric results which it gave, an analysis was also made.

Analysis:

Found: C, 86·26% ; H, 13·81%.

$C_{20}H_{38}$ requires C, 86·33% ; H, 13·67%

PREPARATION of LIQUID DIMENTHYL.

It was noted that when menthyl chloride which had not been treated with alcoholic alkali was treated with sodium in ether, a reaction similar to that undergone by the "stable" chloride took place. On distilling the product, about 75% came over at 165° to 170° and most of the remainder at 310°. Since this is the boiling-point of the solid dimenthyl there can be only dimenthyl present. On cooling the distillate, however, only a small amount of solid dimenthyl separated out, consequently there must also be a liquid dimenthyl formed which would be of interest in this investigation.

80 gm.	menthyl chloride
160 c.c.	absolute ether
20 gm.	sodium wire

The menthyl chloride was treated in the above manner and 10 gm. of liquid dimenthyl was obtained which gave $[\alpha]_D^{20°}$, $-32{\cdot}3°$; $d_4^{20°}$, $0{\cdot}8838$

PREPARATION of *l*-HYDRODICAMPHENE.

1. Preparation of d-Pinene Hydrochloride.

(Cohen, p. 291)

d-α-Pinene, 100 gm., which had been freshly distilled, was treated with dry hydrogen chloride gas, care being taken to exclude the entry of air to keep the temperature below 20°. After several hours, about 50% of the pinene changed to hydrochloride and was filtered off and recrystallised from alcohol.

d-Pinene: $[\alpha]_D^{20°}$, +46·7° ; d_4^{20} , ·866.

d-Pinene Hydrochloride: $[\alpha]_D^{20°}$, +33·24° (c = 5, in benzene).

Yield, 30 gm. M.p., 119-120°.

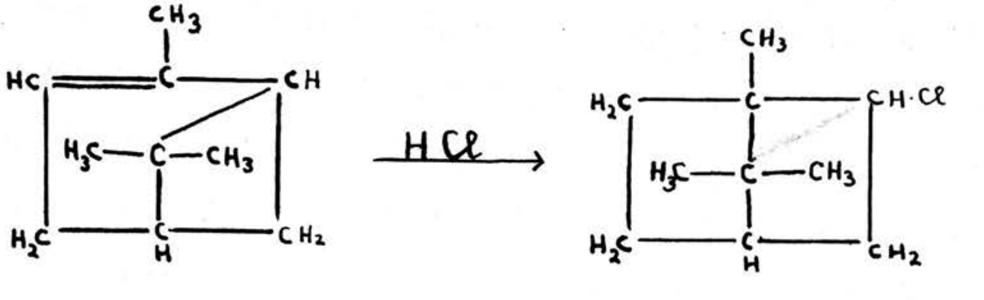
2. Preparation of Hydrodicamphene.

(Sakellarios and Kyrimis, Ber., 1924, 326).

4·2 gm.	magnesium
0·6 gm.	ethyl bromide
27 gm.	absolute ether
24 gm.	anhydrous cupric chloride
30 gm.	pinene hydrochloride

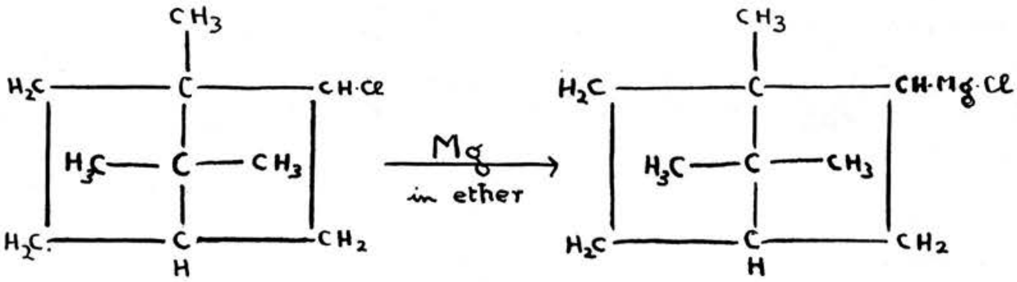
The magnesium, which was contained in a flask fitted with a reflux condenser and closed by a phosphorus pentoxide tube, was acted on by 0·6 gm. of ethyl bromide dissolved in 3 c.c. absolute ether. As soon as the reaction had become vigorous the pinene hydrochloride, dissolved in 24 c.c. of absolute ether, was slowly added, when the reaction proceeded slowly for a short time and then gradually stopped. At this stage it had to be boiled under reflux for 24 hours to complete the reaction. The magnesium compound was then extracted with 75 c.c. of ether and poured on to a suspension of 24 gm. of anhydrous cupric chloride in ether. A slight amount of heat was evolved and the ether boiled. After standing for several hours the mixture was refluxed for 1 hour and the ether extract filtered off from the cupric chloride, which had been changed to a pasty mass. The ether was evaporated off and a solid residue was left which melted at 41°. Since the melting point of pure hydrodicamphene is quoted as 86° it was assumed that this product contained a large amount of impurity such as borneol and camphene. Recrystallisation was therefore attempted using glacial acetic acid but with only a very slight improvement in the melting point. Alcohol was found, however, to raise the melting point to 63° C. after the first recrystallisation, although only about 50% was recovered. Steam distillation was also tried but proved unsuccessful in effecting a separation. After five recrystallisations from alcohol a hydrodicamphene was obtained, of m.p. 85·5 - 86°, the yield being 2 gm. The above experiment was repeated and 4·5 gm. of hydrodicamphene were obtained.

M.p., 85·5 - 86° ; $[\alpha]_D^{20}$, -19·4° (c = 6·056, in benzene).

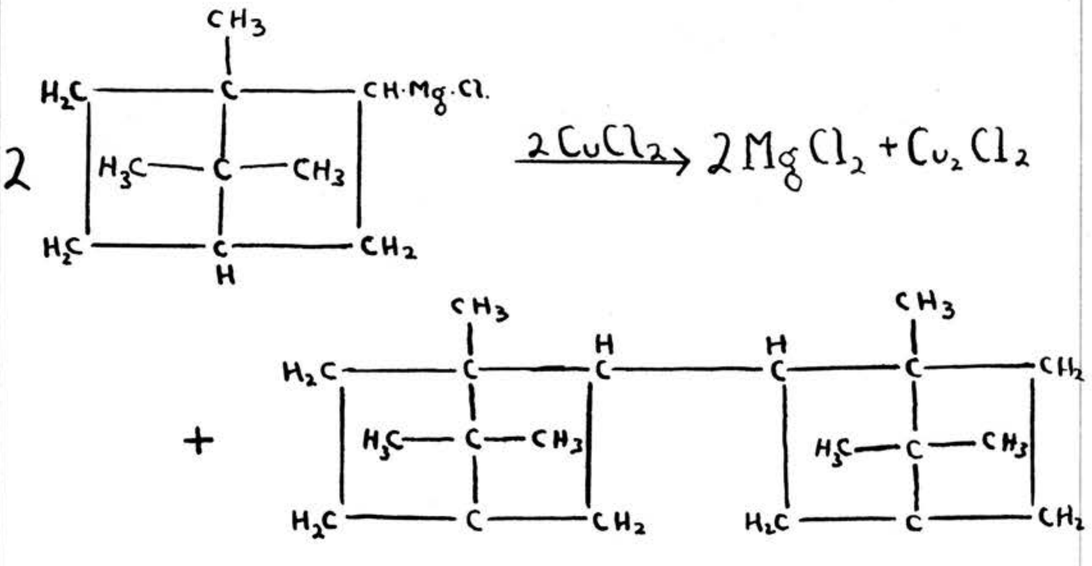


α-Pinene

Pinene Hydrochloride



Bornyl-Magnesium Chloride



Hydrodicamphene

(Dibornyl)

PREPARATION of d-HYDRODICAMPHENE.

This was prepared in the same manner as the l-compound from 150 gm. of l-pinene of $[\alpha]_D^{20^\circ}$, $-33{\cdot}7^\circ$, which in the first stage yielded 60 gm. of ~~d~~ l-pinene hydrochloride; m.p., 125-126°; $[\alpha]_D^{20^\circ}$, $-25{\cdot}1^\circ$. From this was obtained, after five recrystallisations from alcohol, 4 gm. of d-hydrodicamphene which had m.p., 85·5 - 86°; $[\alpha]_D^{20^\circ}$, $+16{\cdot}4^\circ$ ($c = 6$, in benzene).

PREPARATION of d-PINANE.

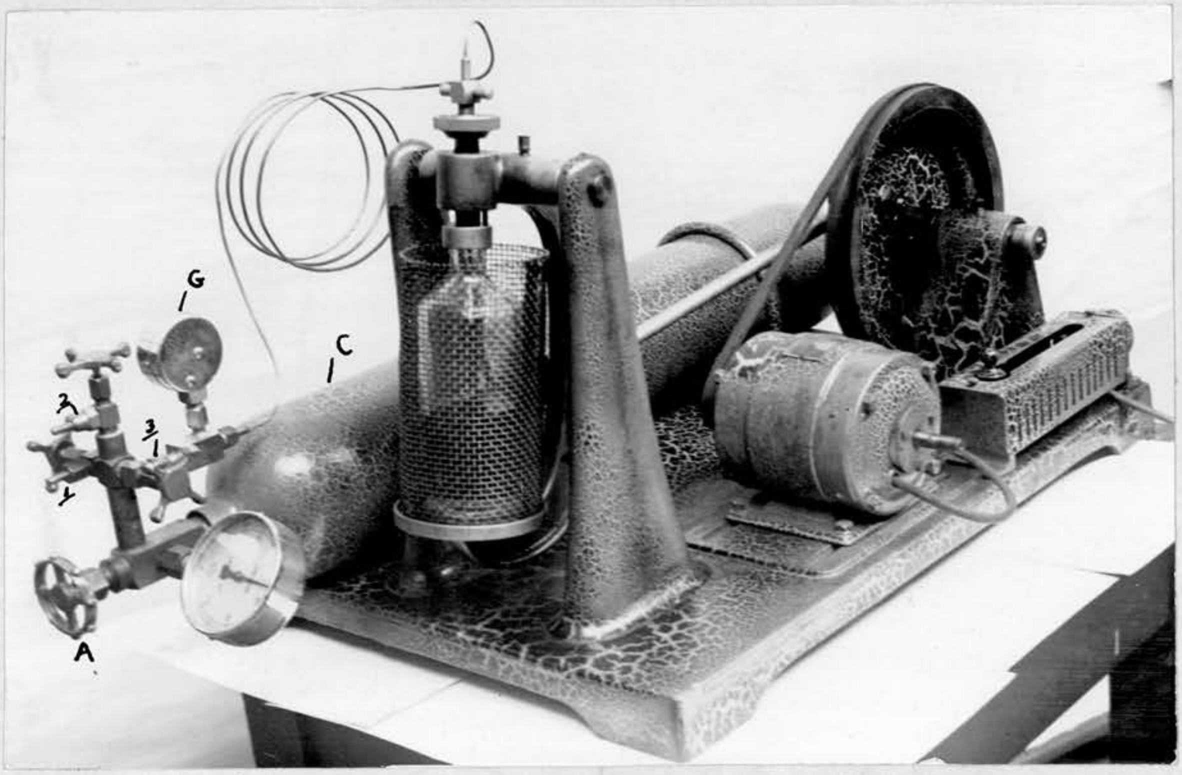
The d-pinene was prepared by catalytic hydrogenation of d-pinene, using platinum-black as a catalyst.

1. Preparation of Platinum Black.

(Houben, Org. Chem., 1928, Vol. II, 496).

7·4 gm.	platinum chloride
7 c.c.	distilled water
25 c.c.	33% formaldehyde
53 gm.	50% solution of potassium hydroxide

The platinum chloride was dissolved in the distilled water and cooled to -10° after adding the formaldehyde. The mixture was stirred vigorously with a mechanical stirrer, whilst the alkali was slowly added so that the temperature never rose above 5°. After all the potassium hydroxide had been added the mixture was heated for half-an-hour at 55-60° with continued vigorous stirring. The solution then became clear and was washed by decantation until free from alkali and chloride, when it was filtered with weak suction so that the platinum was always covered with water. It was then quickly pressed between filter papers and dried in a vacuum desiccator. To avoid


G
C
2
3
1
A

overheating of the catalyst which sometimes takes place in contact with oxygen, the desiccator tap is opened very slowly.

Yield, 2·85 gm.

2. Preparation of d-α-Pinane.

The hydrogenation was carried out in an improved form of apparatus originally designed by Adams and Voorhees (see Organic Synthesis, Vol. VIII (1928), p. 10) and is shown opposite.

The d-α-pinene (Kahlbaum) was purified by distilling in steam with addition of a trace of sodium carbonate, followed by drying over anhydrous sodium sulphate and twice distilling over sodium under atmospheric pressure, the fraction boiling at 154·7°, under 757·5 mm. being collected. This pinene had d_4^{20} 0·8668 and $[\alpha]_D^{20}$, +46·7° (cf. Ross and Somerville, J.C.S., 1926, 220, who quote d_4^{20} = 0·8665 and $[\alpha]_D^{20}$, +47·3°).

Hydrogenation of the d-α-pinene was carried out in the following manner:-

The pure α-pinene, 100 gm., was put into the hydrogenation bottle along with 2·85 gm. of platinum-black catalyst and clamped in the shaker. The pressure in the cylinder C was raised to 80 lbs. per sq. in. from a large hydrogen cylinder by opening tap <u>1</u> and the key A. The bottle was then evacuated by attaching the pump to tap <u>2</u> and opening tap <u>3</u>. When the bottle was fully evacuated, tap <u>2</u> was closed and the valve A was opened so that hydrogen flowed into the vessel to a pressure of 80 lbs. Valve A was closed and also tap 3. The shaker was then started when the hydrogen began to be absorbed so that the pressure fell and the decrease in pressure was registered on the gauge G. When the pressure had fallen off to about 20 lbs. per sq. in. it was raised again by opening valve A and tap 3. The process was repeated in this way until no further fall in pressure was noted after two or three hours shaking. A note of the amount of hydrogen absorbed is kept and from this it is possible to determine the percentage conversion by calibrating the apparatus with a known weight of benzoin.

After hydrogenation, the crude d-pinane was filtered off from the catalyst and was purified by the method of Lipp (Ber., 1923, 56, 2098). The pinane was shaken up with successive small amounts of 1% solution of potassium permanganate in sodium carbonate until the colour persisted for half-an-hour. It was found, however, that the time factor depended on how much permanganate was added and how vigorously it was shaken, so that while with gentle shaking the colour could be made to persist for half-an-hour, more vigorous shaking led to rapid decolourisation. It seemed, therefore, that this was not a very good method. The rest of the purification was, however, carried out. This consisted of refluxing the pinane with sodium to remove the hydroxy compounds formed during the oxidation and then distilling with a long fractionating column. In this way 60 gm. of pinane were obtained, of b.p. 166·5 - 166·7°, and $[\alpha]_D^{20}$ + 24·3° ; d_4^{20} = 0·8594.

Owing to the unsatisfactory results on shaking with permanganate solution it was decided to try to improve the method of purification, especially as the d-pinane obtained by Chambers in this way (see J.C.S., 1937, 145) had been shown by its adsorption spectra to be less than 100% saturated. An experiment was therefore carried out in the following manner. Two 15 c.c. fractions of the pinane obtained by Lipp's method of purification were taken (α_{5461}^{20} + 50·62°, $\ell = 2$).

The first fraction (A) was then shaken for 1 hour with excess of 1% alkaline permanganate, steam-distilled and separated, dried over calcium chloride and again distilled. This sample was then found to have

$$\alpha_{5461}^{20} , \quad + \ 50{\cdot}06^\circ \ (\ell = 2).$$

The other fraction (B) was boiled for 1 hour with acid dichromate, which attacks pinene itself very readily, hence any pinene present should undergo oxidation. The solution was made alkaline and steam-distilled, separated and dried over calcium chloride and distilled. This sample was found to have

$$\alpha_{5461}^{20} , \quad + \ 50{\cdot}60^\circ \ (\ell = 2).$$

The conclusion drawn from these results is that the alkaline permanganate attacks the pinane as well as the pinene. Acid dichromate, on the other hand, does not appear to attack the pinane, as it did not appreciably change the rotation. The indication is, therefore, that acid dichromate is the better agent for eliminating traces of pinene. This possibility was further tested by adding 2 c.c. of d-α-pinene to each of (A) and (B) fractions of 15 c.c. of the pinane, after which the rotations were found to be

(A) α^{20}_{5461}, + 52·2° (ℓ = 2)

(B) α^{20}_{5461}, + 52·8° (ℓ = 2).

