Title	Influence of the triphenyl-methyl grouping on optically active esters and ethers
Author	Bain, James.
Qualification	PhD
Year	1930

Thesis scanned from best copy available: may contain faint or blurred text, and/or cropped or missing pages.

#### **Digitisation notes:**

Page number 52 is missing in the original thesis.

# THE INFLUENCE Of The TRIPHENYL-METHYL GROUPING ON OPTICALLY ACTIVE ESTERS And ETHERS.

By

JAMES BAIN, B.Sc.

Examiner: Prof. J. Read.

Thesis for the Degree of Ph.D.

Chemistry Department, University of Edinburgh.

April 1930.

#### CONTENTS.

		Page
INTRODUCTION .		 1
EXPERIMENTAL .		 20
DISCUSSION OF	RESULTS	 50
SUMMARY		74

#### INTRODUCTION.

During the last ten or fifteen years much work has been done with a view to ascertaining the influence of substituents on the physical and chemical properties of a parent compound. The result of all these investigations shows that a definite influence is at work which is displayed in properties so widely different as benzene substitution, dielectric constant, electrolytic dissociation, velocity of reaction and optical activity. This general polar effect, as it has been called by Robinson (Ann. Rep. Chem. Soc., 1922, p.98), is also sometimes referred to as an inductive effect (J. J. Thomson, Phil. Mag., 1923, 46, 497; Ingold, Ann. Rep. Chem. Soc., 1926, p. 140). The general polar effect of substituents is supposed to propagate itself in two ways, firstly, as a space effect, and secondly by means of a general shift of the valency electrons along the chain of atoms toward an electronegative atom or group such as chlorine, and away from an electropositive one like methyl. From a comparison of the properties of substituted compounds the common substituents have been arranged

in the series

NO<sub>2</sub>, CO<sub>2</sub>H, halogens, OMe, H, Me, N(Me)<sub>2</sub>, NH<sub>2</sub>, passing from the strongly electronegative groups at one end through hydrogen to those of strongly electropositive character at the other. The sequence of the groups in the above series may be derived, for example, from the dissociation constants of aliphatic acids, a property which is generally assumed to be directly dependent on the degree of electronic displacement. In this connection the following table may be quoted for the dissociation constants of the mono-substituted acetic acids (cf. Landolt-Börnstein's Physikalisch Chemische Tabellen, 1923). CH<sub>2</sub>X·GOOH.

TABLE I.

X	NOs	COOH	Cl	Br	I	OCH <sub>3</sub>	н	CH3	NHz
k	-	0.161	0.155	0.138	0.075	0.033	0.005	0.0014	0.0934

In propionic acid CH<sub>3</sub>·CH<sub>2</sub>·COOH the electron shift due to the substituent is supposed to be away from the methyl group, whereas in monochloracetic acid it is in the opposite direction CH<sub>2</sub>·Cl·COOH. This explains the fact that chloracetic acid has a much greater dissociation constant than propionic acid, since the withdrawal of electrons from the carboxylic group would be expected to promote ionisation by facilitating

the transfer of an electron from the hydrogen atom to the adjacent oxygen. The above series accords well with the views of Flürscheim (J.C.S., 1909, 95, 718) on dissociation constants, which he states are dependent for a given solvent on two factors, namely,

- (a) The dissociation constant is <u>directly pro-</u>
  <u>portional</u> to the force with which the negative electron adheres
  to the acidic radical. This force mainly depends on
  the polar nature of the acidic radical, which again is
  affected by the polar nature of the substituents,
  the more electronegative these are the greater that
  force becomes.
- (b) The dissociation constant is inversely proportional to the force with which hydrogen is linked
  to the acidic radical. This chiefly depends on the
  amount of affinity which the atom to which the
  hydrogen is linked can place at the latter's disposal.
  This amount is variable and depends on the force with
  which the substituents are linked to the molecule
  and on their position.

With few alterations the same series was obtained by S. C. J. Olivier (Rec. Trav. Chim., 1923, 42, 516, 775) in his examination of nuclear substituents on the mobility of chlorine in a side chain, by measuring the rate of hydrolysis of the substituted benzyl chlorides in alcoholic solution.

TABLE II.

Rate of Hydrolysis of o-, m-, and p-substituted benzyl chlorides.

			Velocity constants, the constant of CeHs CHe Cl being pu equal to 1 in both cases.			
Substituent	k <sub>30</sub> × 10 <sup>3</sup>	k <sub>83</sub> × 10 <sup>3</sup>	t = 30	t = 83		
p - OMe	1.0400	164.00	9.40	10.60		
o - OMe	0.5500	75.00	4.95	4.84		
m - OMe	0.1440	21.60	1.30	1.39		
CeHs .CH2 .CJ	0.1110	15.50	1.00	1.00		
p - C1	0.0520	9.60	0 • 468	0.620		
0 - 01	•	5.50	•	0.355		
m - C1	0.0152	3*48	0.137	0.237		
p - Br	0.0457	7.80	0.412	0 * 500		
o - Br	0.0236	4.44	0.213	0.286		
m - Br	0.0147	3 • 34	0.135	0.215		
p - I	0.0414	7.40	0.373	0.447		
0 - I	0.0248	4.45	0.223	0.287		
m - I	0.0152	3.11	0.137	0.501		
m - COOH	0.0189	3.79	0.170	0.245		
р - СООН	0.0121	2.56	0.109	0.165		
m - NOg	0.0063	1.40	0.0570	0.090		
0 - NO <sub>2</sub>	0.0052	1.30	0.0468	0.084		
p - NO <sub>s</sub>	0.0049	1.15	0.0442	0.074		

Betti (Gazzetta, 1923, 53, 424) first showed the remarkable parallelism between the influence of substituents on optical activity and dissociation constants in his examination of the Schiff's bases of the type -

$$C_{\bullet}H_{\bullet} - C - N = CH - CH - C_{1,\bullet}H_{\bullet}OH$$

prepared by condensing the optically active base  $\alpha-\beta$ -naphtholbenzylamine,  $C_6H_5$  -  $C_1$  - NHg , with  $C_{10}H_6OH$ 

benzaldehyde, and a number of substituted benzaldehydes.

The dissociation constants quoted were those of the benzoic acids derived from these substituted benzaldehydes.

TABLE III.

+2676       p-dimethylamino-benzoic       1.0         +1507       veratric       3.6         +1220       vanillic       3.0         +1154       anisic acid       3.2         +1049       p-hydroxybenzoic       2.9         +894       o-methoxybenzoic       8.0         +746       cuminic       5.0	<u>1</u> .	plo	ldehyde	2	M] <sub>D</sub>
+1220 vanillic 3.0 +1154 anisic acid 3.2 +1049 p-hydroxybenzoic 2.9 +894 o-methoxybenzoic 8.0		no-	imethyle	p-0	+2676
+1154 anisic acid 3.2 +1049 p-hydroxybenzoic 2.9 +894 o-methoxybenzoic 8.0			atric	vez	+1507
+1049 p-hydroxybenzoic 2.9 +894 o-methoxybenzoic 8.0			11110	var	+1220
+894 o-methoxybenzoic 8.0			sic acid	ani	+1154
		oic	ydroxybe	p-1	+1049
+746 cuminic 5.0		oic	ethoxybe	0-x	+894
			inic	cur	+746
+691 p-toluic 5.1			oluic	p-t	+691

TABLE III. (cont.)