(A) was then treated with alkaline permanganate as before, and eventually refluxed over sodium and distilled. It was obvious that if this method really purified the pinane the rotation ought to have fallen off to the original value observed before adding the pinene, i.e. + 50·06°. The rotation of the final product was found, however, to be +53·9° which is a higher value than that of the mixture of pinene and pinane. It was obvious, therefore, that the permanganate method was useless for purifying d-pinane containing an appreciable proportion of pinene.

Sample (B) was treated, as before, with acid dichromate and finally refluxed and distilled over sodium. The final product had

α^{20}_{5461}, +54·25 (ℓ = 2).

It was therefore obvious that this method also is useless for the purification of d-pinane.

A sample of pinane purified according to Lipp, $[\alpha]_D^{20}$, +24·3°, was then tested with bromine in carbon tetrachloride which was decolourised, indicating unsaturation. Quantitative experiments showed adsorption of bromine corresponding to about 5% of unsaturated ethylenic products, a further proof that the Lipp method is ineffective. It was then considered that treatment with bromine might offer a possible means of purification. Pinene, on bromination, gives a dibromo compound which is stated to decompose on heating to p-cymene which is non-polar and optically inactive and would therefore not seriously affect the optical determinations, even if it could not be entirely removed by fractionation. The bulk of the pinane was therefore treated with bromine until no further rapid decolourisation of the bromine took place. The product was refluxed for three hours with an excess of sodium and then fractionated. This contained no bromine and had b.p., 166·5°/760 mm.; $[\alpha]_D^{20}$, +22·09° ; d_4^{20}, 0·8595 and n_D^{20}, 1·46191.

Zwanziger (Dissert, Munich, 1917) quotes pinane with $[\alpha]_D^{20}$, +23·1° from pinene of $[\alpha]_D^{20}$, 47·5°.

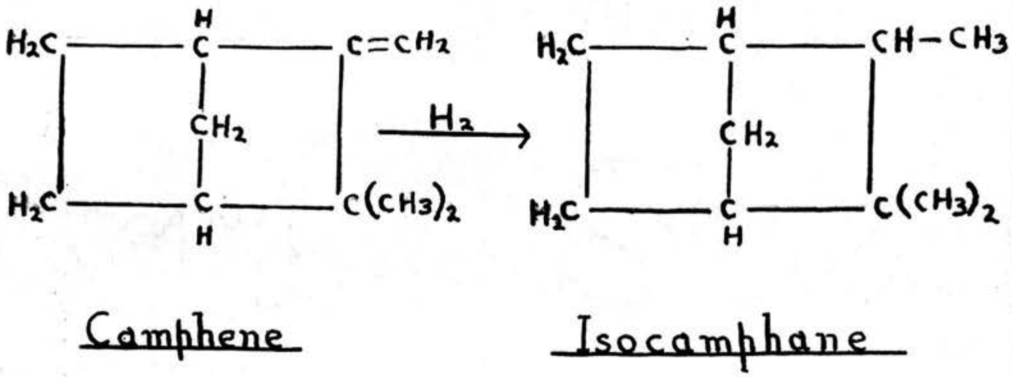
As will be seen later, this sample of d-pinane showed practically the same optical properties in solution as the product obtained by Chambers (loc. cit.) which was purified by Lipp's method.

PREPARATION of ISOCAMPHANE.

When camphene is hydrogenated in a similar manner to pinene a solid product is obtained which is isocamphane (Vavon, C.R. 149, 998).

10 gm. of pure camphene (Schuchardt) were dissolved in 100 c.c. of pure ether and hydrogenated in the same manner as pinene, using 1·8 gm. of platinum-black catalyst. The camphene had $[\alpha]_D^{20°}$, -31·4° (c = 8, in benzene). The initial pressure in the bottle was 77 lbs. per sq. in. Immediately on shaking, the pressure fell off rapidly, reaching a value of 12 lbs. in less than a minute. At this value the rapid fall in pressure stopped, so the vessel was refilled to a pressure of 73 lbs. Even after shaking all night, however, a further fall of only 3 lbs. was noted. The ether solution was then decanted off and filtered, when 9·5 gm. of a solid were obtained which melted sharply at 55°. When dissolved in carbon tetrachloride the compound did not adsorb the least trace of bromine. It must therefore be concluded that complete reduction had taken place and that the product was pure isocamphane. It was found to have a rotation of $[\alpha]_D^{20°}$, +4·7° (c = 6, in benzene).

Vavon quotes m.p. 87° for his isocamphane obtained from camphene, of m.p. 55°, but the melting-point of the isocamphane depends on the optical purity of the camphene and various figures are recorded in the literature.



PREPARATION OF HIGHLY ACTIVE ISOCAMPHANE.

The above isocamphane being of such low activity it was decided to attempt to prepare a more active camphene so that a more active isocamphane would be formed on reduction. This was done according to the method of Reychler (Bull. de la Soc. Chim., 1896, 15, 371).

Preparation of Camphene.

130 gm.	phenol
50 gm.	potassium hydroxide
70 gm.	pinene hydrochloride

The potassium hydroxide was dissolved in the minimum quantity of water and the phenol was added. The solution was then distilled until the temperature of the mixture was 170°. The pinene hydrochloride, which must be freshly recrystallised from alcohol in order to give the maximum yield of camphene, was then added and the mixture allowed to boil gently for 30 minutes under an air condenser acting as a reflux. The mixture was again distilled until the temperature of the mixture in the flask reached 190°, during which all the camphene distilled over and was shaken up with sodium hydroxide solution to remove any phenol. The camphene was finally filtered, washed and melted, and dried over calcium chloride, after which it was refluxed for a short time over sodium and distilled. The pinene hydrochloride employed had $[\alpha]_D^{20}$, +21·3°.

Yield, 40 gm. (73% of theory); b.p., 155-156°/760 mm. m.p., 41°; $[\alpha]_D^{20}$, +59·8° (c = 20, in benzene).

Hydrogenation of Camphene.

The 40 gm. of camphene was dissolved in 100 c.c. of absolute ether and hydrogenated as before, using 3 gm. of platinum-black catalyst. Hydrogen was absorbed very rapidly and a fall in pressure of 250 lbs. was noted, which represents 100% conversion into isocamphane. The catalyst was filtered off, and on evaporating off the ether 40 gm. of isocamphane were left. This was recrystallised from petrol ether and a white crystalline product was obtained, which did not decolourise the least trace of bromine when dissolved in carbon tetrachloride, thus showing it to be completely saturated. It was themdistilled, rejecting the first fraction.

Yield, 33 gm. M.p., 59°; b.p., 162°/760 mm.; $[\alpha]_D^{20}$, -5·41° (c = 6, in benzene).

All rotations for the sodium D wavelength were taken on a Schmidt and Haensch three-field polarimeter of the Lippich type which was illuminated by a monochromator.

All the rotations for the mercury yellow and green lines were taken with a Hilger polarimeter (M 5), also of the Lippich three-field type. The source of illumination was a mercury vapour lamp, the fields for the yellow and green being separated by viewing the field through a prism.

Both instruments were fitted with verniers capable of reading accurately to 0·01°.

Owing to the very small amount of dimenthyl available, ordinary polarimeter tubes could not be employed. A capillary tube, two decimetres in length, was used which had a capacity of 2·1 mls. Solutions were therefore made up in a 2·5 ml. standard flask which was specially prepared for the purpose, the solvent and solution being added to and taken from the flask by means of fountain-pen fillers drawn out to a capillary.

In order to take all readings at 20°C., the tube was first jacketed and water from a thermostat regulated to 20·2° was pumped through the water jacket, when the tube and contents were expected to attain quickly a value of 20°C., since there was a fall in temperature of 0·2°C. when the water flowed through the tubes to the jacket. It was found, however, that no clear reading of the field could be obtained in this manner, even after the water had been flowing through the jacket for an hour. This must have been due to the fact that the metal end-pieces of the polarimeter were not enclosed in the water-jacket and were thus at room temperature of 15°C. This variation in temperature was apparently causing density changes in the liquid which were sufficient to obscure the field. The difficulty was eventually overcome by keeping the whole room at 20°C. This was achieved by means of an electric heater in circuit with a relay and thermostat control, the air being continually mixed by a fan driven by an electric motor. It was possible in this way to control the temperature of the room between the limits of 19·8° and 20·1°. Since a difference of 0·3°C. made no appreciable change in the rotation or the refractive index, the water thermostat was not required, and readings were taken without passing water through the jacket. In this manner a sharp view of the field was obtainable almost immediately after ~~the~~ filling the tube, since all the solvents, flasks, polarimeter tubes, etc. which were employed in taking rotations were kept in this room and therefore maintained at 20°C. All refractive indices were taken with a Pulfrich refractometer which was also kept in the temperature-controlled room.

An Osira sodium-vapour lamp was used for the D line and an Osira mercury-vapour lamp for the mercury green line readings. The Pulfrich refractometer in conjunction with these light sources gave refractive indices correct to the fifth place of decimals.

For each determination the following procedure was found to give best results in the least time. The correct amount of solute was weighed out into the standard flask which was then transferred to the temperature-controlled room. After a few minutes it attained the room temperature of 20°, when solvent was added to it up to the graduation mark by means of the filler. After thorough shaking, the solution was transferred to the polarimeter tube, using a similar filler. The rotation of the solution was then taken for the sodium D line, after which the tube was transferred to the other polarimeter and the rotation taken for the mercury yellow and green lines. The solution was then transferred to the cell of the Pulfrich refractometer, using a clean filler, and the angle of refraction noted for the three wavelengths. After each determination all the apparatus used was washed well with A.R. benzene and dried in a current of air before being used for another determination.

DISCUSSION.

As has already been stated in the Introduction, the investigation of a large number of polar, optically-active substances in solution has shown, in general, the existence of an optical effect related to the polarities of the solute and solvent. In the case of *d*-pinane, however, where the solute is non-polar, Rule and Chambers found that the polarity of the solvent had no perceptible influence on the magnitude of the rotation, the latter being connected with the refractive index of the solution in approximate agreement with the formula of Born:

$$[M] = k(n^2 + 2)^2$$

In a foot-note of a paper by Rule and Chambers (J.C.S., 1937, 145) it is stated that the formula, $[M] = k(n^2 + 2)$, which was deduced by Born in 1935, is incorrect owing to the omission of a factor and that Born gives the corrected version as

$$[M] = k(n^2 + 2)^2$$

In order to obtain further evidence bearing on this point, several optically active, non-polar hydrocarbons of the terpene group have now been prepared, as described in the foregoing section, and their rotations determined in a variety of solvents.

The first compound to be obtained, *l*-dimenthyl,

TABLE 6.

l-DIMENTHYL.

Sodium D line (λ = 5893) ; C ≒ 6.

	Solvent	$[M]_D^{20}$ (solution)	n_D^{20} (solution)	C
1.	Mesitylene	-169·5°	1·49585	6·000
2.	n-Heptane	-169·3°	1·39419	6·000
3.	Hexane	-168·6°	1·38670	6·036
4.	p-Xylene	-167·3°	1·49443	5·740
5.	1-Methyl Naphthalene	-159·8°	1·60591	6·036
6.	Toluene	-155·6°	1·49185	6·216
7.	Carbon Tetrachloride	-155·6°	1·46111	5·968
8.	Carbon Tetrabromide	-155·8°	1·49251	6·012
9.	Cyclohexane	-153·2°	1·42937	5·980
10.	Decahydronaphthalene	-145·3°	1·47614	5·992
11.	Benzene	-141·8°	1·49824	5·800
12.	Carbon Disulphide	-132·2°	1·61581	6·020
	Polar Solvents.			
13.	Acetone	-189·7°	1·36032	1·260
14.	Nitrobenzene	-137·9°	1·55122	1·180

TABLE 7.

l-DIMENTHYL.

Mercury green line (λ = 5461 A) ; C = 6.

	Solvent	$[M]^{20}_{5461}$ (solution)	n^{20}_{5461} (solution)	C
1.	Mesitylene	-203·6°	1·49970	6·000
2.	n-Heptane	-203·2°	1·39628	6·000
3.	Hexane	-202·2°	1·38878	6·036
4.	p-Xylene	-198·2°	1·49870	5·740
5.	1-Methyl Naphthalene	-189·2°	1·61281	6·036
6.	Toluene	-185·6°	1·49594	6·216
7.	Carbon Tetrachloride	-186·3°	1·46381	5·968
8.	Carbon Tetrabromide 33% in Carbon tetrachloride	-184·9°	1·49557	6·012
9.	Cyclohexane	-180·9°	1·43353	5·980
10.	Decahydronaphthalene	-172·6°	1·47890	5·992
11.	Benzene	-169·5°	1·50147	5·800
12.	Carbon Disulphide	-156·1°	1·62276	6·020
	Polar solvents.			
13.	Acetone	-214·2°	1·36259	1·260
14.	Nitrobenzene	-158·5°	1·55820	1·180

was prepared according to the method of Kursanoff (Ann., 1901, 318, 328) in which ℓ-menthol is treated with phosphorus pentachloride to give ℓ-menthyl chloride. This is claimed by Kursanoff to be a mixture of two isomers, one of which is stable towards alcoholic potassium hydroxide, while the other is converted into menthene by this treatment. A separation of the two isomers is thus easily made. Kursanoff claims that the "stable" menthyl chloride, when acted upon with metallic sodium in ether, gives an almost quantitative yield of a solid dimenthyl. It was found, however, during the present work that in no manner could these results be duplicated although the "stable" menthyl chloride was similar in every way to that of Kursanoff. A partial explanation of the low yield of dimenthyl actually obtained is given by the discovery of Corothers (J.A.C.S., 1930, 5279) who found the following changes to take place with similar reactions:

$$R\cdot Cl + Na \longrightarrow R\cdot Na + NaCl$$

$$R\cdot Na + (C_2H_5)_2O \longrightarrow R\cdot H + C_2H_5ONa + C_2H_4$$

This mechanism would account for the large amount of menthane which was actually isolated in the present work although it does not explain why the yield of dimenthyl was so small when using hexane as solvent or by the Grignard method of preparation.

The optical properties of the compound are given in Tables 6 and 7 for the Sodium D line and the

TABLE 8.

l-DIMENTHYL.

Sodium D line (λ= 5893Å ; C = 2.

	Solvent	$[M]_D^{20}$ (solution)	n_D^{20} (solution)	C
1.	Carbon Disulphide	-130·4°	1·62491	2·016
2.	1-Methyl Naphthalene	-160°	1·6129	1·980
3.	Mesitylene	-173·1°	1·49710	2·000
4.	Hexane	-171·0°	1·38176	2·040

Mercury yellow line (λ = 5780).

1.	Carbon Disulphide	-136·5°	1·62681	2·016
2.	1-Methyl Naphthalene	-176·4°	1·61454	1·980
3.	Mesitylene	-182·1°	1·49895	2·000
4.	Hexane	-179·9°	1·38214	2·040

Mercury green line (λ = 5461).

1.	Carbon Disulphide	-153·1°	1·63274	2·016
2.	1-Methyl Naphthalene	-197·7°	1·61995	1·980
3.	Mesitylene	-208·4°	1·50106	2·000
4.	Hexane	-205·0°	1·38342	2·040

TABLE 9.