[M]D	Aldehyde Employed.	$k \times 10^5$ for derived acid.
+589	protocatechuic	3.3
+504	m-toluic	5.1
+373	benzoic	6.0
+363	m-hydroxybenzoic	8.7
+282	p-chlorobenzoic	9*3
+256	m-chlorobenzoic	15.5
+207	p-nitrobenzoic	39 • 6
+168	m-nitrobenzoic	34.5
-85 • 7	salicylic	102.0
-128	o-chlorobenzoic	132.0
-326	o-toluie	12.0
-766	5-nitrosalicylic	890 • 0
-991	o-nitrobenzoic	616.0

From a study of the above table we find that in the case of the para compounds the influence of the subpower stituents on the rotatory/and on dissociation constants gives rise to the same series, but the series do not agree so closely in the ortho compounds. In the latter case, however, there is also the possibility of a space effect (cf. page 12)

p-Compounds.  $\begin{bmatrix} \mathbb{M} \end{bmatrix}_{D} \qquad \text{NO}_{8} < \text{C1} < \text{H} < \text{CH}_{3} < (\text{OH}, \text{OCH}_{3}) < \text{N}(\text{CH}_{3})_{8}$   $\text{k} \qquad \text{NO}_{8} > \text{C1} > \text{H} > \text{CH}_{3} > (\text{OCH}_{3}, \text{OH}) > \text{N}(\text{CH}_{3})_{8}$  o-Compounds  $\begin{bmatrix} \mathbb{M} \end{bmatrix}_{D} \qquad \text{NO}_{8} < \text{CH}_{3} < \text{C1} < \text{OH} < \text{H} < \text{OCH}_{3}$ 

k

 $NO_{s} > C1 > OH > CH_{s} > OCH_{s} > H$ 

Berlingozzi (Gazz. Chim. Ital., 1927, 57, 814;

Atti. R. Acad. Lincei., 1928, 6, 7, 925) obtained a similar correspondence between optical activity and dissociation constants with certain derivatives of asparagine such as p-nitrobenzyl asparagine

NO CO-NH-CH-COOH

Such a correspondence

has also been shown to exist among the optically active esters of monosubstituted acetic acids quoted in Table IV (Rule and co-workers, J.C.S., 1925, 127, 2188; 1926, 3202). Approximately the same order of the groups is found to represent their influence on the velocity of a number of chemical reactions and on the dielectric constants of aromatic and aliphatic compounds (Rule and Paterson, J.CS., 1924, 125, 2155; Errera, Compt. Rend., 1926, 182, 1623).

The interest which at present centres around the dielectric constant arises from the fact that a theory, based on the work of Debye and J. J. Thomson (Phil. Mag., 1923, 46, 513), has been advanced whereby it is possible to trace the

概 也

connection between the constant and certain structural properties of the molecule. This theory assumes that the electrical centre of the electrons in a molecule (analagous to the centre of gravity) does not in general coincide with the electrical centre of the positive atomic nuclei. The distance between these poles multiplied by the total electric charge of either sign is termed the dipole moment of the compound. This electrical doublet, or dipole, the magnitude of which can be calculated from Debye's formula relating to dielectric constant and refractivity, is a characteristic of the substituent group and largely independent of the hydrocarbon radical to which it is attached. By making use of Thomson's suggestion (loc. cit.) relating to the dielectric constants of disubstituted benzenes it has been found possible to arrange substituents into two classes according to the manner in which the dipoles are linked to the parent In the case of a disubstituted benzene compound. containing groups of similar type, Thomson predicted that the influence of the two groups on the dielectric constant increases the value in the ortho compound and decreases it in the para substituents are of the opposite type the reverse will hold. From results obtained by Smyth, (J. Amer. Chem. Soc., 1927, 49, 1038) Hojendahl and Williams, with

disubstituted benzene derivatives it follows that dipoles due to NO<sub>2</sub>, COOH, Cl, Br, OMe are of the same sign, whilst those due to CH<sub>2</sub>, NH<sub>2</sub> are of the opposite sign. Since the dipole due to NO<sub>2</sub> must be in the direction of its semi-polar double bond these results are taken as establishing permanent electron shifts in the directions:-

C<sub>6</sub>H<sub>5</sub>·CH<sub>2</sub> C<sub>6</sub>H<sub>5</sub>·Hal. C<sub>6</sub>H<sub>5</sub>·NO<sub>2</sub>
which are the same as that deduced by Robinson and Ingold (loc. cit.) for the inductive displacement from aromatic substitution data.

A comparison of the dipole moments of substituent groups reveals the close agreement between their magnitude (D.M.) and other chemical and physical properties of compounds, as may be seen from a study of the following table relating to monosubstituted acetic acids X\*CH<sub>2</sub>\*COOH.

#### TABLE IV./

<sup>(1)</sup> Given by H. G. Rule in Hons. lectures Nov. 1929.

TABLE IV.

Х	D	.M.	k (	î	acid	$[\mathtt{M}]_{\mathtt{D}}^{\mathtt{zo}}$ for $\ell$ -Menthyl and Esters	l-Octyl Esters
N(CH <sub>3</sub> ) <sub>2</sub>	+1 • 4	× 10 <sup>-18</sup> e.s.u	. 1.8	3 >	10-10	-157·1	-
н			1.8	3 >	10-5	157•4	-11.8
CHa	÷0*4		1.4	4	n	160.5	-13.0
СООН	-0.9	11	160		n	160 • 2	-
OC <sub>2</sub> H <sub>5</sub>			23		n	160.6	-
OCH <sub>3</sub>	-1.8	11	33		11	165.0	-16.3
ОН	-1.7	n	15		n	165°0 (at 94°C)	- *
Br	-1.5	n	138		n	169.0	-28.8
Cl	-1*5	n	155		n	171.0	-17.9
CN	-3.8		370		11	174.0	
ON .	-0 0		010			174.0	

From an examination of the \(lambda\)-menthyl (I) and sec-β-octyl (II) esters of various substituted benzoic acids it has been shown (Cohen, J.C.S., 1914, 105, 1892; Rule, Miles and MacGillivray, J.C.S., 1929, 2276) that the influence of orthosubstituents is as follows:

I  $NO_{s} > COOH > NH_{s} > OH > H > I > Me > Br > NMe_{s} > C1 > OMe$ 

II NO<sub>2</sub>> COOH> H,OH> Me> Br> Cl> I> OMe> NMe<sub>2</sub>> NH<sub>2</sub>
On the whole, these groups are here arranged in the general polar series, except that OMe and the halogens (which raise the rotation of the acetic esters) produce an abnormal effect in

the ortho position, resulting in a lowering of the of the rotation. Among the  $\ell$ -menthyl esters the effect produced by substituents in the p-substituted benzoic acids is very small, the molecular rotations of these compounds only varying slightly from that of the unsubstituted  $\ell$ -menthyl benzoate. With the sec- $\beta$ -octyl series, however, the general effect of the p-substituents is plainly visible. The following table shows the influence of p-substituents on the rotation of octyl benzoates (Rule, J.C.S., 1928, 178),

TABLE V.

Subst.	+ N·Me <sub>2</sub> H	NO2	COSH	Br	OMe	Cl	Me	н
[M]D	147	145.2	145	140	136	124	123.5	92

where the order of the groups agrees approximately with that deduced from the rate of hydrolysis of p-substituted benzyl chlorides (loc. cit.). An increase in the rotatory power of the benzoate, following on p-substitution by NO<sub>2</sub>, Cl, or a similarly oriented dipole grouping, might have been anticipated from a knowledge of the rotatory powers of the substituted acetic esters. In both cases the increduction of the dipole should result in a shift of the electrons away from the asymmetric atom and hence to similar

changes in rotation

The abnormal lowering effect produced by the substituents Cl, Br, I, OMe, in the ortho position to the carboxylic complex among the  $\ell$ -menthyl and sec- $\beta$ -octyl esters of substituted benzoic acids is assumed to be due to the dipole grouping acting through space, instead of through the chain of atoms.