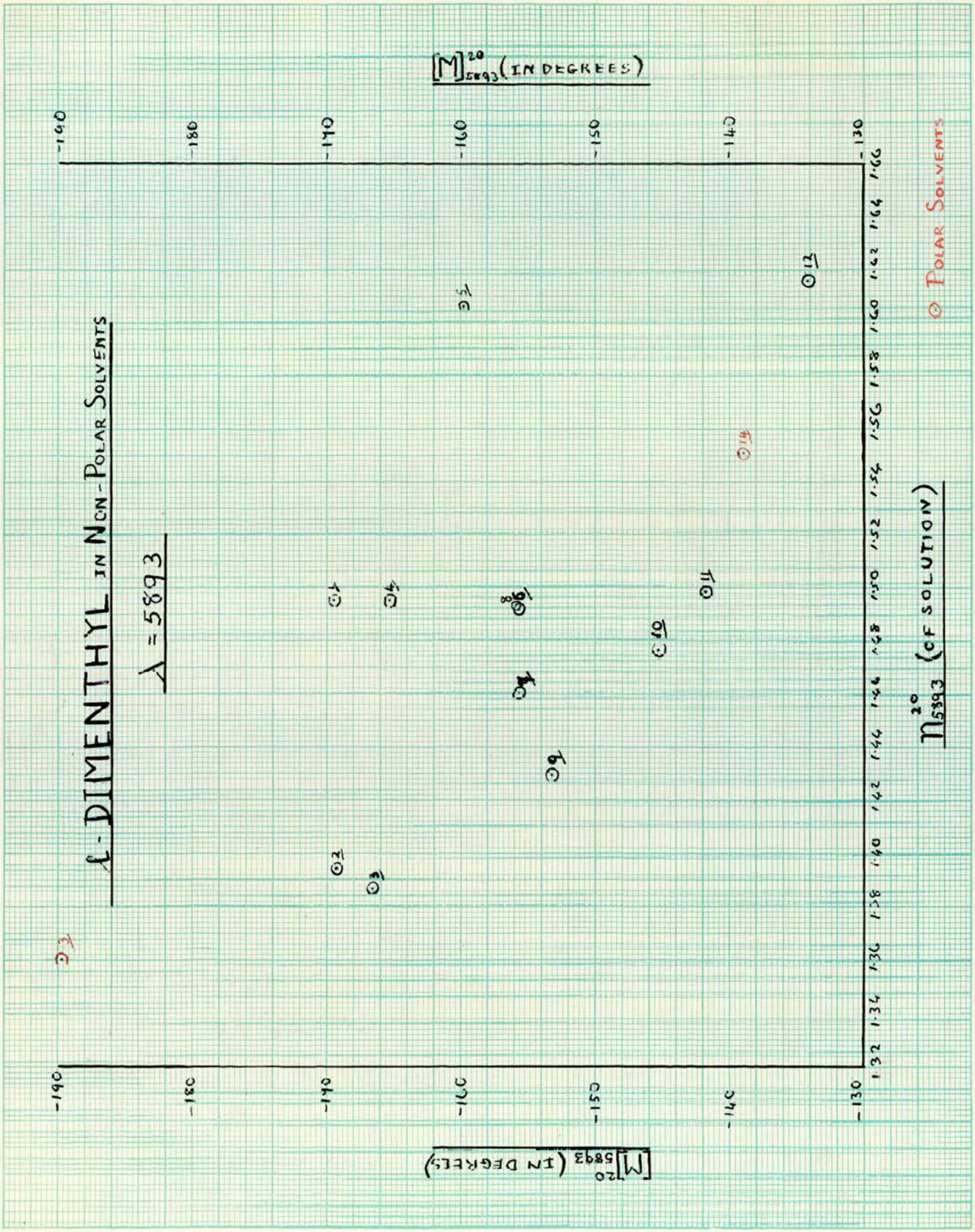
EFFECT Of CONCENTRATION On ROTATION Of ℓ-DIMENTHYL.

Solvent - Decahydronaphthalene.

	C	$[\alpha]^{20}_{D}$ (solution)	$[\alpha]^{20}_{5780}$ (solution)	$[\alpha]^{20}_{5461}$
1.	2·996	-52·96°	-56·06°	-63·05
2.	5·988	-53·20°	-56·30°	-63·2
3.	11·992	-53·40°	-56·58°	-63·36
4.	14·196	-53·45°	-56·40°	-63·46

	C	n^{20}_{D} (solution)	n^{20}_{5780} (solution)	n^{20}_{5461} (solution)
1.	2·996	1·47594	1·47693	1·47860
2.	5·988	1·47609	1·4 7673	1·47880
3.	11·992	1·47634	1·47690	1·47900
4.	14·196	1·47653	1·47721	1·47929

GRAPH I


l-DIMENTHYL in Non-Polar Solvents
λ = 5893
$[M]^{20}_{5893}$ (IN DEGREES)
-190
-180
-170
-160
-150
-140
-130
n^{20}_{5893} (OF SOLUTION)
1·32
1·34
1·36
1·38
1·40
1·42
1·44
1·46
1·48
1·50
1·52
1·54
1·56
1·58
1·60
1·62
1·64
1·66
⊙ Polar Solvents
1
2
3
4
5
6
7
8
9
10
11
12
13
14

mercury green line. The results are summarised in graphical form in Graph I which is for the Sodium D line. The graph for the green line is not included, since it is almost exactly similar to that for the D line. It is clear from both table and graph that there is no tendency of the rotation to increase with rise in the refractive index of the solution. If anything, the refractive index effect is in the other direction, a high value of refractive index tending to give low rotations and *vice versa*. In this connection it may be noted that the extreme values are for solutions in carbon disulphide (point 12) and in n-heptane (point 2) and acetone (point 13). Only two polar solvents were examined, viz., acetone and nitrobenzene (point 14). One of these stands at the top of the list and the other at the bottom, thus showing that there is no appreciable polar effect in these cases. An interesting comparison is given by the four liquids, benzene, toluene, p-xylene and mesitylene (points 11, 6, 4 and 1 respectively), all of which have approximately the same refractive index and only differ from each other in respect of a progressively increasing number of methyl groups. Nevertheless, these solvents give very large differences in the rotatory power of their solutions. The rotatory powers in the case of these four liquids appear to be arranged in increasing magnitude as the number of methyl groups attached to the benzene ring increases, which may be connected with the fact that the methyl groups tend to screen the double bonds of the benzene ring. Some of the rotations were redetermined at a lower concentration (c = 2), the results of which are given in Table 8. The values, however, do not differ appreciably from these already quoted which were determined at c = 6. In a further attempt to determine whether concentration had any marked effect on the rotation, the rotatory powers were measured, using decahydronaphthalene as solvent at concentrations ranging from c = 3 to c = 14 (see Table 9). Over this range there was only a negligible change in refractive index, since the addition of dimenthyl to decahydronaphthalene has very little effect on the refractive index of the solution. There was no marked change in the rotatory power which only rose from -52·96° at c = 3 to -53·45° at c = 14. This alteration corresponds, however, to a slight rise in rotation as the refractive index increases and is thus not in agreement with the general conclusion to be drawn from the diagram opposite p. 62. Owing to the limited solubility of the dimenthyl this point could not be put to further test at higher concentrations. These results obtained with l-dimenthyl are so completely at variance with those already quoted for d-pinane that another compound of the same non-polar type was prepared and examined, viz., hydrodicamphene. This was prepared according to the method of Sakellarios and Kyrimis (Ber., 1924,326), in which pinene hydrochloride is treated with magnesium in presence of absolute ether. The reaction is very slow and is started by firstly treating the magnesium with a small amount of ethyl bromide in ether. This treatment activates the magnesium which is then slowly attacked by the pinene hydrochloride to form bornyl magnesium chloride. In this connection it was found advisable to continue this part of the reaction rather longer than was recommended by Sakellarios. The Grignard reagent is then treated with a suspension of anhydrous cupric chloride in ether, when hydrodicamphene is formed. The ether extract, when evaporated, gave a hydrodicamphene, of melting-point about 40°. Since the melting-point of pure hydrodicamphene is quoted as 86° it was obvious that it contained a large amount of impurity, which might have been borneol produced by the action of oxygen on the Grignard compound, or a reduced compound of camphane type formed by the action of water. This impurity was removed by repeated crystallisation from alcohol, the product finally giving a pure hydrodicamphene, of m.p. 85·5 - 86°. From d-pinene hydrochloride an *l*-hydrodicamphene was obtained, the rotation of which was only about half the value of the pinene hydrochloride employed. From *l*-pinene hydrochloride was obtained a d-hydrodicamphene which had also only about half the rotation of the pinene hydrochloride

TABLE 10.

d-HYDRODICAMPHENE.

Sodium D line ($\lambda = 5893$); $c = 6$.

	Solvent	$[M]_D^{20°}$ (solution)	$n_D^{20°}$ (solution)	c
1.	1-Methyl Naphthalene	+52·4°	1·60894	6·036
2.	p-Xylene	+48·8°	1·49595	6·204
3.	Toluene	+47·1°	1·49395	6·156
4.	Benzene	+44·9°	1·50067	6·276
5.	Carbon Disulphide	+44·1°	1·61920	6·196
6.	Carbon Tetrachloride	+44·1°	1·46340	6·036
7.	Cyclohexane	+43·8°	1·43147	6·280
8.	n-Heptane	+43·8°	1·39584	6·252
9.	Hexane	+43·7°	1·38802	6·068
10.	Mesitylene	+43·6°	1·49755	6·200
11.	Decahydronaphthalene	+43·3°	1·478800	6·024

Polar Solvents.

12.	Nitrobenzene	+47·4°	1·54956	4·74
13.	Acetone	+45·2°	1·36469	4·032
14.	Bromoform	+41·1°	1·59211	5·108

TABLE 11.

d-HYDRODICAMPHENE.

Mercury green line (λ = 5461); c = 6.

	Solvent	$[M]^{20}_{5461}$ (solution)	n^{20}_{5461} (solution)	c
1.	1-Methyl Naphthalene	+65·2°	1·61567	6·036
2.	p-Xylene	+57·5°	1·50004	6·204
3.	Toluene	+56·7°	1·49813	6·156
4.	Benzene	+55·6°	1·50492	6·276
5.	Carbon Disulphide	+55·0°	1·62686	6·196
6.	Carbon Tetrachloride	+54·8°	1·46619	6·036
7.	Cyclohexane	+54·5°	1·43378	6·280
8.	n-Heptane	+54·3°	1·39790	6·252
9.	Hexane	+53·9°	1·39011	6·068
10.	Mesitylene	+53·7°	1·50164	6·200
11.	Decahydronaphthalene	+53·2°	1·48037	6·024

	Polar solvents.			
12.	Nitrobenzene	+57·3°	1·55598	4·74
13.	Acetone	+55·5°	1·36663	4·032
14.	Bromoform	+51·2°	1·59658	5·108

GRAPH II

d-HYDRODICAMPHENE IN NON-POLAR SOLVENTS

$\lambda = 5893$

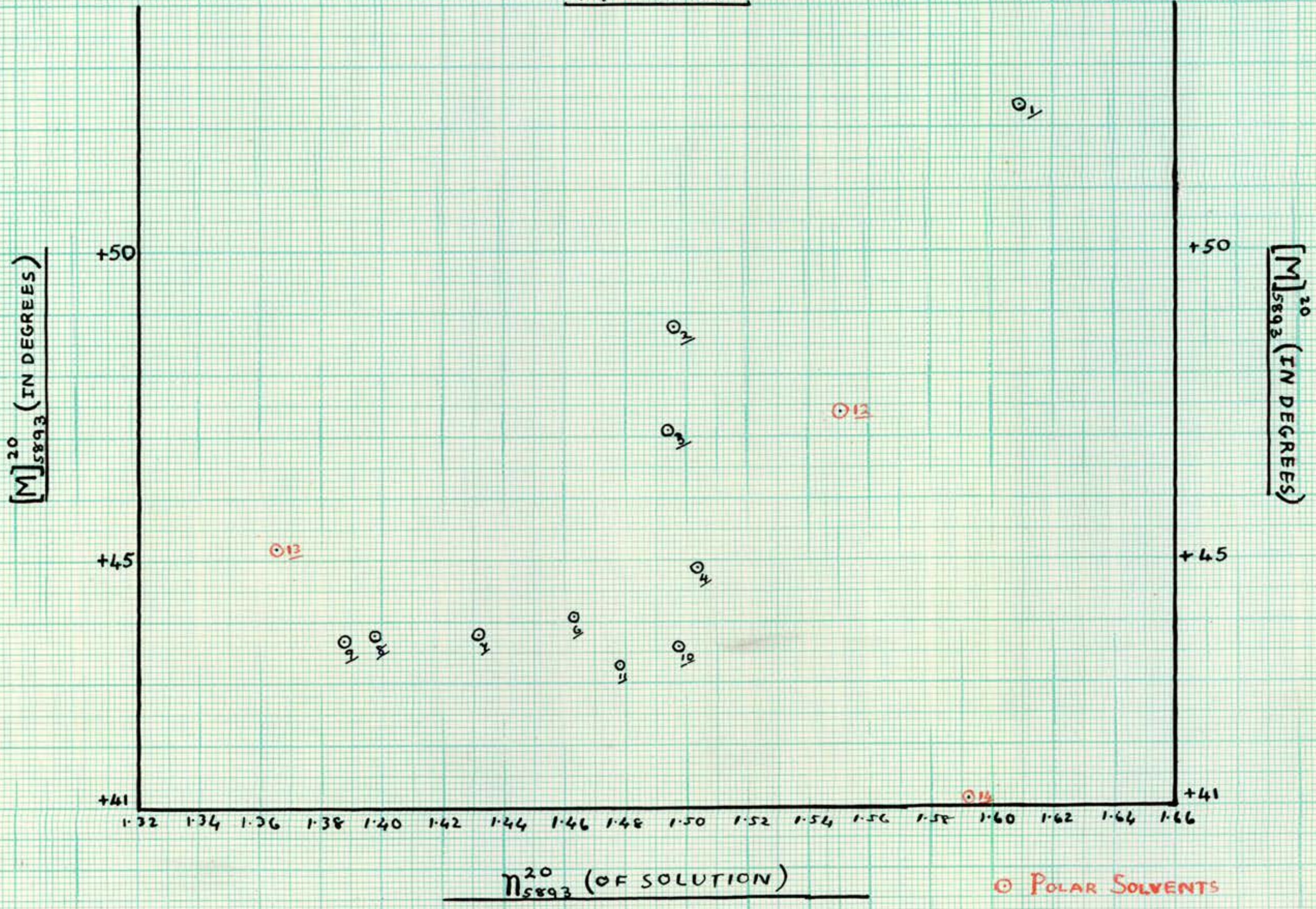


TABLE 12.

l-HYDRODICAMPHENE.

Sodium D line (λ = 5893); C = 6.

	Solvent	$[M]_D^{20}$ (solution)	n_D^{20} (solution)	C
1.	1-Methyl Naphthalene	-63·6°	1·60773	5·968
2.	p-Xylene	-55·9°	1·49614	6·060
3.	Toluene	-53·7°	1·49405	6·128
4.	Benzene	-52·2°	1·49973	6·056
5.	Carbon Tetrachloride	-52·3°	1·46320	5·984
6.	Carbon Disulphide	-51·8°	1·61858	6·032
7.	Cyclohexane	-51·7°	1·43077	5·988
8.	n-Heptane	-51·6°	1·39554	6·024
9.	Hexane	-51·2°	1·38793	6·024
10.	Mesitylene	-51·0°	1·49756	6·020
11.	Decahydro-naphthalene	-50·9°	1·47780	6·024

<u>Polar Solvents.</u>

12.	Nitrobenzene	-56·0°	1·54958	4·560
13.	Acetone	-53·5°	1·36550	4·404

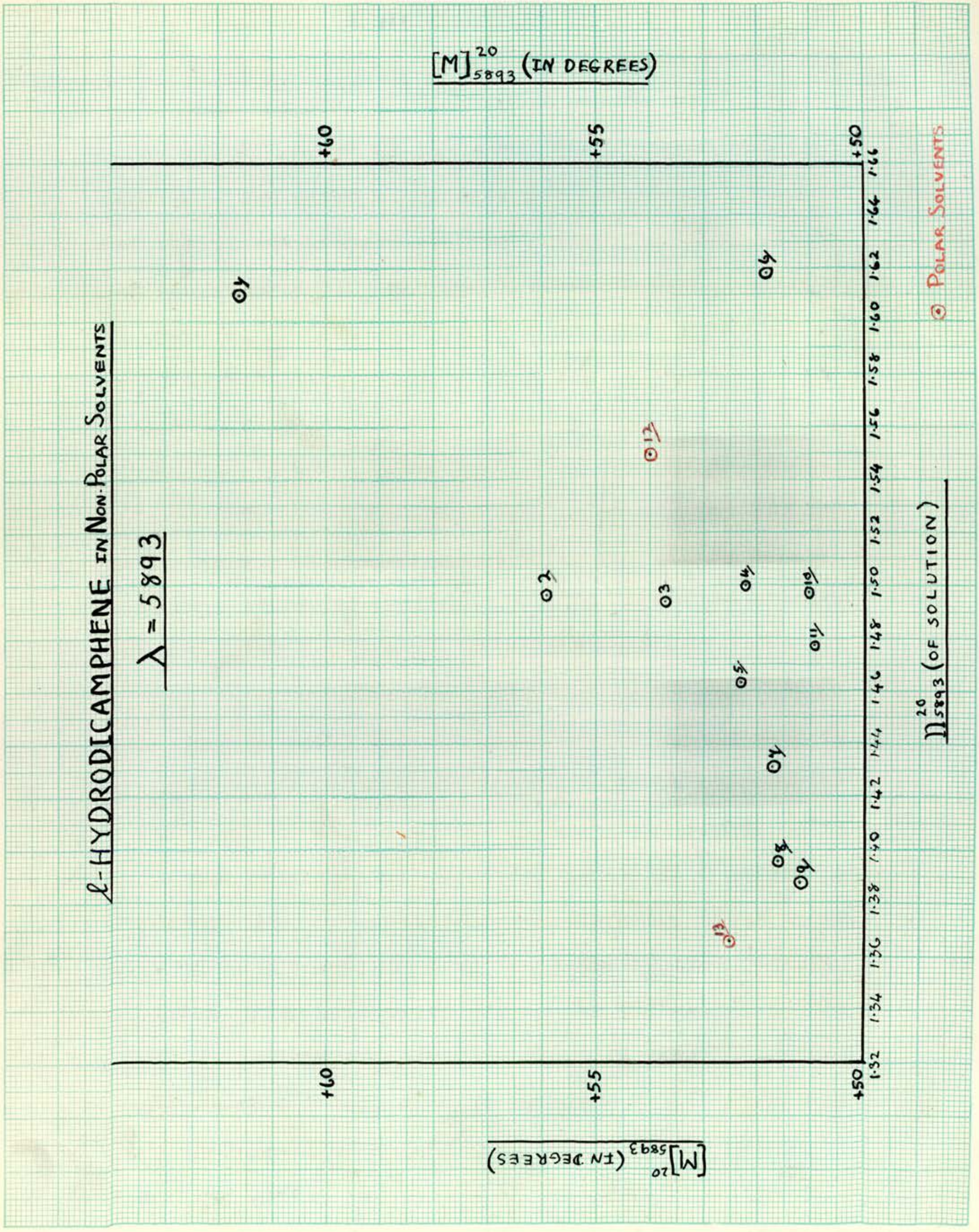
TABLE 13.

l-HYDRODICAMPHENE.