A close relationship also exists between the influence of substituents on the  $\ell$ -menthyl and sec- $\beta$ -octyl esters of o-substituted benzoic acids and the magnitude of the directive power of the group on benzene substitution (Rule, J.C.S., 1924, 125, 1122).

TABLE VI.

[M]D of o-	Nitration of CeHs'X			
Subst. X	L-octyl series	l-menthyl series.	% m.	% p.
NOs	-122°	<b>-</b> 381·0	93	0.4
COgH	-(90+117°)	-332	76	1.5
Н	-77.8	-239		
Me	-68.1	-231	3.1	41
ı	-44.3	-237	-	66
Br	-49.2	-205	0.3	62
Cl	-47.1	-195	•	70
OMe	-33 •0	-148	(	
NMe)g	-28 • 1	+200	Chiefly	o and

These o-substituents which raise the rotation of the benzoic esters are m-directive in their effect on benzene substitution, while those which depress the rotation are o,p-directive. This powerful influence of o-substituents on the rotatory power of the benzoic esters is also observed with the ortho-derivatives of α- and β-naphthoic acids (Rule, Bretscher and Spence, J.C.S., 1928, 1493; 1929, 2516).

#### TABLE VII.

As may be seen from the above, the influence of the methoxyl group in position-2 is similar to that in the benzoic esters, whilst in position-4 the effect of the -OME appears to be of the general polar type as in the acetic and p-benzoic esters. The position-8 in the naphthoic derivatives is of great importance, as it affords strong evidence in favour of a space effect. If the influence were transmitted through the chain the rotation ought to be near to that of the unsubstituted derivative, but instead we have a very marked diminution in the rotatory power due to the substituent -OME, and a large increase due to the -NO<sub>2</sub>

grouping. This similarity between peri- and ortho- compounds is also observed in their chemical behaviour, e.g., anhydride formation and steric hindrance.

The powerful effect produced by ionisation on benzene substitution led Rule to postulate (J.C.S., 1927, 54) that similar well-marked changes in the rotatory power ought to be observed on the introduction of ionisable complexes into the molecule. When aniline is nitrated the NH<sub>2</sub> group directs to the para and ortho positions, but when the substituent is present in the form NH<sub>3</sub>, charged that is, as a positively/ionic complex (obtained by using aniline sulphate dissolved in excess of sulphuric acid) it is chiefly the meta derivative which is formed. Some of the results obtained for the rotation of the  $\ell$ -menthyl and sec- $\beta$ -octyl benzoates containing ionisable substituents (Rule and co-workers, J.C.S., 1927, 54; 1929, 401, 2275) are quoted below:-

FABLE VIII.

[M] 5461 for o-Substituted Benzoic Esters in Alcohol Solution.

Subst.	N_one	соон	COONa	NHa	H <sub>a</sub> cī	NMez	NH(Me) <sub>s</sub> Cl	ОН	oĸ
-Menthyl	-239	-345 • 6	-260 • 5	(-313)	-290	-250	-292	(-299)	-246
-Octyl	-77.8	-163.0	-88.3	-21	-63 . 7	-31 .7	-68.5	-105	+24.4

As may be sceen, the ionisation produces a marked effect on the fotation: a positive charge raising the rotation and a negative charge lowering the value. The abnormally high rotations of  $\ell$ -menthyl anthranilate and  $\ell$ -menthyl salicylate have been ascribed to

chelation (loc. cit.) which is assumed to occur less readily with octyl esters since we have a completely different type of structure, viz., an open octyl chain as compared with the rigid menthyl ring. Further evidence of the powerful effect of ionisation is shown by the reversal of sign undergone by many optically active acids and bases when converted into their salts. Ionisation of the amino group in certain amyl alcohol derivatives also produces a well-marked reversal in the sign of the rotations:-

TABLE IX.

Amyl derivatives C<sub>5</sub>H<sub>11</sub>X.

14 4

x	·NH3	COSH	I	Et	Br	Cl	OMe	ОН	NHg
[M] 5461	+11.5	+10.5	+11.17	+6.2	+5•6	+1.8	+0 •41	-5.1	-5.2

At the one end of the series, which is of the general polar type, we have the positively charged (electron attracting) ionic complex NH<sub>3</sub> and at the other the electropositive (electron repelling) amino group.

An examination of the variations undergone by active amino acids in alkaline, neutral, and acid solutions, supports the above views regarding the definite influence of ionisation.

An extensive study of the influence of

saturated and unsaturated groups, and in particular the influence of phenyl groups, has been made by Rupe, Hilditch, Frankland and others. Walden (Zeit. physikal. Chem., 20, 569, 1896) discovered that a double bond in close proximity to the asymmetric atom produces a powerful effect on rotation, while later Frankland (J.C.S., 1912, 101, 654) coheluded that the presence of unsaturation leads to an irregularity in the rotatory effect and not necessarily to an increased rotation.

An influence of an apparently different type was discovered by Frankland (J.C.S., 1899, 75, 368) in examining the molecular rotatory powers of a homologous series. Frankland observed that a periodic rise or fall in the rotation took place when the carbon chain contained five or a multiple of five carbon atoms. This "growing chain effect", which was later examined by Pickard and Kenyon (J.C.S., 1911. 99, 46), was explained by Frankland as being due to the chain returning upon itself, a view quite in accordance with Baeyer's Strain Theory and the commonly accepted views of stereochemistry. Similar conclusions were arrived at, for example, by Pickard and Macnicol (J.C.S., 1923, 123, 14) in investigating a series of octyl ethers and by Philips (ibid., p. 29) for the thers derived from benzyl methyl carbinol.

A further investigation into the "growing chain effect" has been carried out in the case of the aliphatic menthyl esters (Rule, Hay and Paul, J.C.S., 1928, 1347). According to the last authors, if the o-effect in the benzoic esters is transmitted through space. similar differences might be exhibited in the behaviour of growing chains possessing terminal groups of different types, e.g., the carboxyl and alkoxy groups. examined the two series of optically active esters of the menthyl n-alkoxy acetates and the menthyl hydrogen esters of n-dicarboxylic acids. Their results appear to show that the fifth carbon effect due to the return of the carboxyl group produces an opposite type of effect to that due to the return of the alkoxy group which is in agreement with the differences found for the ogsubstituted benzoic esters.

When the phenyl group is displaced away from the asymmetric carbon atom in the  $\ell$ -menthyl esters of aliphatic acids, its effect in increasing the rotation diminishes until it becomes less than that of an alkyl group, and finally the effect may even become negative. From the following table we see that the introduction of four methylene groups between the phenyl and menthyl groupings results in a big fall in the rotation, the greatest effect being observed at or about the fifth carbon atom.