Mercury green line (λ = 5640); C = 6.

	Solvent	$[M]^{20}_{5460}$ (solution)	n^{20}_{5460} (solution)	C
1.	1-Methyl Naphthalene	-77·1°	1·61449	5·968
2.	p-Xylene	-66·8°	1·50022	6·060
3.	Toluene	-65·1°	1·49794	6·128
4.	Benzene	-63·1°	1·50371	6·056
5.	Carbon Tetrachloride	-62·8°	1·46589	6·032
6.	Carbon Disulphide	-62·5°	1·62617	5·984
7.	Cyclohexane	-62·7°	1·43308	5·988
8.	n-Heptane	-61·9°	1·39752	6·024
9.	Hexane	-61·2°	1·39002	6·024
10.	Mesitylene	-60·6°	1·50145	6·020
11.	Decahydronaphthalene	-60·5°	1·48057	6·024
	Polar Solvents			
12.	Nitrobenzene	-67·0°	1·55586	4·560
13.	Acetone	-63·7°	1·36735	4·404

GRAPH III


l-HYDRODICAMPHENE IN NON-POLAR SOLVENTS
λ = 5893
[M]$^{20}_{5893}$ (IN DEGREES)
+60
+55
+50
n^{20}_{5893} (OF SOLUTION)
1.32
1.34
1.36
1.38
1.40
1.42
1.44
1.46
1.48
1.50
1.52
1.54
1.56
1.58
1.60
1.62
1.64
1.66
⊙ POLAR SOLVENTS
1
2
3
4
5
6
7
8
9
10
11
12
13

from which it was prepared.

The experimental results obtained with d-hydrodicamphene are contained in Tables 10 and 11 and are illustrated graphically in Graph II. On the whole, it will be seen that the results are of the same erratic nature as those found for *l*-dimenthyl, although in this case there is a barely perceptible tendency for the rotations to rise with increasing refractive index. The rotations fall within a much narrower range than with dimenthyl and vary from $[M]_D$, +52·6°, in 1-methyl naphthalene, to +41·1° in bromoform. As will be seen from Graph II, the majority of the rotations approximate closely to 44° to 45°. The rotatory powers obtained for 1-methyl naphthalene at the top and bromoform at the bottom appear to be somewhat exceptional. An examination of the positions in the graph of the strongly polar nitrobenzene and acetone shows that they group themselves normally with the bulk of the other solvents. It cannot therefore be said that any appreciable polar effect is evident. The results obtained with d-hydrodicamphene were confirmed by preparing a quantity of *l*-hydrodicamphene which had a somewhat higher rotation than the d-compound. The rotatory powers observed in this case are summarised in Tables 12 and 13 and graphically in Graph III. A slightly wider range of rotations was noted, but the arrangement of the solvents is practically identical with that found for the d-derivative.

In view of the unexpected nature of these results it was determined to obtain further confirmation of the work of Chambers by repeating the preparation of d-pinane. The d-pinane was formed by catalytic hydrogenation of d-α-pinene, using platinum black as catalyst. Hydrogenation took place slowly and could not be carried to 100% completion, this being in agreement with the conclusions of earlier workers. Purification was attempted by the method of Lipp (Ber., 1923, 56, 2098), in which the crude pinane is shaken up with small amounts of a 1% solution of potassium permanganate until the colour of the permanganate persists for thirty minutes, followed by steam-distillation and distillation over sodium. It was found, however, as is seen from the experimental part of this work, p. 45, that this method proved to be of very little use in removing any considerable amount of pinene mixed with pinane, and a more efficient method was evolved, in which the pinene-pinane mixture was treated with bromine until the bromine was no longer decolourised. This product was then distilled in steam, which would remove pinane from the bulk of the bromo-compounds formed. The partially purified pinane was then fractionated, rejecting the last fraction which might contain a trace of bromo-derivatives. In this treatment, the dibromopinene formed tends to decompose on heating to yield

TABLE 14.

d-PINANE.

Sodium D line (λ = 5893) ; C = 12.

	Solvent	$[M]_D^{20^\circ}$ (solution)	$n_D^{20^\circ}$ (solution)	C
1.	Carbon Disulphide	+37·0°	1·60174	12·024
2.	1-Methyl Naphthalene	+34·1°	1·59410	11·848
3.	Benzene	+31·6°	1·49357	12·252
4.	Toluene	+31·6°	1·48682	12·300
5.	p-Xylene	+31·5°	1·48994	12·036
6.	Mesitylene	+31·1°	1·49184	12·328
7.	Decahydro-naphthalene	+30·6°	1·47405	12·144
8.	(Homogeneous)	+30·4°	1·46191	100
9.	Carbon Tetra-chloride	+30·4°	1·46051	12·280
10.	Cyclohexane	+28·4°	1·43107	12·000
11.	Hexane	+27·6°	1·39155	12·128
12.	n-Heptane	+27·2°	1·39855	12·488

TABLE 15.

d-PINANE.

Mercury green line (λ = 5461) ; C = 12.

	Solvent	$[M]^{20}_{5461}$ (solution)	n^{20}_{5461} (solution)	C
1.	Carbon Disulphide	+44·9°	1·60883	12·024
2.	1-Methyl Naphthalene	+42·4°	1·60070	11·848
3.	Benzene	+38·7°	1·49756	12·252
4.	Toluene	+38·7°	1·49162	12·300
5.	p-Xylene	+38·2°	1·49387	12·036
6.	Mesitylene	+37·8°	1·49564	12·328
7.	Decahydronaphthalene	+37·3°	1·47653	12·144
8.	(Homogeneous)	+36·6°	1·46420	100
9.	Carbon Tetrachloride	+36·6°	1·46301	12·28
10.	Cyclohexane	+34·2°	1·43327	12·00
11.	Hexane	+33·1°	1·39455	12·128
12.	n-Heptane	+32·8°	1·40062	12·488

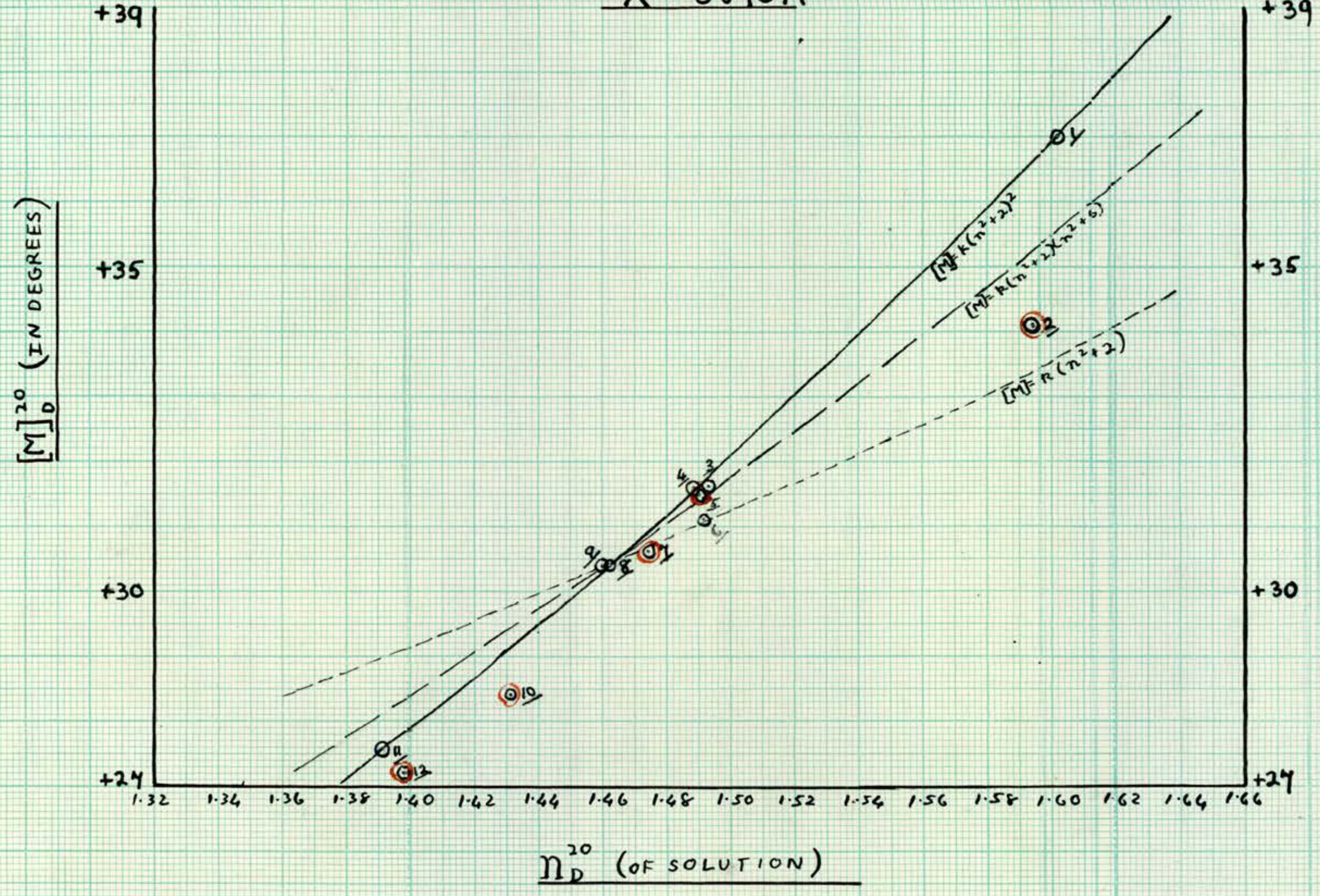
C = 48·012

Solvent	$[M]^{20}_{5461}$ (solution)	n^{20}_{5461} (solution)	C
Carbon Disulphide	+40·4°	1·53403	48·012
1-Methyl Naphthalene	+38·9°	1·53175	48·488

GRAPH IV

d-PINANE in Non-Polar Solvents

$\lambda = 5893A$



p-cymene which should be almost completely removable by fractionation. Since p-cymene, however, is non-polar, traces of this compound in the pinane - if they are actually present - should not appreciably affect the results in the non-polar solvents. The pinane obtained in this way was found to be completely saturated and of slightly lower rotation than that obtained by Chambers. Pinene, it may be noted, has a higher rotation than pinane. The rotations for solutions of d-pinane were determined in the non-polar solvents employed by Chambers and also in additional non-polar liquids, namely, cyclohexane, n-heptane, p-xylene, 1-methyl naphthalene and decahydronaphthalene. The results found fully bear out Chambers' conclusions, as may be seen by reference to Tables 14 and 15 and to Graph IV. In the diagram the continuous line represents the theoretical relationship $[M] = k(n^2 + 2)^2$ as calculated from the value obtained for homogeneous pinane. The dotted lines represent the theoretical relationships $[M] = k(n^2 + 2)(n^2 + 5)$ and $[M] = k(n^2 + 2)$ respectively. It will be seen that except for the rotation obtained in 1-methyl naphthalene, all the experimental points lie on or close to the line corresponding to $[M] = k(n^2 + 2)^2$. In this connection it may be noted that 1-methyl naphthalene gave abnormal rotations, both for ℓ-dimenthyl and hydrodicamphene.

In considering the results so far recorded we may therefore state that the behaviour of d-pinane in non-polar solvents is in close accordance with that to be expected on theoretical grounds, whereas the behaviour of hydrodicamphene, and to a still greater extent *l*-dimenthyl, diverges very strongly from the theoretical. In view of the non-polar nature of the compounds under examination, it is difficult to suggest any reason for these variations except on the assumption that the intermolecular forces existing between the molecules of dimenthyl and hydrodicamphene are of a very different order of magnitude to those existing in the case of d-pinane, and that their difference produces optical changes in the case of the more complex hydrocarbons. In some respects this assumption is not unwarranted; dimenthyl, for example, is a solid of relatively high melting-point (105°), and the forces between the molecules of the compound which are responsible for their deposition from solution in the crystal form must therefore be relatively great. Hydrodicamphene has a lower melting-point and has thus a lower tendency towards crystallisation. For this compound, therefore, it appears that the intermolecular forces in question are not so strong as those existing in the case of *l*-dimenthyl. d-Pinane, for which the solvent effect approximates to theory, is, on the other hand, a liquid under ordinary conditions with no tendency

TABLE 16.

LIQUID DIMENTHYL.

Sodium D line (λ = 5893) ; c = 8

	Solvent	$[M]_D^{20}$ (solution)	n_D^{20} (solution)	c
1.	Hexane	-97·6°	1·38925	8·136
2.	Mesitylene	-97·4°	1·49575	7·856
3.	n-Heptane	-96·6°	1·39640	8·04
4.	p-Xylene	-95·1°	1·49405	8·276
5.	Toluene	-92·0°	1·49275	8·06
6.	Carbon Tetrachloride	-92·0°	1·46191	8·128
7.	Cyclohexane	-91·7°	1·43117	8·244
8.	1-Methyl Naphthalene	-90·6°	1·60297	8·148
9.	Benzene	-90·3°	1·49832	8·288
10.	(homogeneous)	-88·8°	1·48191	100
11.	Decahydronaphthalene	-90·0°	1·47653	8·276
12.	Carbon Disulphide	-84·8°	1·61312	8·056

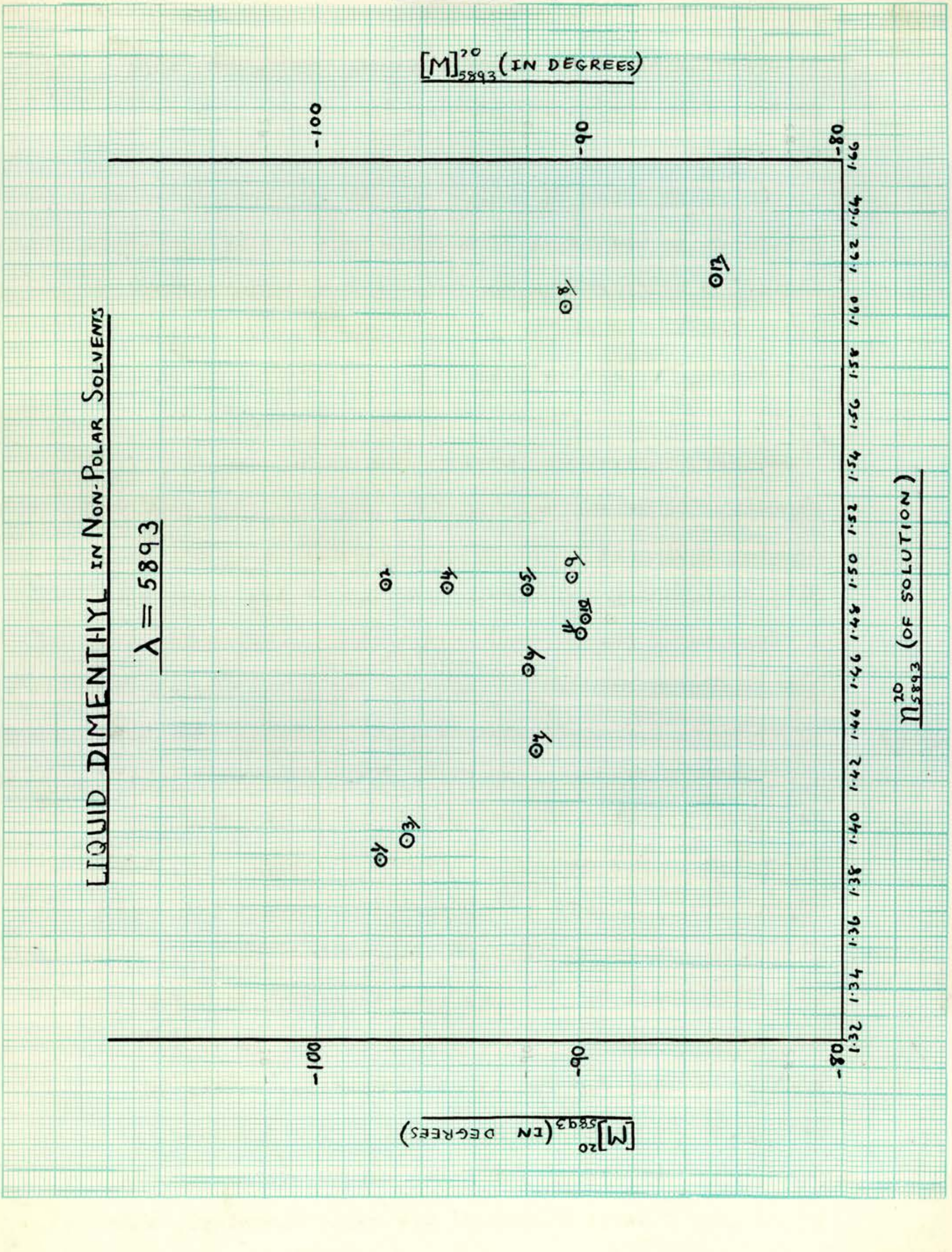
TABLE 17.

LIQUID DIMENTHYL.

Mercury green line (λ = 5461) ; C = 8

	Solvent	$[M]^{20}_{5461}$ (solution)	n^{20}_{5461} (solution)	C
1.	Hexane	-116·0°	1·39130	8·136
2.	Mesitylene	-115·4°	1·49944	7·856
3.	n-Heptane	-114·9°	1·39868	8·04
4.	p-Xylene	-113·4°	1·49792	8·276
5.	Toluene	-110·1°	1·49681	8·06
6.	Carbon Tetrachloride	-109·2°	1·46440	8·128
7.	Cyclohexane	-109·2°	1·43338	8·244
8.	1-Methyl Naphthalene	-108·1°	1·60956	8·148
9.	Benzene	-108·4°	1·50211	8·288
10.	(Homogeneous)	-107·0°	1·48438	100
11.	Decahydronaphthalene	-105·6°	1·47910	8·276
12.	Carbon Disulphide	-100·9°	1·62165	8·056

GRAPH V



LIQUID DIMENTHYL IN NON-POLAR SOLVENTS

$\lambda = 5893$

to crystallise. It may be assumed, therefore, that in this case the intermolecular forces are at a minimum.

In order to obtain further information on this point, it is desirable to examine more optically active, non-polar hydrocarbons which are liquid under normal conditions. As has already been indicated, little information regarding compounds of this type is to be found in the literature. In the preparation of *l*-dimenthyl, however, Sakellarios states that a liquid dimenthyl is formed when menthyl chloride (not previously treated with alkali) is acted on by sodium in ether. This preparation was carried out and it was found that a fraction of the extract distilled at a temperature of 310° which is the same as that of the solid dimenthyl. On standing for a few days, a small amount of the solid *l*-dimenthyl crystallised out and was removed. The remaining liquid dimenthyl was found to be quite saturated in its behaviour towards bromine. The experimental values of the rotation obtained for this liquid in non-polar solvents are given in Table 16 and 17 and in Graph V. It is seen from this that the general arrangement of the points on this is exactly similar to that for the solid dimenthyl. This is perhaps not surprising, since the liquid dimenthyl is probably a mixture of solid and liquid dimenthyls containing a large amount of the solid dimenthyl, which would thus be expected to give a similar arrangement for the optical rotations in the various solvents. These results for liquid dimenthyl are therefore of little value in testing the validity of the above assumption as to the magnitude of the intermolecular forces.

Some information was found in the literature relating to the reduction of ℓ-camphene to the saturated hydrocarbon isocamphane, although no figures were quoted for the optical activity of the latter. Isocamphane, however, is not a liquid at ordinary conditions, but a waxy solid of low melting-point (55°). On the above reasoning it would thus be expected that the rotatory powers of this compound in non-polar liquids would be in closer agreement with the refractive index values than those found for dimenthyl and hydrodicamphene, although probably not so close as the figures obtained for pinane. *d*-Isocamphane was therefore prepared from a small amount of ℓ-camphene which was available by catalytic hydrogenation, using ether as solvent and platinum black as catalyst. The hydrogenation took place very rapidly - in a few seconds - and was found to be complete, since the isocamphane produced did not decolourise the least trace of bromine vapour when dissolved in carbon tetrachloride. Although the ℓ-camphene used had $[\alpha]_{D}^{20°}$, -31·4°, the resulting isocamphene had a very low rotation of

TABLE 18.

d-ISOCAMPHANE.

Sodium D line (λ = 5893); C = 6.

	Solvent	$[M]_D^{20}$ (solution)	n_D^{20} (solution)	C
1.	1-Methyl Naphthalene	+7·67°	1·60365	6·696
2.	Carbon Disulphide	+6·87°	1·61491	6·080
3.	Mesitylene	+6·86°	1·49490	6·032
4.	p-Xylene	+6·56°	1·49242	6·680
5.	Toluene	+6·37°	1·49051	6·240
6.	Benzene	+6·32°	1·49718	6·068
7.	Decahydro-naphthalene	+6·10°	1·47486	6·060
8.	Carbon Tetrachloride	+5·87°	1·46012	6·300
9.	n-Heptane	+5·44°	1·39293	6·048
10.	Cyclohexane	+5·42°	1·42867	6·192
11.	Hexane	+5·38°	1·38679	7·400

Table 19.

d-ISOCAMPHANE.

Mercury green line ($\lambda = 5460$); $c = 6$.

Solvent	$[M]^{20}_{5460}$ (solution)	n^{20}_{5460} (solution)	c
1. 1 Methyl Naphthalene	+8·50°	1·61120	6·696
2. Carbon Disulphide	+7·61°	1·62268	6·080
3. Mesitylene	+7·63	1·49870	6·032
4. p-Xylene	+7·59°	1·49652	6·680
5. Toluene	+7·47°	1·49452	6·240
6. Benzene	+7·40°	1·50126	6·068
7. Decahydronaphthalene	+7·01°	1·47754	6·060
8. Carbon Tetrachloride	+6·74°	1·46262	6·300
9. n-Heptane	+6·00°	1·39592	6·048
10. Cyclohexane	+5·98°	1·43079	6·048
11. Hexane	+6·02°	1·38779	7·400

TABLE 20.

ℓ-ISOCAMPHANE.

Sodium D line (λ = 5893).   c = 12

	Solvent	$[M]^{20}_{D}$ (solution)	n^{20}_{D} (solution)	c
1.	1-Methyl Naphthalene	-9·21°	1·59393	12·144
2.	Carbon Disulphide	-8·25°	1·60047	12·704
3.	Mesitylene	-8·02°	1·49285	12·048
4.	p-Xylene	-7·79°	1·48956	12·664
5.	Toluene	-7·40°	1·48820	12·308
6.	Benzene	-7·30°	1·49347	13·244
7.	Decahydro-naphthalene	-6·80°	1·47418	12·184
8.	Carbon Tetrachloride	-6·83°	1·46021	12·128
9.	Cyclohexane	-6·21°	1·43017	12·064
10.	n-Heptane	-6·00°	1·39797	12·212
11.	Hexane	-5·79°	1·39138	12·432
	Polar Solvents.			
12.	Acetophenone	-8·29°	1·52297	12·400
13.	Bromobenzene	-8·19°	1·54518	12·052
14.	Anisole	-7·95°	1·50793	12·068
15.	Chlorobenzene	-7·71°	1·51491	12·004
16.	Nitrobenzene	-7·55°	1·53903	12·072
17.	Acetone	-5·56°	1·37160	12·036

TABLE 21.

ℓ-ISOCAMPHANE.

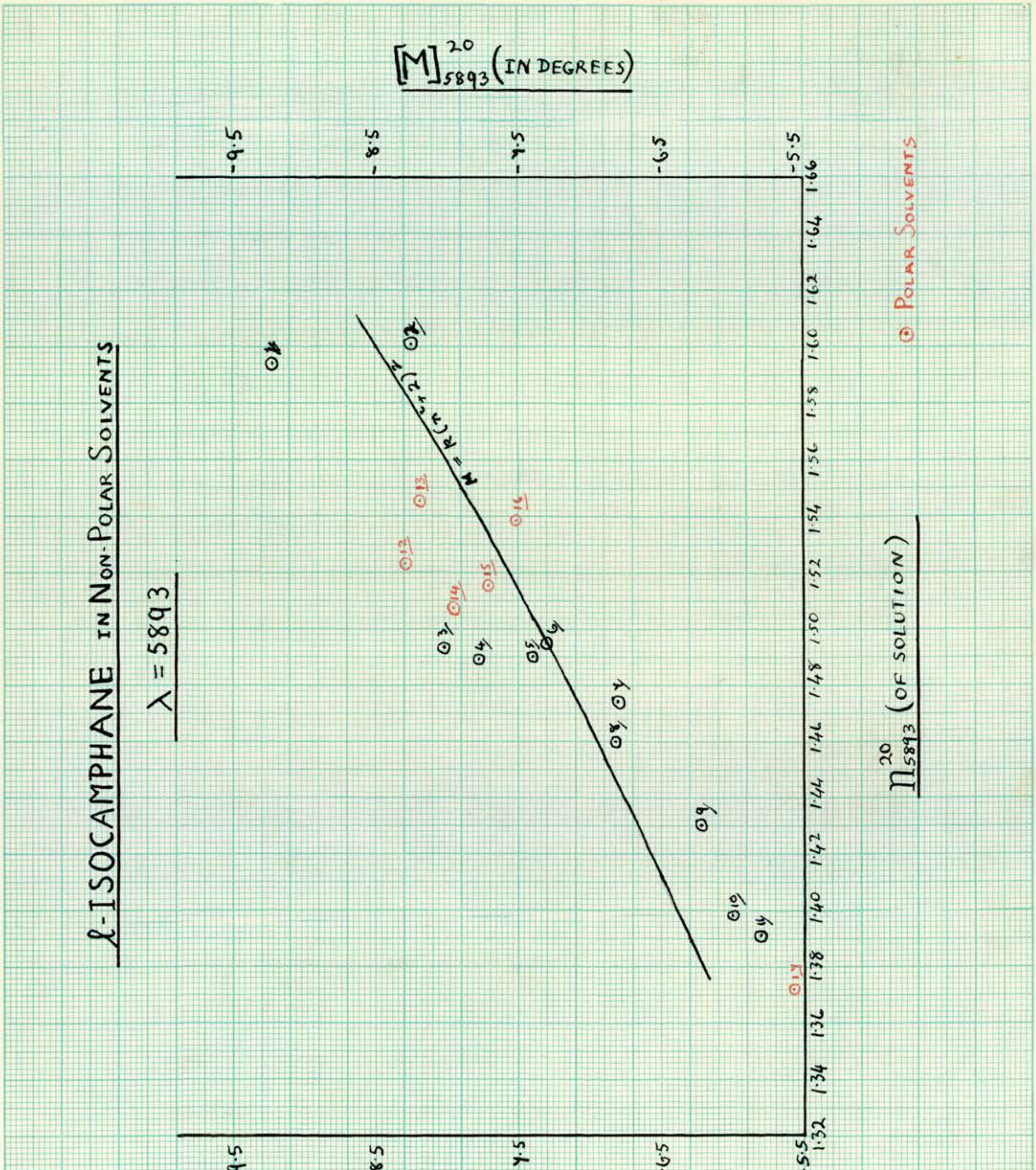
Mercury green line ($\lambda = 5460$). c = 12.

Solvent	$[M]^{20}_{5460}$ (solution)	n^{20}_{5460} (solution)	c
1. 1-Methyl Naphthalene	-11·14°	1·60024	12·144
2. Carbon Disulphide	-9·99°	1·60756	12·704
3. Mesitylene	-9·73°	1·49565	12·048
4. p-Xylene	-9·56°	1·49327	12·664
5. Toluene	-9·34°	1·49202	12·308
6. Benzene	-8·90°	1·49756	13·244
7. Decahydro-naphthalene	-8·39°	1·47677	12·184
8. Carbon Tetrachloride	-8·25°	1·46271	12·128
9. Cyclohexane	-7·70°	1·43317	12·064
10. n-Heptane	-7·38°	1·40004	12·212
11. Hexane	-7·26°	1·39330	12·432

<u>Polar Solvents</u>.

12. Acetophenone	-9·74°	1·52763	12·400
13. Bromobenzene	-9·56°	1·54968	12·052
14. Anisole	-9·44°	1·51210	12·068
15. Chlorobenzene	-9·03°	1·51896	12·004
16. Nitrobenzene	-9·03°	1·54470	12·072
17. Acetone	-6·77°	1·37354	12·036

GRAPH VII


l-ISOCAMPHANE in Non-Polar Solvents
λ = 5893
$[M]^{20}_{5893}$ (in degrees)
n^{20}_{5893} (of solution)
⊙ Polar Solvents
$M = k(n^2+2)^2$
-9.5
-8.5
-7.5
-6.5
-5.5
1.32
1.34
1.36
1.38
1.40
1.42
1.44
1.46
1.48
1.50
1.52
1.54
1.56
1.58
1.60
1.62
1.64
1.66
1
2
3
4
5
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$[\alpha]^{20^\circ}_{D}$, +4·70° (c = 6, in benzene). Owing to the small amount of *d*-isocamphane available, a concentration of c = 6 only could be used for the optical determinations, giving an α_D of about 0·4°, so that the experimental error is more than 5%, allowing a possible error of about 0·02° in making the determination. The results for *d*-isocamphane in non-polar solvents are given in Tables 18 and 19 and in Graph VI. Owing to the relatively large experimental error in these results it was decided to prepare a more active isocamphane from highly active *d*-camphene, which was readily prepared from d-pinene hydrochloride. A sample of d-camphene was prepared of $[\alpha]^{20^\circ}_{D}$, +59·8° (c = 20, in benzene), and hydrogenated in the hope that a much more active isocamphane would be obtained. Hydrogenation took place very quickly, but the final product had a rotation very little greater than that obtained from the ℓ-camphene, namely, $[\alpha]^{20^\circ}_{D}$, -5·29° (c = 12, in benzene). Since, however, a much greater amount of this product was now available, greater accuracy was obtained in measuring the rotations in the various solvents by using a concentration of c = 12, giving an actual α_D of about 1·4°. The results for this ℓ-isocamphane in a variety of polar and non-polar solvents are given in Tables 20 and 21 and Graph VII. It will be observed that the rotations vary from $[M]^{20^\circ}_{D}$ = -9·21° in 1-methyl naphthalene to $[M]^{20^\circ}_{D}$ = -5·79°

in hexane. When plotted in diagram form it is noted that values rise more or less steadily with increase in refractive index. The general trend of the points on the diagram corresponds possibly to a somewhat steeper rise with refractive index than that indicated by the theoretical relationship $[M] = k(n^2 + 2)^2$ It should be noted, however, that no absolute curve can be obtained for this expression, since values of $[M]_D^{20}$ and n_D^{20} are not available for the homogeneous hydrocarbon. The curve indicated is calculated from values of $[M]_D^{20}$ and n_D^{20} of the solution of l-isocamphane in benzene. On the other hand, the experimental figures approximate more closely to this relationship than they do to the equations of Boyes, $[M] = k(n^2 + 2)(n^2 +5)$, and of Gans, $[M] = k(n^2 + 2)$, which have a smaller inclination to the horizontal than that of Born. Reference to the points indicated in red, recorded for polar liquids, shows that it is the refractive index and not the polarity of these solvents which controls the magnitude of the rotatory power, since these points fall approximately into position with the rest of the liquids.

In conclusion, it would appear that in all probability the theoretical relationship which represents the rotatory power as increasing with the refractive index of the solution, in accordance with the mathematical equations of Born and others, will only be realised experimentally in the case of optically active, non-polar compounds which are liquids of low solidification point. When optically active, non-polar solids are employed, the somewhat limited experimental evidence produced in this thesis suggests that the intermolecular forces between the solute molecules bring about deviations from the theoretical values. These deviations appear to become greater as the melting-point of the solid rises, and with it the magnitude of the forces in question.

SUMMARY.

The optical rotatory powers of a number of non-polar, terpinic hydrocarbons in a variety of non-polar solvents have been examined in dilute solutions, with a view to testing the theory of Born

$$[M] = k(n^2 + 2)$$

which had been confirmed by Rule and Chambers in the case of d-pinane.