## Molecular Rotations of $\ell$ -Menthyl Esters (Frankland, loc. cit.).

Ester	$[M]_{\mathbf{D}}$
CH3 . COOC 1 0 H 1 9	146 • 2 •
CHaCHa .COOC, oH, e	160 • 2
CH3.(CH5)8.COOC10H18	156.9
CH3 (CH2) 4000C10H19	157.7
CH; (CH2) 5 .COOC 10H18	157.7
CeHs .COOC10H18	236 • 5
CeH2.CH5.COOC10H10	185.0
CeHe.(CHE)E.COOCIOHIA	168.4
CeH; (CH2) 4 COOC10H19	107.0

The molecular rotation at the 4th carbon atom (-107°) is very much lower than that of the average aliphatic ester (-157°) and this may be regarded as further evidence in favour of a space effect, since a similar fall in rotation is observed when we introduce a phenyl group into the o-position in menthyl benzoate (Bretscher, Rule and Spence, J.C.S., 1928, 1493)

$$\begin{bmatrix} \mathbb{M} \end{bmatrix}_{D} = -239^{\circ}$$

$$\begin{bmatrix} \mathbb{M} \end{bmatrix}_{D} = -201^{\circ} \text{ (in benzene)}$$

Homee the introduction of a phenyl group into the o-position in the benzoate does not lead to an increase in the rotatory power as might be expected

from its cyclic and conjugated unsaturated character, but has the usual depressing effect of an o,p-directive grouping in this position.

When we examine the effect of substituting phenyl groups for the methyl hydrogen atoms in menthyl esters of acetic acid we observe the depressing effect of the unsaturated nucleus in the low rotatory power of the triphenyl acetate (Rupe, Trans. Faraday Soc., 1914, 10, 46).

	$[\alpha]_{\mathbf{D}}$	$[M]_{\mathbf{D}}$
CH3 · CH2 · COOC 10H19	-75.51	-1\$0.2
CeHs *CH2 *COOC10H19	-67.57	-185·1
(CeHs) CH · COOC 10H10	-66 • 70	-226.8
(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> C • COOC <sub>19</sub> H <sub>19</sub>	- 3.44	- 14.6 (in toluene)

The work of this thesis deals with the changes in the rotatory powers of esters and ethers of the type  $R \cdot 0 \cdot COCH_3$  and  $R \cdot 0CH_3$ , which occur when the hydrogen atoms of the methyl group are successively replaced by phenyl radicals. Derivatives of  $\ell$ -menthol and  $\sec -\beta$ -octyl alcohol were examined in the greatest detail, but the triphenyl substituted derivative of d-borneol was also prepared for the purpose of comparison. The only complete example of this kind quoted in the literature is that of the  $\ell$ -menthyl esters of mono-, di-, and triphenyl acetic acids mentioned above.

#### EXPERIMENTAL.

The active  $\beta$ -octyl alcohol required for this investigation was obtained by resolving the racemic form by the method of Pickard and Kenyon (J.C.S., 1907, 2058; 1922, 2540). The octyl hydrogen phthalate had a rotatory power  $[\alpha]_{5461}^{20}$  =  $^{\pm}58.^{\circ}3$  to  $^{\pm}58.^{\circ}6$  (in alcohol, c=5), and gave a homogeneous octyl alcohol with  $[\alpha]_{5461}^{20}$  =  $^{\pm}9.6^{\circ}6$ . The  $\ell$ -menthol (B.D.H., "recrystallised") gave  $[\alpha]_{D}^{20}$  =  $^{-49.75^{\circ}}6$  in alcoholic solution (c=10).

## Triphenylmethyl $\ell$ -Menthyl Ether.

#### (a) Triphenylmethyl chloride.

A mixture of dry benzene (500 gm.) and dry carbon tetrachloride (175 gm.) was brought to the boiling point, and powdered aluminium chloride (120 gm.) added in small amounts so as to keep the reaction mixture boiling. When all the aluminium chloride had been added, the reaction was completed by boiling gently for an hour on the water-bath. On cooling. the mixture was poured on to crushed ice and well The benzene layer was separated off, washed with moderately concentrated hydrochloric acid, the acid removed by washing with water, and the dark green benzene solution dried over calcium chloride. The benzene was distilled off on the water-bath, and the residue, which solidified on cooling, was recrystallised from hot benzene, from which it separated in very fine white needles, m.p. 110°. Yield, 100 gm.

(Gomberg, Ber., 33, 3144, quotes 105 - 110°).

(b) Triphenylmethyl  $\ell$ -Menthyl Ether (Schmidlin, Ber., 45, 3188, 1912).

Well-dried triphenylmethyl chloride (14 gm.)
was dissolved in pure dry pyridine (46 gm.), menthol (20 gm.)
added, and the mixture heated for four hours at 100°

on an oil-bath. On cooling, the contents of the flask were poured into cold water (600 c.c.) and stirred vigorously, when a pale yellow oil was precipitated. This was washed three times with dilute hydrochloric acid to remove pyridine, and the resulting yellow solid was dissolved in ether. The ethereal layer after washing with moderately concentrated hydrochloric acid to remove the last traces of pyridine, was allowed to stand over calcium chloride. On removing the solvent, a pale yellow solid remained which was crystallised from hot ethyl alcohol.

Yield of pure ether, 15 gm., m.p. 136°. (Schmidlin, loc, cit., records 135 - 136°). The rotation in benzene (c = 5) was unchanged on further recrystallisation.

#### Analysis:

Found: H = 8.52%, C = 87.54%  $C_{89}H_{34}O$  requires H = 8.54%, C = 87.44%Rotatory Power.

The observed and molecular rotations are given in the table on the following page.

## Observed Rotations.

Solvent	c	l(mm.)	t°C	Œ 6708	α 5893	a 5461	a 4358
Benzene	5.670	100	11	-5*20	-6 • 73	-7.83	-13.78
Acetone	4.624	100	18.5	-4.04	-5-27	-6.50	-10.53
Ethyl acetate	4.706	100	18.5	-3.95	-5.12	-6.13	-9.76

## Molecular Rotations.

Solvent	[M]8708	[M] sees	[M]s481	[M]4358 ·
Benzene	-365	-473	<b>-</b> 550	-968
Acetone	-348	-454	-532	-881
Ethyl acetate	-335	-434	-518	-826

## Triphenylmethyl $\ell$ - $\beta$ -Octyl Ether.

manner in the l-menthyl ether, using 10 gm. octyl alcohol, 9 gm. triphenylmethyl chloride, and 23 gm. of pyridine. After removing the excess of octyl alcohol under diminished pressure a yellow semi-solid mass remained, which deposited very fine crystals on standing. These crystals were separated and found to melt at 159°C, which is the melting-point of triphenyl carbinol. The remaining liquid was distilled under reduced pressure and the fraction boiling at 178° under 0.28 mm. collected. If this ether is allowed to stand in contact with moist air a crystalline precipitate of triphenyl carbinol gradually appears. Yield of pure ether, 6 gm.

#### Analysis:

Found: H = 8.59%, C = 87.00% $C_{27}H_{32}O$  requires H = 8.66%, C = 87.06%

#### Density Determination.

The density of the liquid was determined at 16.5°, the temperature at which the rotations for the homogeneous liquid were measured.

D 4 = 1.0262.

Rotatory Power. /

#### Rotatory Power.

The succeeding page contains a table of the observed and molecular rotations. In order to see if the ether combined additively with hydrogen chloride, the rotation of the triphenylmethyl l- $\beta$ -octyl ether in alcohol was repeated, using alcohol containing an equivalent of hydrochloric acid. From the falling values obtained with the solution it was seen that hydrolysis was taking place, giving rise to l-octyl alcohol, and the solution had the strong odour of this alcohol on removal from the polarimeter tube. Owing to absorption no readings could be obtained for l-octyl alcohol on the homogeneous ether.

Solvent	c	l(mm.)	to	a <sub>6708</sub>	a5893	a5461	<b>4358</b>
Homogeneous	(D4 = 1.0262)	25	16*5		+4.107	+4*903	
Alcohol	5.714	100	16.5	+0*82	+1.110	+1 •41	+2*68
Benzene	3*566	100	16.5		+0 • 45	+0.54	+0.99

Molecular Rotations.