(a) *l*-Dimenthyl is shown to be strongly exceptional to this law, since no regular effect of the type can be traced, and indeed there is a strong tendency for high refractive index to correspond to low rotations and vice versa.

(b) d- and *l*-Hydrodicamphenes are shown to be also exceptional in that there is no regular refractive index effect. There is, however, no tendency for a reversal of the relationship, as is shown by dimenthyl.

(c) The results of Chambers with d-pinane are repeated and confirmed.

(d) A possible explanation of the anomalous effects given by dimenthyl and hydrodicamphene is put forward. It is assumed that since dimenthyl and hydrodicamphene are both solids, the intermolecular forces must be of a much higher order than in the case of liquid pinane, and that these forces are also present in solution and cause changes in the normal relationship.

(e) On the above basis, it is argued that a non-polar solid of low melting-point ought to give rotations much closer to the theoretical values than hydrodicamphene and dimenthyl. This is proved to be the case with d- and ℓ-isocamphane.

PART II.

OPTICAL ACTIVITY INDUCED BY LARGE ELECTROSTATIC FIELDS.

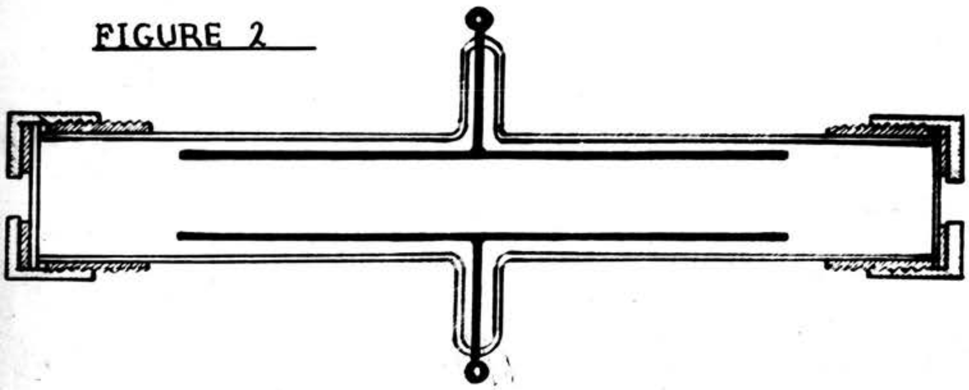


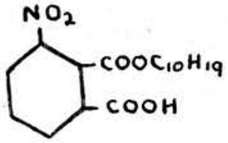
FIGURE 2

Dr A. McLean, while in America on a Commonwealth Scholarship, was working on problems of optical activity with Professor Kunz of the University of Illinois and discovered that an electrostatic field was capable of producing rotations in solutions of certain organic compounds (cf. Nature, Nov. 1935, p.795). Before any exhaustive investigation had been carried out on it, however, McLean had to return to Edinburgh where he continued the work for a few weeks before having to discontinue it in favour of an appointment.

McLean's apparatus consisted of a transformer capable of stepping up 230 v. A.C. to about 20,000 v. A.C. This was connected in series with a cell, which will be described, in parallel with which was a calibrated spark-gap, by means of which the potential across the electrodes of the cell could be varied (cf. Fig. 1, p. 98). The cell was a specially constructed polarimeter tube of length 10 cm., with screw-on end-plates. Fused into the sides of this, at right angles to one another, were two short limbs carrying stout platinum electrodes measuring about 8 cm. by 1 cm. which were parallel to each other at a distance of 1 cm. apart (cf. Fig. 2). The tube was filled through a stoppered opening on top.

The effect was first discovered by McLean using ℓ-menthyl hydrogen 3-nitro-phthalate in 4% solution in benzene. The following is an extract from McLean's results:-

<u>Solute</u>:



<u>Solvent</u>, benzene.

$t = 26°$; $c = 4.$

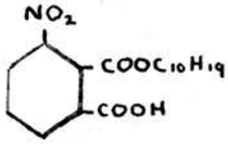
Contents of tube.	Potential Difference	Angle between field and plane of polarisation	α_{5893}	Induced Rotation.
Air	zero	0°	-·03°	-
Benzene	zero	0°	-·03°	-
Benzene	11,000 v.	0°	-·03°	-
Benzene	16,000 v.	0°	-·03°	-
Solution	zero	0°	-5·02°	0°
"	11,000 v.	0°	-5·01°	-·01°
"	16,000 v.	0°	-5·00°	-·02°
"	16,000 v.	30° to left	-4·75°	-0·27°
"	16,000 v.	30° to right	-5·28°	+0·26°
"	16,000 v. (reversed)	30° to right	-5·28°	+0·26°

These results were repeated with toluene as solvent with very similar results except that the maximum rotation was found to be -0·59°, and a lag of

5 seconds was noted before the rotation fell back to its original value, on switching off the field.

With a similar solution the effect of gradual increase in voltage was studied and the following results were found:-

Solute:



Solvent, toluene.

t = 20° ; = 5463 ; c = 3·9584.

P.D.	Angle of field	Induced Rotation.
3,500 v.	20° ℓ	-0·53°
	40° ℓ	-0·63°
5,000 v.	20° ℓ	-0·73°
	40° ℓ	-0·90°
7,500 v.	20° ℓ	-0·73°
	40° ℓ	-0·93°
10,000 v.	20° ℓ	-0·73°
	40° ℓ	-0·94°
12,500 v.	20° ℓ	-0·73°
	40° ℓ	-0·94°

From this it was concluded that there was a saturation value for this solution at about 5,000 v.

The next discovery by McLean was that the cyclohexyl ester of the acid, which was itself optically inactive, became active under the influence of the field. Moreover, a 1% solution in toluene was found to give a maximum rotation of 3·71° which is about twelve times as great as that of the *l*-menthyl ester. It must be added, however, that the solution was made up hot and allowed to cool in the tube, when part of the solute crystallised out, which later investigations have now shown to have a very important effect on the result. It was found that results were not easily repeated and that the solutions, on standing, lost the power to rotate the plane of polarised light under the influence of an electrostatic field. The maximum rotation was found to be given in every case, when the angle ~~of~~ between the plane of polarisation of the light and the direction of the field was 45° .

At this stage McLean had to discontinue the work, but it was thought of sufficient interest to warrant further investigation which was begun by me a few months later. It was obvious from the start that the effect was very similar to the Kerr effect in reaching a maximum at a field angle of 45° . The Kerr effect, however, was not known to produce rotation of the plane of polarisation. The new effect also differs from the Kerr effect in that the latter shows no saturation value, but increases with the square of the field, nor is there any time lag with the Kerr effect. Due to the above noted points of similarity, however, it was thought necessary to become familiar with the Kerr effect, and so the following references were studied:-

H. A. Stuart, Z. Physik., (1929) 55, 358.
" " (1929) 59, 13.
" " (1930) 63, 533.
H. A. Stuart and Volkmann, Ber., 17, 429.
Raman and Krishnin, Annalen, (1927) 397.
" " (1932) 900.
Meyer and Otterbein, Physikal. Z., (1931) 32, 290;
34, 645;
35, 249.
Iwatake, Tech. Rep. Tohoku (1929) 8, 399.
Martin, J. Physical Chem., (1924) 28, 1284.
Briegleb, Z. physikal. Chem., B, 14, 97.
Rocard, J. Phys. Radium, (4) VII, 247.
Hilke, Z. Physik (1936), 103, 350.
Hootman, Physical Rev., 43, 749.
Serber, Physical Rev., 43, 1003.
Stuart and Volkmann, Z. Physik, 83, 444.
Ingersoll and Wrinch, Physical Rev., 44, 399.
Schwab, Compt. Rend., 197, 615.
Meyer, Physikal. Z., 36 (1935), 212.
Hehlgans, Physikal. Z., 33 (1932), 378.

Attempts were then made to measure the ordinary Kerr effect in the solutions in question, using fields similar to those employed by McLean. The first method was to place the cell between crossed Nicol prisms with a strong light source at one end and a sensitive photoelectric cell connected to a sensitive galvanometer at the other. On switching on the field there should have been a deflection of the galvanometer due to the fact that the emergent light, after passing through the cell, ought to be elliptically polarised if there is an appreciable Kerr effect. It was found, however, that there was no measurable deflection of the galvanometer. As a final test of this method it was decided to use nitrobenzene in the cell. The references showed that in determining the Kerr constants of liquids very high purity was required. To purify the nitrobenzene it was washed with sodium carbonate solution, dried over phosphorus pentoxide and distilled from apparatus that had previously been heated to 150° to expel any water adsorbed on the glass. It was then partly crystallised out and the crystals separated from the remainder of the liquid. This fraction was then distilled in vacuo directly into the polarimeter tube by a series of distillations, first from a flask containing a few grams of freshly-prepared lime, which reduces the conductivity of the nitrobenzene, and then from a second flask containing a little silver oxide which investigators have found to reduce the conductivity of the nitrobenzene still further. Even with nitrobenzene thus purified, however, there was no appreciable Kerr effect noticeable. It seemed practically certain, then, that the ordinary Kerr effect, under the conditions of the experiment, was too small to be measured. Moreover, this nitrobenzene, when placed in the cell in the polarimeter, showed no rotation on switching on the field. Since nitrobenzene has a much greater Kerr constant than any of the other liquids it seemed reasonably certain from this that the rotation was caused by something other than the ordinary Kerr effect. It was therefore decided to continue the investigations dealing especially with the aspect of the problem concerning organic chemistry.

On the assumption that the rotation was produced by the electric field acting on the molecules in the solution it seemed possible that this was related to the high dipole moment of these molecules. The mechanism of the effect might thus have been an orientation of the molecules by the electric field or some distortion of the molecule itself, although this explanation seems unlikely in view of the enormous magnitude of the intermolecular forces. It seemed possible, therefore, that the magnitude of the rotation would bear some relationship to the dipole moment of the compound under examination.

It was, therefore, decided to continue the work along the following lines:

(1) relationship of dipole moment of solute and magnitude of the rotation;

(2) the type of compound exhibiting the effect.

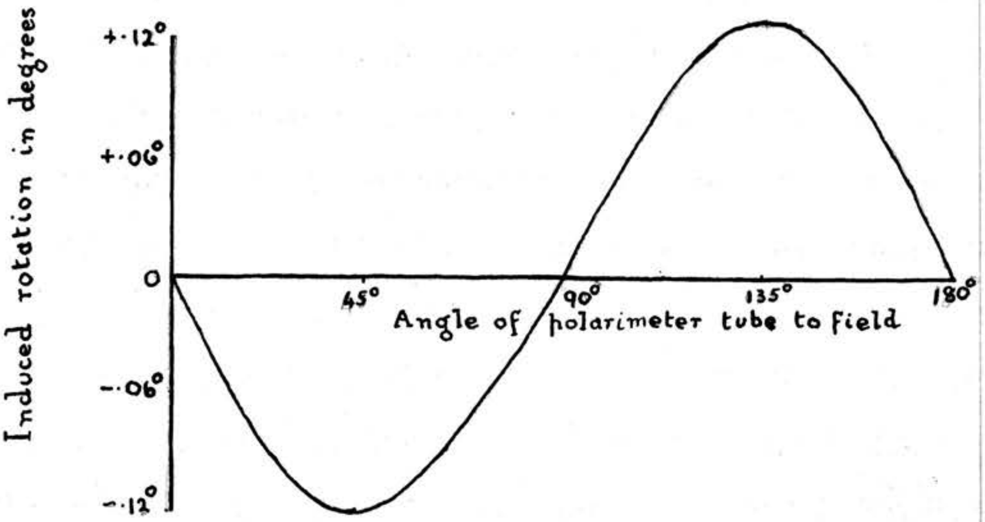
In order to find a suitable type of compound for investigation, certain compounds which were at hand were used, and the following results found when V = 20,000 v. and angle between field and plane of polarisation was 30°.

1.	Benzoic acid (saturated solution) in benzene	α	-·03°
2.	Ethyl benzoate (5% solution) in benzene	α	nil.
3.	Phenyl benzoate (5%, in benzene)	α	-·12°
4.	Ethyl lactate (5%, in benzene)	α	nil.
5.	Salicylic acid (saturated in benzene)	α	-·05°
6.	Methyl salicylate (5%, in benzene)	α	nil.
7.	Phenyl salicylate (5%, in benzene)	α	-·07
8.	Cyclohexanone (5%, in benzene)	α	nil.
9.	Dimethyl malonate (5%, in benzene)	α	-·01°
10.	Benzophenone (5%, in benzene)	α	-·02°
11.	Benzaldehyde (5%, in benzene)	α	nil.
12.	m-Dinitrobenzene (5%, in benzene)	α	nil.
13.	Amyl acetate (5%, in benzene)	α	nil.

Since phenyl benzoate gave the greatest rotation it was decided to investigate the change produced in the induced rotation by substituting polar groups into the phenyl benzoate nucleus, e.g., phenyl o-nitro-benzoate, phenyl o-iodo-benzoate, etc., and also to study the effect of different esters of benzoic and substitutdd benzoic acids.

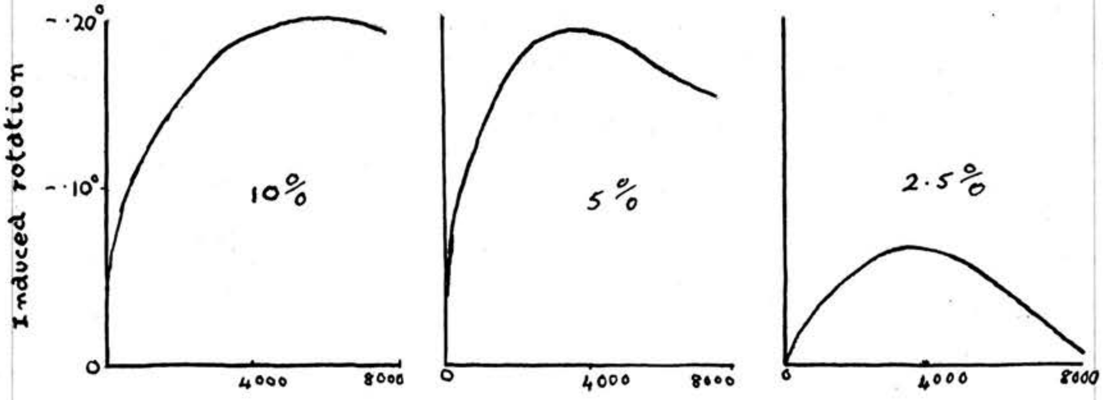
While the preparative work for this was being carried out a paper was published by Kunz and Babcock in America (Phil. Mag. (1926), 22, 616). In their experiments, rectified D.C. smoothed by condensers was used, the various voltages being tapped off from a potentiometer and measured by an electrostatic voltmeter. The polarimeter tube was of similar dimensions to that used by McLean. It was thought by Kunz that the Kerr effect ought to occur under the conditions of the experiment. For this reason the tube was filled with benzene, toluene, nitrobenzene, etc., but it was found that no rotation resulted. It was therefore concluded that no rotation could be produced as a result of the Kerr effect. An attempt was made to distinguish between simple rotation of the plane of polarisation and elliptical polarisation. They used the method of Rayleigh in which a strip of flint glass is placed in front of the analyser; the strip is supported at each end and stressed in the middle. No satisfactory results were, however, obtained.

Using a 3% solution of 2-l-menthyl hydrogen 3-nitro-phthalate in benzene with a field of 6,000 volts, it was found by Kunz that a sine curve relationship existed between the angle and the magnitude of the rotation, thus:-



A similar curve was obtained for *l*-menthyl o-nitro-benzoate.

The relationship between the strength of the field and the rotation produced was next studied by Kunz and a maximum field strength was noted, above which the induced rotation fell off slightly. In the Kerr effect the magnitude increases with the voltage and does not show any saturation value. The results for 2·5%, 5% and 10% solutions of the ester were as shown

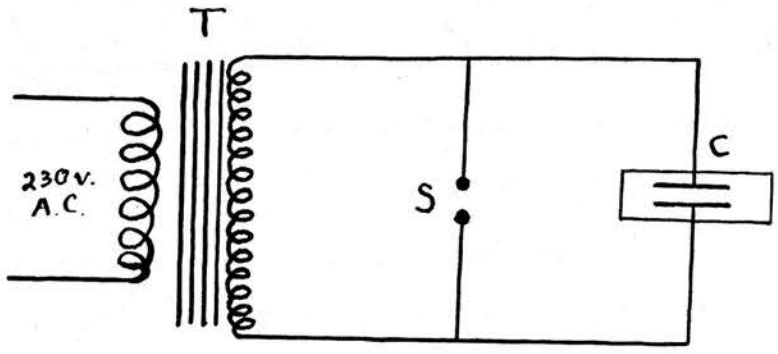


It was noted by Kunz that the magnitude of the effect decreased markedly with increase in the dipole moment of the solvent and he explains the change in rotation caused by the electrostatic field as due to the induced moment in the solvent molecules. It was finally found that ethyl (2) hydrogen 3-nitrophthalate showed the effect, and this obviously cannot be explained in this way since it is itself inactive.