Solvent	[M]16.5	[M] 16.5	[N]16.5 5461	[M]18.5
Homogeneous	•	+59•6	+71.1	-
Alcohol	+54	+72	+92	+175
Benzene		+47	+57	+104

#### Triphenylmethyl d-Bornyl Ether.

Since the d-borneol (from British Drug Houses, Ltd.) probably contains a small amount of t-isoborneol, it was thought advisable to purify it. and an attempt was made, following the method of Ross and Somerville (J.C.S., 1926, 2773). The final product after drying carefully gave [a] 16 = +16.3 in alcohol (c = 5), so that in the process of purification the product had become isomerised, probably during the heating with zinc chloride. As the d-bornyl ether was only required to determine whether the triphenylmethyl derivative had an abnormally low rotation - as was found for the 1-menthyl ether - the original borneol was used, for which  $[a]_D^{17} = +30.5$  in alcohol (c = 5). (Ross and Somerville, loc. cit., quote  $[a]_D^{18} = +37.1$ in toluene (c = 8) for the purified compound). method of procedure was similar to that for the l-menthyl and l-octyl ethers, using 20 gm. d-borneol, 14 gm. triphenylmethyl chloride, and 46 gm. pyridine. The white crystalline solid obtained was recrystallised for methyl alcohol. Yield of ether, 10 gm. M.p. 116°.

#### Analysis.

Found: H = 8.30%, C = 87.65%

CsoHoso requires H = 8.15%, C = 87.82%

Rotatory Power.

The observed and molecular rotations are given on the following page.

## Observed Rotations

Solvent	c	L(mm.)	t°	G6708	a <sub>sgs</sub>	05461	a4358
Benzene	4.952	100	19	+1.80 (e=5.18)	+2-37	+2*80	+4.81
Ethyl acetate	4.514	100	19	+1*07	+1*88	+2*20	+3*84
Acetone	4.448	100	19	+1*23	+1.78	+2-15	+3 • 56

## Molecular Rotations.

Solvent	[N] 19 6708	[M] 10 5803	[N] 5461	[M]4358
Benzene	138	190	225	385
Ethyl acetate	94	165	193	337
Acetone	109	159	191	317

## Diphenylmethyl L-Menthyl Ether.

#### (a) Preparation of Benzhydrol.

Phenyl magnesium bromide was prepared by treating freshly-distilled bromobenzene with magnesium ribbon (dried for four hours at 110 - 120° in the air-oven) in ether which had been dried over sodium. Breshly-distilled benzaldehyde was added in small amounts in ethereal solution and the mixture well shaken. After all the benzaldehyde had been added the solid compound obtained was decomposed by treating with concentrated hydrochloric acid, and the green ethereal layer separated off and dried over anhydrous potassium carbonate. The ether was distilled off on the water-bath and the solid compound crystallised from hot ligroin. M.p. 68°.

(Tschelinzeff, Ber., 37, 4539, quotes 67°.)

#### (b) Preparation of Diphenylmethyl chloride.

Pure dry benzhydrol (14 gm.) was dissolved in dry benzene (100 c.c.) and some fused calcium chloride added to take up the water produced in the reaction. The solution was kept boiling gently while a stream of dry hydrochloric acid gas was passed in; the reaction being complete in about two hours. The benzene layer was separated from the calcium chloride, the solvent distilled off on the oil-bath,

and the remaining liquid distilled under reduced pressure. The colourless liquid distilling between 155 - 157°/12 mm. was collected. Yield, 14 gm.

## (c) Preparation of Diphenylmethyl &-menthyl ether.

Sodium (1.2 gm.) was added to excess of menthol (20 gm.) dissolved in toluene, and the mixture kept gently boiling until all the sodium had disappeared. Diphenylmethyl chloride (14 gm.), dissolved in toluene, was added, and the mixture boiled gently for eight hours on an oil-bath at 120°. The sodium mentholate reacted with the chloro-compound, giving sodium chloride and the other. A slow evolution of hydrochloric acid gas took place, due to the action of menthol on diphenylmethyl chloride. On cooling, the liquid was dissolved in ether, the ethereal layer was separated from sodium chloride and acid by washing with water, and was then dried over calcium chloride. The ether and toluene were distilled off and the excess of menthol removed by distillation under reduced pressure. The reddishyellow oil obtained solidified on cooling, and was crystallised from hot methyl alcohol, giving fine white needles of the ether, m.p. 67°. Yield of pure ether, 15 gm.

#### Analysis.

Found: H = 9.34%, C = 85.50%  $C_{23}H_{30}O$  requires H = 9.38%, C = 85.64%

## Rotatory Power.

A table of the observed and molecular rotations is given on the following page.

## Observed Rotations.

Solvent	c	l(mm.)	t°	C.6768	α <sub>5893</sub>	a <sub>5461</sub>	a4358
Benzene	5.106	200	17	-1.5*01	-19.87	-23 • 70	-41.15
Ethyl acetate	5*090	200	17	-13-29	-17.75	-21.10	-36*53
Acetone	5.070	200	17	-12*95	-17-13	-20.44	-35-13

## Molecular Rotations.

Solvent	[1]27 [2708	[H 17 5892	[M] 17 5461	M 4358
Benzene	-474	-627	<b>-74</b> 8	-1299
Ethyl acetate	-421	-562	-668	-1157
Acetone	-412	-545	-650	-1117

### Diphenylmethyl $\ell$ - $\beta$ -Octyl Ether.

This compound was prepared in a similar manner to the menthyl ether, using potassium octyloxide (obtained by dissolving 2 gm. potassium in 10 gm. octyl alcohol contained in toluene) and diphenylmethyl chloride (15 gm.). Much difficulty was encountered during the preparation of the pure octyl ether, however, and it was only after a number of experiments had been carried out that sufficient of this compound was obtained.

In the preparation of this ether it was found that on removing the excess of octyl alcohol under diminished pressure a crystalline solid was deposited on the sides of the flask. In the first experiment this solid also appeared in the liquid after distillation. These crystals were filtered off, dried on porous plate, and found to melt between 215 and 220°, which indicated that the substance might be tetraphenyl-ethylene (m.p. 221°), since diphenyl-methyl chloride is known to decompose at high temperatures to give tetraphenyl-ethylene and hydrochloric acid:-

 $2(C_6H_5)_2GH \cdot C1 \longrightarrow (C_6H_5)_2C = C(C_6H_5)_2 + 2HC1$ The liquid distilling at  $169^\circ/0 \cdot 1$  mm. from the first preparation (preparation A) was collected, and this gave a rotation  $a_{5461}^{26} = -1.13$  in the homogeneous state. On a single redistillation the value rose to  $a_{5461}^{20} = -1.41$ . Yield, 3 gm.

A number of experiments were carried out varying the conditions, but without leading to better results.

- (B) Inactive octyl alcohol (13 gm.) was added to diphenylmethyl chloride dissolved in pyridine (50 c.c.), and the mixture heated for some time. This method, however, was discarded, as the diphenylmethyl chloride reacted vigorously with the tertiary base pyridine to give an additional compound.
- (6) In this experiment potassium octyloxide was added to diphenylmethyl chloride dissolved in ether, and the mixture heated for twenty-five hours at 35 40° on a water-bath, but no yield whatever was obtained.
- (D) The reaction was carried out again under similar conditions to the first preparation, employing active potassium octyloxide prepared from 15 gm.

  l-β-octyl alcohol and 1.7 gm. potassium, but using a smaller proportion of diphenylmethyl chloride (7 gm.). The octyl ether obtained in this case gave

  conditions was widely different from that obtained in (A), a further amount was prepared under the same conditions. The liquid boiling at 202.5°/10 mm.

was collected and found to be of the same rotation as that from the previous preparation <u>D</u>. The two yields were mixed and purified. Yield of pure ether, unchanged by further fractionation, 3 gm.