After the necessary preparative work had been completed, the further investigation of this problem was continued along the lines previously mentioned.

The apparatus adopted was the same as that used by McLean, being as shown in the following figure.

FIGURE I



T - a transformer capable of giving a potential difference of 20,000 v.;

S - a calibrated spark gap;

C - a cell of similar dimensions to that used by McLean (see figure).

In each case the solution was made up and immediately transferred to the cell which was arranged so that the field could be applied at an angle of 45° to the plane of polarisation of the light. After the zero reading had been taken, the field was switched on so that a potential difference of 2,500 volts was applied across the electrodes, and the angle of rotation again taken. The voltage was then increased to 5,000 and the rotation again taken. In this way the value of the induced rotation was obtained for voltages from 2,500 v. to 20,000 v., with the following results:-

1. Phenyl Benzoate ($\frac{M}{2}$ solution in benzene)

Temp. = 15°.

Maximum rotation, -0·12°

Saturation voltage, 7,500 v.

λ = 5893.

2. Phenyl o-nitro-benzoate ($\frac{M}{2}$ solution in benzene)

λ = 5893. Temp. = 15°

Maximum rotation, -0·19°.

Saturation voltage, 7,500 v.

3. Phenyl o-iodo-benzoate ($\frac{M}{2}$ solution in benzene)

λ = 5893. Temp. = 15°.

Maximum rotation, -0·03°

Saturation voltage, 10,000 v.

4. Phenyl Salicylate ($\frac{M}{2}$ in benzene)

$\lambda = 5893.$ Temp. = 15°.

Maximum rotation, -0·07°.

Saturation voltage, 7,500 v.

5. Phenyl o-bromobenzoate ($\frac{M}{2}$ solution in benzene)

$\lambda = 5893.$ Temp. = 15°.

Maximum rotation, -0·07°.

Saturation voltage, 10,000 v.

From these results it is immediately apparent that there is no relationship between the dipole moment of the solute and the induced rotation, but it was decided to confirm this conclusion using a similar series of substituted ethyl benzoates and a few esters of phthalic acid.

1. Methyl Benzoate ($\frac{M}{2}$ solution in benzene)

$\lambda = 5893.$ Temp. = 15°.

Maximum rotation, nil, even at 20,000 v.

2. Methyl o-chlorobenzoate ($\frac{M}{2}$ solution in benzene)

$\lambda = 5893.$ Temp. = 15°.

Maximum rotation, nil.

3. Methyl o-bromobenzoate ($\frac{M}{2}$ solution in benzene)

$\lambda = 5893.$ Temp. = 15°.

Maximum rotation, nil.

4. Ethyl o-nitrobenzoate ($\frac{M}{2}$ solution in benzene)

λ = 5893. Temp. = 15°.

Maximum rotation, 0·49°.

Saturation voltage, 10,000 v.

It was obvious from these results also that there was no apparent relationship between dipole moment and induced rotation. It was noticed, however, that all the compounds showing a high value of induced rotation were solids. Liquids, on the other hand, gave little or no induced rotation. For this reason the rotations of other solid esters were taken and also a few more liquids, with the following results.

Liquids.

Solute	Solvent	Concentration.	Induced Rotation.
1. α-Naphthyl benzoate	benzene	$\frac{M}{2}$	nil
2. Ethyl α-naphthoate	benzene	$\frac{M}{2}$	nil
3. Cyclohexyl benzoate	benzene	$\frac{M}{2}$	nil
4. Dimethyl malonate	benzene	$\frac{M}{2}$	nil

Solids.

1. α-Naphthyl benzoate	benzene	$\frac{M}{2}$	-0·10°
2. β-Naphthyl benzoate	benzene	$\frac{M}{2}$	-0·08°
3. Diphenyl phthalate	benzene	$\frac{M}{2}$	-0·03°
4. Diethyl 4-nitro phthalate	benzene	$\frac{M}{2}$	-0·05°
5. -Menthyl benzoate	benzene	$\frac{M}{2}$	-0·02°

These results confirmed the observation that liquids did not give induced rotations but that some solids did do so.

The ethyl o-nitrobenzoate used in the above experiments was the B.D.H. product which had not been re-purified and was obviously not quite pure. In view of its rather high rotation it was decided to recrystallise it and repeat the experiment. The ester was recrystallised from alcohol and the induced rotation was then found to have fallen to -0·12°. Another recrystallisation lowered the value to -0·09°, and still another to -0·05°. It was obvious, therefore, that the induced rotation must be due to some impurity in the solute.

Before further investigation was carried out on this point a communication was received from Professor Kunz, stating that the effect could be completely eliminated in the case of *l*-menthyl hydrogen 3-nitro-phthalate by filtering the solution through a very fine filter paper immediately before the experiment (cf. Nature, July 31, 1937, 194). Experiments were therefore repeated with all the above solutes after filtration through a very fine filter paper (and in no case was any induced rotation noticed. It was obvious from this either that the filter paper was removing the impurity that was causing the rotation or that the filter paper was adding something to the solution such as fibrous material which was eliminating the induced rotation. An experiment was therefore performed in which the rotation induced in ethyl o-nitrobenzoate was measured, after which a few pieces of filter paper were added to it and shaken. The filter paper was then extracted and the induced rotation was again measured. There was, however, only a very slight change, thus showing that the filtration was probably removing some impurity. The cause of the rotation must therefore be fine particles in suspension in the solution, which would explain why rotations were given by the solid esters but not the liquid esters, since these were all purified by distillation which would remove any insoluble impurity. The solid exters, however, were purified by recrystallisation without filtration of the solution before cooling, since it was believed that contact with filter paper might add cellulose fibres to the solution. The presence of fibres of this kind has been quoted in the literature as being one of the causes leading to inaccuracy in the determination of the Kerr Constant of liquids.

Further and more direct proof that the rotation was caused by particles in suspension was obtained by adding dust to pure benzene. The benzene itself showed no induced rotation, but on adding a small quantity of dust a rotation of -0·51° was induced on switching on the field. The rotation of the esters could therefore be explained by the presence of dust in the crystals, since only a minute quantity of dust would be required to produce the small rotations which were noted. In the case of the original compound, *l*-menthyl hydrogen 3-nitro-phthalate, however, the rotation is of a slightly higher order than would be given by the trace of dust that might be present. It was later found that 3-nitro-phthalic acid was insoluble in benzene and gave a high rotation under the electric field. If, therefore, a trace of the free acid was present, this would account for the high rotation given by the solution of the ester. This explanation is highly probable, since traces of the free acid are quite likely to occur in the ester, either due to its method of preparation from the anhydride, or owing to slight hydrolysis. The latter was proved to be the actual cause by dissolving the ester in benzene and filtering it, after which it showed no induced rotation. The benzene was then evaporated off and the solid ester kept in a stoppered bottle for a month. It was then dissolved in benzene, when a rotation of -0·13° was induced, proving that the ester must have decomposed slightly to the free acid. Precaution was taken to prevent the entry of dust.

The discovery that the induced rotation was not a molecular phenomenon greatly diminished its interest to the organic chemist. It was decided, however, to investigate the effect further by using different materials in suspension. The shape and size of the particles was determined in each case by examining the suspension under a microscope fitted with a scale. Results were made as nearly as possible comparable by powdering each substance for thirty minutes, using the same quantity of each and allowing the suspension to settle for the same length of time. Rotations of the following order were obtained in benzene suspensions:-

Suspensoid	Size and shape of particles.	Rotation
1. Wood dust	·0001 to ·001 cm. of irregular shape	-4·67°
2. Aluminium oxide	·0003 to ·002 cm. of more or less round shape	-0·04°
3. Calcium carbonate	·0005 to ·001 cm. of irregular shape	+0·25°
4. Ferric oxide	·0001 to ·001 cm. of rounded shape	nil
5. Carbon	·0002 to ·0008 irregular particles	-0·85°
6. Sulphur (powdered flowers of sulphur)	·0001 to ·002 irregular particles	-0·19°
7. Water (milky suspension in benzene)	round globules	nil
8. Starch	oval-shaped globules of size ·0001 to ·0006 cm.	+0·14°

Suspensoid	Size and shape of particles	Rotation
9. Dextrin	Oval-shaped globules of average size about ·001 cm.	+·11°
10. Maltose	Irregular bunches of crystals of ·001 cm. average size	+1·30°
11. Magnesium Oxide	Round lumps of ·0001 to ·002 cm.	nil
12. Colloidal Silver in benzene		nil
13. Colloidal Silver (coagulated)		-1·7°
14. "Colloidal" Carbon (Oildag)	Average size 1 μ.	-1·6°
15. Sodium Chloride		nil
16. Phthalic Acid	Long, broken crystals	+6·7°
17. 3-Nitro-phthalic Acid	Elongated, broken crystals.	+5·6°

By using a suspension of phthalic acid in benzene at the maximum turbidity a rotation of nearly 30° was obtained.

Certain general rules can be deduced from the above results.

(1) Irregular and elongated crystals gave the greatest rotations (e.g., phthalic acid).

(2) Completely spherical or symmetrical particles produce no rotation (e.g., magnesium oxide, sodium chloride).

(3) Particle size has some effect on the induced rotation since true colloids do not show any induced rotation.

Shortly after these observations had been made, references were found in the literature which showed that optical rotations induced in suspensions by electric fields had already been studied, cf.

Meslin, Compt. Rend., 1903, 137, 182.

Meslin, Compt. Rend., 1908, 146, 1208.

Chaudier, Ann. Chim. et Physique, 1908, 15, 67.

Diesselhorst and Freundlich, Physikal. Z., 16, 419; 17, 117.

Procopiu, Annales de Physique, 1924, 213.

The early work by Meslin and Chaudier was mainly concerned with establishing the existence of dichroism in suspensions of a considerable number of solids in a variety of liquids, observing the sign of the rotation produced by the applied field and connecting the sign and the magnitude of rotation with the difference between the refractive indices of the solid and the liquid. The rotation is produced by the different absorption of the light perpendicular and parallel to the field, and it is to this difference in the absorption that the term dichroism is applied. Chaudier observed that whereas with a magnetic field the light was polarised rectilinearly, with the electric field there was also a notable double refraction with all the liquids used. The double refraction is great when the difference in the refractivity of liquid and solid is small, but the dichroism is then also small. Meslin noticed that no cubical crystals gave the effect. He also observed that the greater the difference between the index of refraction of the liquid and of the substance in suspension, the less was the double refraction. The work of Procopiu in 1924, sixteen years after the last paper by Chaudier, aimed at greater precision in the measurements. He points out that whereas the electrical effect for pure liquids (Kerr effect) requires thousands of volts and is proportional to the square of the field, the effect in the case of suspensions tends towards saturation at much smaller voltages. Also, the Kerr effect in pure liquids is instantaneous but there is an appreciable lag with suspensions. This absence of lag is one of the reasons why the Kerr effect was employed in the earlier methods of television. Lack of extreme precaution in preparing pure liquids may, however, lead to delay in the Kerr effect, as early experimenters on the subject found. Procopiu worked on the double refraction and also on the dichroism, as the two are always produced together by suspensions. Pure liquids do not produce dichroism.

In the case of homogeneous liquids the double refraction is caused by the orientation of the molecules in the applied field. In the case of suspensions the orientation may be due either to anisotropy of the particle or to its shape not being spherical, even though its material is isotropic. In some simple cases Procopiu showed that the effect was due to the structure and others to the shape of the particle.

He measured the dichroism by applying the electric field at an angle of 45° to the plane of polarisation, and if h and v are the amplitude along a perpendicular to the lines of force, v^2 and h^2 are the intensities and the angle of rotation, then

$$\frac{v}{h} = \tan(45^\circ \pm \rho) \quad \text{and} \quad \frac{v^2 - h^2}{v^2 + h^2} = \sin 2\rho$$

But when the substance is simultaneously doubly refractive and dichroic, the actual measurement of ρ does not give the true dichroism, for the emergent light is elliptically polarised and the axis of the ellipse is not in the direction of the rectilinear vibration. To show the magnitude of this effect, for a double refraction of 10° and a dichroism of 10° the observed rotation would be about 6% higher than the value due to the double refraction alone. He found very little variation in the rotation with different wavelengths. In some cases the double refraction is the greater and in others the dichroism, depending on the liquid medium employed.

Experimentally, the procedure is to measure the ellipticity, using a compensator to convert the elliptical into rectilinear polarisation and then to measure the rotation of this rectilinear light and so obtain the dichroism. For this purpose a thin mica strip was interposed between the polariser and the tube containing the liquid to cover only part of the field, and a quarter-wave plate capable of rotation was placed between the tube and the analyser.

The work of Chaudier was concluded by a number of quantitative experiments to establish certain simple relationships, such as:

(a) influence of the nature of the liquid medium;

(b) influence of the thickness of the suspension through which the light is passing. A direct proportionality was found in this case;

(c) influence of concentration. Chaudier made no direct measurement of this but assumed a linear relationship to exist, since the concentration and the number of particles in suspension are directly proportional;

(d) influence of the intensity of the field. Chaudier found a saturation value when the spark length was 9 mm.

It was decided to confirm some of these results by more accurate methods if possible.

To Determine the Relationship between Length of Electrode and the Rotation Produced.

This had not been determined by Procopiu or any of the previous workers on the subject. In order to be able to attain reasonable accuracy in this determination it was necessary to prepare a suspension which would have a large rotation and yet be practically stable for the period of the experiment. After many unsuccessful attempts to find such a suspension, it was decided that phthalic acid in benzene gave the greatest rotation without obscuring the field too much although the suspension was not very stable. Another difficulty was that internal electrode length could not be quickly changed, using simple internal electrodes. Experiments with external electrodes were carried out and these were found as satisfactory as internal ones. A cell in which the electrode length could be quickly changed was made from a two decimeter polarimeter tube of 1 cm. cross-section by sticking two strips of silver foil along opposite sides of the tube, contact to the electrode being made by copper wire. The tube was then coated with candle-wax which served to keep the electrodes in place and also as in insulator to prevent sparking between the electrodes.

The suspension was prepared by shaking finely-ground phthalic acid with benzene and allowing the mixture to stand for thirty minutes, after which the supernatant liquid was decanted off and transferred to the cell. The stability of the suspension was tested by taking readings of the induced rotation every few minutes, and it was found that the value fell appreciably with time. It was therefore necessary to apply a correction for this change.

The polarimeter tube was filled with suspension and values of the rotation were taken at intervals, with the following results:

Time (in mins.)	Rotation	Correction	Time (in mins.)	Rotation	Correction.
0	+2·78°	0°	30	+1.82°	+0.96°
5	+2·58°	+0·20°	35	+1·76°	+1·02°
10	+2·32°	+0·46°	40	+1·72°	+1·06°
15	+2·12°	+0.66°	45	+1·68°	+1·10°
20	+1·98°	+0·80°	50	+1·66°	+1·12°
25	+1·90°	+0·88°	55	+1·64°	+1·14°

The experiment was repeated with the same solution, except that 1 cm. of the electrodes was scraped off each time. The results were as follows:

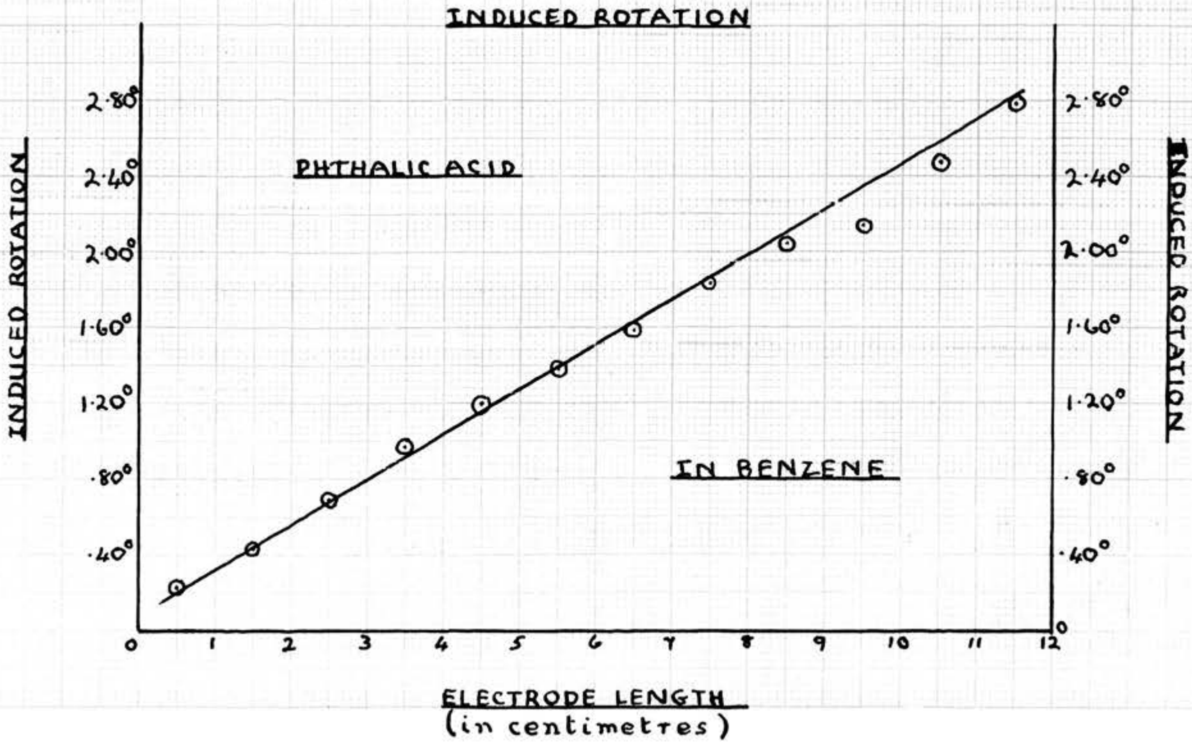
Time (in mins.)	Rotation	Length of electrode	Time (in mins.)	Rotation	Length of electrode
0	+2·77°	11·5 cm.	30	+0·92°	5·5 cm.
5	+2·30°	10·5 cm.	35	+0.74°	4·5 cm.
10	+1·76°	9·5 cm.	40	+0·60°	3·5 cm.
15	+1·55°	8·5 cm.	45	+0·41°	2·5 cm.
20	+1·31°	7·5 cm.	50	+0·26°	1·5 cm.
25	+1·10°	6·5 cm.	55	+0·17°	0·5 cm.