Density Determinations gave D47 = 0.9675

#### Analysis.

Found: H = 9.60%, C = 84.83%

 $C_{21}H_{23}O$  requires H = 9.52%, C = 85.08%

#### Rotatory Power.

The observed and molecular rotations are contained in the table on the following page.

#### 6

## Observed Rotations.

Solvent	c	l(mm.)	t°	<b>G</b> 6708	a <sub>5893</sub>	a <sub>5461</sub>	04358
Homogeneous	$(D_4^{17} = 0.9675)$	25	17	-7-24	-9.62	-11.34	-20,10
Benzene	4.369	100	17	-1-23	-1.53	-1.82	-3.36
Ethyl alcohol	6*263	100	17	-1.52	-1.92	-2.59	-4.08

## Molecular Rotations.

Solvent	[M] 17 0708	[M] 17 5895	[M] 17 8461	[M]17
Homogeneous	-88•7	-117.7	-138.9	-246 • 2
Benzene	-83	-103	-123	-228
Ethyl alcohol	-72	-91	-108	-193

## $\ell$ - $\beta$ -Octyl Benzyl Ether.

Benzyl chloride was freshly distilled and the portion boiling at 175° collected. Fifteen grams were dissolved in toluene and potassium octyloxide (prepared from 2 gm. potassium and 11 gm. l-octyl alcohol) added. The mixture was heated at 110° on the oil-bath for two hours, when the flask became filled with a white precipitate of potassium chloride. This was filtered off and the toluene and excess of benzyl chloride distilled under diminished pressure. The benzyl octyl ether subsequently distilled over at a constant temperature of 154°/18 mm. Yield, 6 gm. The mixture of toluene, benzyl chloride and octyl alcohol which was collected before the ether distilled was treated with a gram of potassium, when a further quantity of benzyl octyl ether was obtained boiling at 147-148°/12 mm. Total yield of pure ether, 10 gm.

Density Determinations gave  $D_4^{20} = 0.8974$ Analysis.

Found: H = 10.80%, C = 81.70% C<sub>18</sub>H<sub>84</sub>O requires H = 10.98%, C = 81.74% Rotatory Power.

Observed and molecular rotations given on the following page.

# Observed Rotations.

Solvent	c	l(mm.)	t°	C6708	a <sub>5893</sub>	a <sub>5481</sub>	a4388
Homogeneous	$(D_4^{29} = 0.8974)$	50	20	-9*33	-12-24	-14.55	-24.56
Benzene	5.002	200	20	-2.09	-2.67	-3*08	-5*25
Ethyl alcohol	4.799	200	20	-1.85	-2.35	-2.78	-4.76

# Molecular Rotations.

Solvent	[M] 80 6708	[M]20 5693	[M] 5461	[M]4358
Homogeneous	<b>-45</b> *8	-60-1	<b>-71 ·</b> 3	-120 -4
Benzene	-46.0	-59°0	-68.0	-116.0
Ethyl alcohol	-42*0	-54.0	-64.0	-109.0

## $\ell$ - $\beta$ -Octyl Phenylacetate.

#### (a) Preparation of Phenylacetic acid.

was heated gently with 300 gm. of a mixture of three volumes concentrated sulphuric acid and two volumes water until bubbles of steam were evolved, when the heating was stopped. The reaction then proceeded vigorously, steam and unchanged benzyl cyanide being evolved and trapped by leading into water. The cold product separated into two layers, the lower being concentrated sulphuric acid. Addition of water precipitated the phenylacetic acid which was filtered at the pump. On crystallisation from hot water, q quantitative yield of acid, m.p. 74.5°, was obtained. (Houben, Kesselkaul, Ber., 35, 2523, quote m.p. 75°).

## (b) Preparation of Phenylacetyl chloride.

Twelve grams of the acid were heated with excess of thionyl chloride for four hours at 120° on an oil-bath. After removal of the thionyl chloride, under reduced pressure, the residual liquid was distilled, giving a colourless liquid, b.p. 94°/10 mm. (Rupe, Ann., 369, 330, quotes 101°/16 mm.)

Yield, 8 gm.

## (c) Preparation of l-β-octyl phenylacetate.

Phenylacetyl chloride (8 gm.) was added to \$\ell\$-\$\sigma\$-octyl alcohol (8 gm.) in pyridine (20 gm.) and the mixture heated for four hours at 120°. The liquid was extracted with ether, the extract washed with water and alkali, and dried over calcium chloride. The ether was distilled, excess of octyl alcohol removed under diminished pressure, and the liquid boiling at 173 - 175°/12 mm. collected. The ester was obtained as a yellow liquid which still retained its colour on further fractionation, b.p. 174°/12 mm. Yield of purified ester, 6 gm.

Density Measurements gave D4 = 0.9578

#### Analysis.

Found: H = 9.81%, C = 77.12%  $C_{10}H_{84}O_{8}$  requires H = 9.75%, C = 77.35%

#### Rotatory Power.

The table of observed and molecular rotations is given on the following page. No readings could be obtained for  $\lambda_{4388}$  with the homogeneous ester, owing to absorption.

## Observed Rotations.

Solvent	c	l(mm.)	to	C8708	α5893	a <sub>5461</sub>	C4858
Homogeneous	(D4 = 0.9578)	50	20	-13.07	-16.73	-20.16	-1-
Benzene	4.900	100	20	-0*39	-0.49	-0.61	-1.37
Ethyl alcohol	5*168	100	20	-0*88	-1.27	-1.49	-2.36

# Molecular Rotations

Solvent	[M]20 6708	[M] 80 8895	[M] 80 8461	[N] 20 4358
Homogeneous	-33•9	-43 • 4	<b>-52</b> •3	-
Benzene	-20.0	-25.0	-31.0	-70
Ethyl alcohol	-42.0	-61.0	-72*0	-113

#### d-β-Octyl Diphenylacetate.

#### (a) Preparation of Diphenyl-acetic acid.

Fifty grams of benzilic acid (m.p. 150°), 12 - 13 gm. dry red phosphorus, 12 - 13 gm. of hydriodic acid (constant boiling, 125 - 130°), and 200 gm. glacial acetic acid were heated together on a water-bath for an hour. The mixture was filtered hot into a large beaker containing water, when the acid was precipitated as a yellowish-grey substance. This was filtered off, dissolved in hot glacial acetic acid, and the solution filtered hot into cold water, when the acid separated in colourless crystals, m.p. 144°. This product contained no benzilic acid, since addition of concentrated sulphuric acid gave no violet coloration. Recrystallisation from hot ethyl alcohol gave fine colourless needles, m.p. 146°. (Symons, Zincke, Ann., 171, 126, quote 145 - 146°). Yield, 33 gm.

## (b) Preparation of Diphenyl-acetyl chloride.

Well-dried diphenyl-acetic acid (16 gm.) and thionyl chloride (24 gm.) were heated together on the oil-bath until the evolution of hydrochloric acid gas had ceased (2 hours). After removing the

the excess of thionyl chloride under diminished pressure a pinkish-brown crystalline mass remained.

#### (c) Preparation of d-β-Octyl diphenylacetate.

The above mass was dissolved in pyridine (20 gm.) and d-\$\beta\$-octyl alcohol (12 gm.) added, when copious fumes of hydrochloric acid were evolved and pyridine hydrochloride was thrown out of solution. The reaction was completed by heating for four hours at 110 = 120°, and the mixture cooled and extracted with ether. The ethereal layer, after drying and purifying in the usual manner, was distilled, finally under reduced pressure. The ester was obtained as a colourless liquid boiling at 221°/17 mm. Yield of pure ester, 20 gm.

Density determinations gave D4 = 0.9974.

## Analysis.

Found: H = 8.80%, C = 81.44%

CasHasOs requires H = 8.69%, C = 81.43%

#### Rotatory Power.

The table of observed and molecular rotations is given on the following page.

# Observed Rotations.

Solvent	C	l(mm.)	to	a <sub>3798</sub>	Œ5893	C5482	a4358
Homogeneous	$(D_4^{15.5} = 0.9974)$	100	15.5	+16*3	+21.68	+26.05	+45 • 48
Benzene	5.910	100	20	+0.53	+ 0.72	+ 0.87	+ 1.58
Ethyl alcohol	5*386	100	14	+1.30	+1.65	+ 1.98	+ 3*65

# Molecular Rotations.

Solvent	[M]8708	[M]sees	[M]5461	[M]4356
Homogeneous	+53 • 0	+70.5	+84 • 7	+147.8
Benzene	+29.0	+39.5	+48.0	+ 85.0
Ethyl alcohol	+73*0	+99•0	+119.0	+220 • 0

#### d-β-Octyl Triphenyl Acetate.

#### (a) Preparation of Triphenyl-acetic acid.

Well-dried triphenyl-methyl chloride (33 gm.) was mixed with magnesium turnings (5 gm.) which had been thoroughly washed with other to remove grease, and then doried for 3 - 4 hours at 100°. mixture was placed in a 500 c.c. flask, fitted with a cork bearing a mercury seal and stirrer, a reflux condenser, a small glass tube for addition of ether, and a wide glass tube bent at right angles through which carbon dioxide was passed into the mixture. A rapid stream of dry carbon dioxide was passed into the flask, and when all the air had been displaced 300 c.c. of dry ether were added. The mixture was well stirred and the flask warmed gently on the waterbath, when the triphenyl-methyl chloride went into solution. The experimental details given by Schmidlin and Hodgson (Ber., 39, 634) were found to be incomplete, and great trouble was encountered in the formation of triphenyl-methyl magnesium chloride. This difficulty was overcome after a number of experiments and the above conditions arrived at. conditions have since been worked out by Gilman and Zoelnner (J. Amer. Chem. Soc., 1929, 51, 3493).

The stream of CO2 was stopped when the

flask was filled with a lemon-yellow precipitate which occurred after about four hours. The contents of the flask were then allowed to cool, and decomposed by pouring into a large quantity of water with vigorous stirring. Excess of magnesium was decomposed by addition of hydrochloric acid, and the yellow solid was filtered off and washed thoroughly with water. The crude triphenyl-acetic acid was powdered in a mortar and boiled with the requisite amount of sodium hydroxide (600 c.c. of 10% NaOH and 300 c.c. water) whereby the greater part of the substance went into solution. Cold water (900 c.c.) was now added and the cold solution filtered from the insoluble matter, consisting of triphenyl methane and insoluble magnesium compound. To the clear solution of the sodium salt a slight excess of concentrated hydrochloric acid was added, when a white flocculent precipitate of somewhat colloidal nature was obtained. This was converted into a crystalline powder by boiling the solution for some time. powder was filtered off and recrystallised from glacial acetic acid, when it was obtained in the form of glistening needles, m.p. 263° (Schmidlin quotes 263 - 265°). Yield, 27 gm.

(b) Preparation of Triphenyl-acetyl chloride.

Triphenyl-acetic acid (20 gm.), after being

in an air-oven, was boiled gently for twenty minutes with the equivalent by weight (15 gm.) of phosphorus pentachloride and five parts by weight (50 gm.) of phosphorus oxychloride. After cooling, the mixture was poured on to crushed ice. The white oil which separated became solid on vigorous stirring. This was washed thoroughly with water to remove phosphorus compounds, dried on porous plate, and finally by standing over sulphuric acid in a vacuum dessicator. Yield, 20 gm.; m.p. 126 - 127°.

(Bistrzycki and Landtwing, Ber., 41, 687, quote 128 - 129°).

#### (c) Preparation of d-β-Octyl Triphenylacetate.

Potassium octyloxide was prepared as before, 18 gm. d-β-octyl alcohol and 2.5 gm. potassium being used. The cold potassium octyloxide solution in toluene was treated with triphenylacetyl chloride (20 gm.). A great evolution of heat occurred and the chloride passed into solution followed immediately by a bulky precipitation of potassium chloride. The reaction was completed by heating for half an hour at 120° on an oil-bath; the mixture cooled and ether added. The ethereal layer was washed in the usual way and dried over calcium chloride. After distilling off ether and toluene, the excess of octyl alcohol

was removed under diminished pressure. The remaining liquid was distilled, giving a pale yellow viscous liquid, b.p. 206°/0.03 mm. Yield, 14 gm. The rotation in benzene was unchanged on further fractionation.

#### Analysis.

Found: H = 8.00%, C = 83.80% $C_{88}H_{38}O_{2}$  requires H = 8.06%, C = 83.92%

#### Rotatory Power.

The table of observed and molecular rotations is given on the following page. It was found impossible to obtain readings with the homobeneous liquid, owing to a slight persistent cloudiness.

## Observed Rotations.

Solvent	e	l(mm.)	to	a <sub>6708</sub>	a <sub>5895</sub>	a <sub>5461</sub>	<b>4358</b>
Alcohol	5 • 576	200	20	+0.77	+0*92	+1.14	+1.78
Chloroform	5 • 234	200	20	+0*60	+0.76	+0.92	+1.46
Acetone	5.030	200	20	+0.54	+0.71	+0.87	+1*40
Benzene	5.371	200	20	+0.03	-0.02	-0.06	-0.16
Carbon disulphide	5.460	200	20	-0.66	-0.92	-1.19	-2.58

## Molecular Rotations,

Solvent	[M] <sub>6708</sub>	[M] <sub>5893</sub>	[M] <sub>5481</sub>	[M]4358
Alcohol	+28	+33	+41	+64
Chloroform	+23	+29	+35	+56
Acetone	+21	+28	+35	+56
Benzene	+ 1.3	- 0.6	- 2	- 6
Carbon disukphide	-24	-34	-44	-94

#### DISCUSSION.

"The presence of unsaturation leads to an irregularity in the rotatory effect and not necessarily to an increased rotation." This statement from Frankland's Presidential Address (J.C.S., 1912, 101, 654) is so worded in order to take account of the abnormally low rotatory power obtained for certain unsaturated compounds, particularly phenyl derivatives in which there are unsaturated groupings in close proximity to the asymmetric complex. The presence of these phenyl groups had been expected to increase the rotation, as was to be anticipated from the cyclic and conjugated unsaturated nature of the benzene nucleus. On the contrary, in the menthyl ester of  $\beta$ -phenyl-cinnamic acid,  $[M]_D = -137^{\circ}$ , where there is a heavy accumulation of unsaturated groups, we encounter an unusually small rotation for a menthyl ester of this type. This low rotation produced by the accumulation of unsaturated groups is also observed in an even more pronounced degree in the menthyl ester of triphenyl acetic acid. successively substitute phenyl groups for the methyl hydrogen atoms in the parent acetic ester, the first

effect is to increase the rotatory power. But in the triphenyl acetate the depressing effect of the three unsaturated nuclei is so powerful that there is actually a reversal in the sign of the rotation in some solvents. (Rupe, loc. cit.).