On the assumption that a straight line relationship exists between length of electrode and the magnitude of the rotation it is possible to calculate the correction to be applied at each electrode length. Should the relationship not be linear, these corrections will not be accurate but the error will be, in any case, small and the corrected graph will give a rough idea as to what form the curve is likely to take. The corrected results are as follows:-

Length of electrodes	Rotation	Correction	Corrected rotation.
11·5 cm.	+2·77°	0°	+2·77°
10·5 cm.	+2·30°	$\frac{\cdot 20 \times 10\cdot 5}{11\cdot 5} = 0\cdot 18^\circ$	+2·48°
9·5 cm.	+1·76°	$\frac{\cdot 46 \times 9\cdot 5}{11\cdot 5} = 0\cdot 38^\circ$	+2·14°
8·5 cm.	+1·55°	$\frac{\cdot 66 \times 8\cdot 5}{11\cdot 5} = 0\cdot 49^\circ$	+2·04°

GRAPH VIII

RELATIONSHIP BETWEEN ELECTRODE LENGTH AND THE INDUCED ROTATION



(contd.)

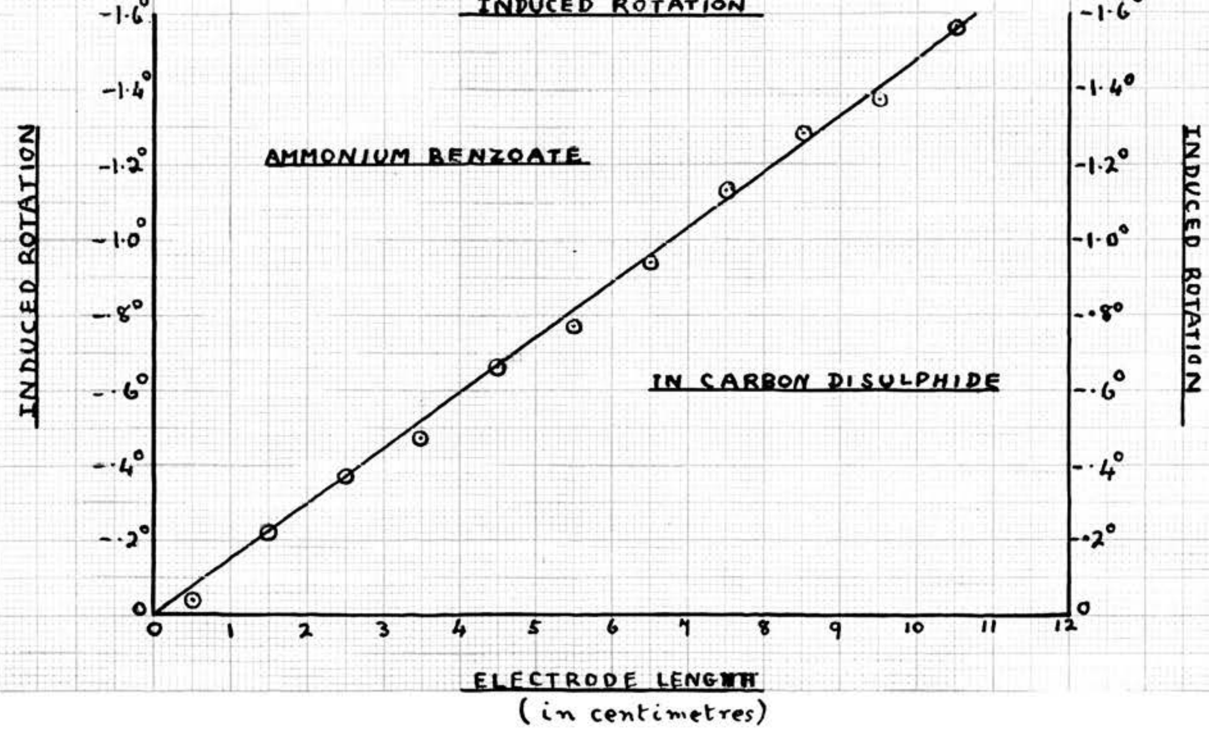
Length of electrodes	Rotation	Correction	Corrected rotation.
7·5 cm.	+1·31°	$\frac{\cdot 80 \times 7\cdot 5}{11\cdot 5} = 0\cdot 52°$	+1·83°
6·5 cm.	+1·10°	$\frac{\cdot 80 \times 6\cdot 5}{11\cdot 5} = 0\cdot 48°$	+1·58°
5·5 cm.	+0·92°	$\frac{0\cdot 96 \times 5\cdot 5}{11\cdot 5} = 0\cdot 46°$	+1·38°
4·5 cm.	+0·74°	$\frac{1\cdot 02 \times 4\cdot 5}{11\cdot 5} = 0\cdot 46°$	+1·20°
3·5 cm.	+0·60°	$\frac{1\cdot 06 \times 3\cdot 5}{11\cdot 5} = 0\cdot 37°$	+0·97°
2·5 cm.	+0·41°	$\frac{1\cdot 10 \times 2\cdot 5}{11\cdot 5} = 0\cdot 28°$	+0·69°
1·5 cm.	+0·26°	$\frac{1\cdot 12 \times 1\cdot 5}{11\cdot 5} = 0\cdot 17°$	+0·43°
0·5 cm.	+0·17°	$\frac{1\cdot 14 \times 0\cdot 5}{11\cdot 5} = 0\cdot 06$	+0·23°

When these results are plotted, a straight line relationship is apparent (see Graph VIII).

This result was later confirmed more directly with a suspension of ammonium benzoate in carbon disulphide. This suspension did not change appreciably in rotation over one hour, but has the disadvantage of being rather opaque, making readings of the rotation difficult. The following results were obtained:-

GRAPH IX

RELATIONSHIP BETWEEN ELECTRODE LENGTH AND THE INDUCED ROTATION



Length of electrode	Rotation	Length of electrode	Rotation.
10·5 cm.	-1·56°	4·5 cm.	-0·66°
9·5 cm.	-1·37°	3·5 cm.	-0·47°
8·5 cm.	-1·28°	2·5 cm.	-0·37°
7·5 cm.	-1·13°	1·5 cm.	-0·22°
6·5 cm.	-0·94°	0·5 cm.	-0·04°
5·5 cm.	-0·77°		

This also gives a linear relationship (see Graph IX).

An attempt was also made to determine the effect of concentration on the rotation of suspensions of various ammonium salts in benzene. Ammonium benzoate, ammonium phthalate, ammonium chloride, etc. were finely powdered and shaken up with benzene, and the suspension allowed to settle for 30 minutes, after which the top layer was withdrawn and the rotation taken. Exactly 5 c.c. of the suspension of ammonium phthalate was withdrawn and the benzene evaporated off. The residue was dissolved in water and an attempt was made to estimate the amount of ammonia present with Nessler's colorimetric method. No appreciable yellow colour was developed, however. It was thought that the ammonium salt may have sublimed when driving off the benzene. An experiment was therefore tried of shaking up 5 c.c. of the suspension with 25 c.c. of water and separating the aqueous layer. No greater success was attained by this method, however. Since the rotation given by this suspension was 2·8° it was concluded that very minute quantities of ammonium phthalate were sufficient to cause an appreciable rotation. It was possible, however, that the ammonium phthalate contained some free phthalic acid which might remain in suspension after all of the ammonium salt had settled out. A known weight of ammonium phthalate was therefore weighed out and the ammonium content of this estimated by Nessler's colorimetric method, comparing it with a standard ammonium chloride solution. It was found that the amount of ammonia present corresponded to only 75% purity. Since ammonium benzoate, chloride, nitrate, etc., which could be obtained in A.R. purity, did not give suspensions in benzene stable enough to give any rotation after a few seconds, it appears probable that free phthalic acid was causing the rotation and that the method was therefore useless. By using the denser liquid carbon disulphide it was possible to obtain suspensions of A.R. ammonium oxalate, ammonium benzoate, etc., giving rotations up to about one degree. On evaporating off the carbon disulphide, however, and attempting to estimate the ammonium content, a brown colour was immediately developed, due to some impurity in the carbon disulphide which could not be removed. This method was therefore also abandoned. After unsuccesful attempts to obtain other suitable suspensions the experiment was discontinued.

An attempt was then made to obtain permanent rotations in jellies by the use of electric fields. It was hoped to suspend particles in unset aqueous gelatine in a cell, switch on the field and measure the rotation produced. It seemed possible that if the gelatine were allowed to set while the field was still on, the rotation could persist after the field was switched off, since the rotation could be explained by orientation of the particles in the field. If this were so, then by examining the jelly under the microscope this orientation would become evident. No success was attained, however, since no suspensions in gelatine could be found which gave a rotation when the field was applied.

It was apparent that no further progress in the study of the effect can be made until some method is found for controlling the variables such as the stability of the suspension, the size and shape of the particles and the number of particles in suspension. This, unfortunately, is a task beyond even the most expert colloid chemists at the present time. For this reason the work was discontinued in favour of the preceding investigation.

PREPARATIVE.

PREPARATION of PURE BENZENE.

B.D.H. "extra pure" benzene was partly crystallised out and the crystals filtered off, melted and dried over phosphorus pentoxide and finally distilled, the middle fraction being collected. B.p., 80·3°/760 mm.

PREPARATION of PHENYL o-NITRO BENZOATE.

50 gm. o-nitro benzoyl chloride
50 gm. phenol

The ester was prepared by the Schotten-Baumann method. The solid which separated out was dark-brown in colour, since the o-nitro benzoyl chloride used was impure. The crude ester was purified by dissolving it in the minimum amount of boiling alcohol, adding animal charcoal and refluxing for several hours. It was then filtered. The resulting product was still very dark brown. It was found that, in recrystallisation from alcohol, the first part of the ester separated out on cooling as a dark brown liquid but eventually, on further cooling, light brown crystals were deposited on the sides. As soon as this second deposition started, the mother liquor was poured into andher vessel, when light brown crystals were deposited. By repeating this process several times from petrol-ether, light yellow crystals were obtained.

Yield, 12 gm. M.p., 54°.

Analysis: found N, 5·91% ;

calculated for $C_{13}H_9O_4N$, N, 5·76%

PHENYL o-IODO BENZOATE.

(a) Preparation of o-iodo benzoyl chloride.

20 gm. o-iodobenzoic acid

20 gm. PCl_5

These were heated together on an oil-bath under reflux for half-an-hour. The $POCl_3$ was removed by vacuum distillation on a water-bath, when the acid chloride distilled over as a colourless liquid.

Yield, 18 gm. (90% theory);

b.p., 153-154°/20 mm.

(b) Phenyl o-iodobenzoate.

15 gm. o-iodobenzoyl chloride

10 gm. phenol

These were heated together, when a vigorous reaction started and much HCl was evolved. After the reaction had stopped, the mixture was shaken up with dilute sodium hydroxide solution until any excess of acid chloride was removed and the liquid ester which remained was washed with water, extracted with ether, dried over calcium chloride and the ether removed on the steam-bath. The oily ester was then distilled under reduced pressure. The first two or three c.c.'s were rejected as they were highly-coloured with iodine. The ester did not solidify, even on standing for a few weeks, but on cooling to -110° for a few hours it became crystalline and was recrystallised from alcohol to give colourless crystals.

Yield, 12 gm. (50% of theory); m.p., 47°.

Analysis: Found: I, 38·44%.

Calculated for $C_{13}H_9O_2I$, I, 39·2%.

CYCLOHEXYL BENZOATE.

This was prepared according to the method of Brunel (B., 3 , 33, 273) from 20 gm. cyclohexanel.

Yield, 30 gm. (75% of theory);

b.p., 157-159°/14 mm. (quoted 192-193°/61 mm.).

α-NAPHTHYL BENZOATE.

This was prepared according to the method of Autenreith, Muhlinghaus (Ber., 40, 748).

The product was recrystallised from alcohol.

Yield, 20 gm. (50% of theory);

m.p., 56° (quoted 56°).

β-NAPHTHYL BENZOATE.

This was prepared from β-naphthol and benzoyl-chloride in the same manner as the α-naphthyl ester.

Yield, 25 gm. (55% of theory); m.p., 106° (quoted 107°)

l-MENTHYL BENZOATE.

Prepared from *l*-menthol and benzoyl chloride by the method of Rupe, Silverberg (Annalen, 327, 194).

Yield, 50 gm. (90% of theory);

m.p., 55·5° (quoted 55°).

DIPHENYL PHTHALATE.

(a) PHTHALYL CHLORIDE (symmetrical).

This was prepared from phthalic anhydride and phosphorus pentachloride by the method given in Organic Synthesis II (New York 1931) p. 88.

Yield, 45 gm. (89% of theory);

b.p., 155-157°/23 mm. (quoted 131-133°/10 mm.).

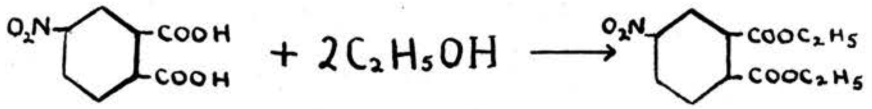
(b) DIPHENYL PHTHALATE.

Prepared from phthalyl chloride and phenol by the method of Schreider (Ber., 7, 705).

Yield, 25 gm. (47% of theory);

m.p., 71° (quoted 69-73°).

DIETHYL 4-NITRO PHTHALATE.



Prepared from a mixture of 3-nitro-phthalic acid and 4-nitro-phthalic acid by the method given in Organic Syntheses, Vol. 7, p. 70.

Yield, 25 gm. (33% of theory); m.p., 32° (quoted 33-34°).

ETHYL α-NAPHTHOATE.

(a) α-NAPHTHOYL CHLORIDE.

Prepared from α-naphthoic acid by treating it with phosphorus pentachloride according to the method of V. Braun (Ber., 38, 180).

Yield, 45 gm. (90% of theory);

b.p., 170-172°/15 mm.

(b) ETHYL α-NAPHTHOATE.

Prepared from α-naphthoyl chloride and ethyl alcohol by the method of Hofmann (Ber., 1, 42).

Y ield, 30 gm. (59% of theory);

b.p., 185-189°/22 mm.

Methyl o-chlorobenzoate and methyl o-bromobenzoate were available in the pure state, having been prepared for former work, while ethyl o-nitrobenzoate was obtained from The British Drug Houses.

SUMMARY.

(a) The discovery by Dr McLean that solutions of certain esters of 3-nitro-phthalic acid in benzene are capable of giving a rotation or increase in rotation when an electric field is applied at right angles to the plane of propagation of the light is proved to be due to particles of 3-nitrophthalic acid in suspension, which causes dichroism under the influence of the electric field. This is already a well-known effect.

(b) A linear relationship is proved to exist between the length of the electrodes and the magnitude of the induced rotation.

In conclusion the author wishes to express his gratitude to Dr H. G. Rule and Dr E. B. Ludlam for much valuable advice and guidance which they gave so willingly during the course of this work.