Since the influence of electronegative groups in the acetic acid molecule has been found to increase the rotatory power of \( \ell \)-menthyl and sec-βoctyl esters (Rule and Smith, loc. cit.) it would be expected that the optical changes in the phenyl substituted esters would go hand in hand with corresponding changes in the strengths of the acids. general considerations, the effect of replacing a methyl hydrogen atom by a phenyl group in acetic acid would be supposed to increase the strength of the acid. This is actually the case with phenyl acetic acid (k = 5.3 × 10 ), which is a much stronger acid than acetic acid (k = 1.86 × 10 ). Hence we would expect the dissociation constant to be largely increased by the introduction of two phenyl groups, whilst the presence of three such radicals would still further enhance the value. On reference to the literature we find that although no quantitative measurements are recorded, the trisubstituted acid is definitely described as being a very weak acid by Elbs and Tolle (J. pr. Chem., 1895, 2, 32, 625).

Schmidlin and Hodgson (Ber., 41, 441) also comment upon the weakly acidic properties, their conclusions being borne out by the fact that the salts are easily decomposed by hydrolytic dissociation, the solution of the sodium salt being strongly alkaline. Further, the latter investigators found it impossible to prepare a solution of the sodium salt of sufficient concentrations to separate triphenyl methyl by electrolysis, since the principal condition - a sufficiently high concentration - only leads in the case of triphenyl acetic acid to a decomposition of water.

The result of introducing phenyl groups into the molecule of  $\ell$ -menthyl acetate is shown in the following table of specific and molecular rotations.

TABLE I. (Rupe).

Compound	[a]D	$[M]_{\mathbf{D}}$
CH3 · CH8 · COOC10H19	-72.18	-156 • 9
CeHs · CHz · COOC10H19	-67.57	-185 • 1
(CeH2) CH . COOC 18H18	-66.70	-226 •8
(CeHs)3C.COOC16H18	- 3*44	- 14.6

Before discussing the results described in the experimental section of this thesis, the molecular

rotations and dispersion ratios observed for the different compounds may be summarised. Although the values for the mercury green line,  $\lambda_{5461}$ , can be more accurately determined than those for the D line, it is necessary to make use of the latter, since the corresponding values for the menthyl derivatives are the only ones recorded in the literature.

The octyl ester of phenyl acetic acid quoted in table II was actually obtained from  $\ell$ - $\beta$ -octyl alcohol, but in order to avoid confusion this is recorded here with change of sign as the d-ester.

Molecular Rotatory Powers, [M]<sub>D</sub>, of d-β-Octyl Esters of Substituted Acetic Acids, R.COOH, at approx. 20°.

R	CeH5 CH2 *	(CeHs)cH*	(CeHa)aC.
Homogeneous	+43 • 4	+70 • 5	•
Benzene	+25.0	+40 • 0	-0.6
Alcohol	+61.0	+99•0	+33
Chloroform	-	•	+29
Acetone	•	•	+28
CS <sub>2</sub>			-34

TABLE III.

Molecular Rotatory Powers, [M]<sub>D</sub><sup>29</sup>, of the Optically
Active l-β-Octyl Ethers, C<sub>8</sub>H<sub>17</sub>O·R.

R	Homogeneous	Benzene	Alcohol
CeHs · CH2 ·	- 60.1	- 59	-54
(CaHa)aCH.	-117.7	-103	-91
(CeHs)C.	+ 59*6	+ 47	+72

TABLE IV.

Molecular Rotatory Powers, [M]D, of the Optically Active &-Menthyl Ethers, C10H100 R.

R	Homogeneous	Benzene	Acetone	Ethyl Acetate
<sup>⊙</sup> C <sub>6</sub> H <sub>5</sub> ·CH <sub>2</sub> ·	-232.7		•	-
(CaHa) CH.		-627	-545	-562
(CoHs)aC.		-473	-454	-434

Tschugaeff, Chem. Zentr., 1902, [2], 1238.

For comparison, the values obtained for d-bornyl triphenyl methyl ether are given (the compound being prepared from borneol having  $[\alpha]_D = +30.5^{\circ}$  in ethyl alcohol).

TABLE V.

Molecular Rotatory Powers, M D, of Triphenylmethyl d-Bornyl Ether, (CeHs) 3C.OC, 0H, 7.

Solvent	Benzene	Acetone	Ethyl Acetate
M D	190	159	165

The values of the dispersion ratio  $\alpha_{5461}/\alpha_{5893}$  are given for all the above compounds in the following tables. It was found advisable to use this ratio instead of the more usual  $\alpha_{4358}/\alpha_{5893}$ , since the value  $\alpha_{4358}$  could not be employed throughout.

## TABLE VI./

TABLE VI.

Values of α<sub>5461</sub>/α<sub>5893</sub> for d-β-Octyl Phenylacetates.

Solvent	Homogeneous	Benzene	Alcohol
CaHs *CHz *COOCaH17	1.50	1.24	1.17
(CaHs) 2CH • COOC 8H17	1.50	1.50	1.50
(CeHs) 3C . COOC 8H24		3.35	1.25

TABLE VII.

Values of α<sub>5461</sub>/α<sub>5893</sub> for ℓ-β-Octyl Ethers.

Solvent	Homogeneous	Benzene	Alcohol
CeHa *CHa *OCeH17	1.19	1.15	1.18
(CeHa) 2CH .OC 8H14	1.18	1.19	1.19
(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> C·OC <sub>6</sub> H <sub>17</sub>	1.50	1.50	1.27

Values of  $\alpha_{5462}/\alpha_{5893}$  for  $\ell$ -Menthyl Ethers and d-Bornyl Ether.

Solvent	Benzene	Acetone	Ethyl Acetate
(CeHs)2CH •OC10H19	1.19	1.19	1.19
(CeHs) aC .OC 10H18	1.16	1.18	1.50
(CeHs) 3C .OC 10H12	1.18	1.50	1.17

#### Dispersion.

When the reciprocal of the rotation is plotted against the square of the wave-length it is found that deviations from the linear are very small for the majority of the compounds, as may be seen from the accompanying graphs. The dispersion ratios asas/assas vary from 1.15 to 1.27, except for triphenyl octyl acetate in benzene, for which the In the majority of cases the disvalue is 3.35. persion observed may be described as normal and simple. In some cases complex dispersion is exhibited. particularly for the d-bornyl ether in acctone and ethyl acetate solutions. With triphenyl octyl acetate in benzene solution, however, the rotatory dispersion is distinctly anomalous, as was also found to be the case by Rupe for the corresponding \( \ell \)-menthyl derivative. This abnormality is not unexpected, as the rotation is not far removed from zero in both these compounds, the specific rotations falling between the limits 0 and 13.5. Pickard and Kenyon (J.C.S., 1914, 105, 830) have commented upon the phenomenon of anomalous rotatory dispersion as occurring near these limits in esters of secondary alcohols.

According to Tschugaeff, (Ber., 45, 2759) who investigated the rotation dispersion of the

triphenyl menthyl acetate, this abnormal behaviour is connected with a selective absorption in the ultra-violet spectral region. Rupe (Ann., 395, 129) has shown this to be dependent on the great amount of unsaturated residue present in the molecule, because as was first established by Hartley ("Cotton Phenomenon", Ann. Chim. phys., 1896, [7], 8, 347), the direct condensation of three phenyl residues with a methane residue, in the formation of the group (CeHe) aC - , causes a displacement of absorption bands (in comparison with the single benzene derivatives) to the limit of the visible spectrum. With the \(l-\)bornyl and fenchyl esters of triphenyl acetic acid, however, this irregularity is not observed, for here the dispersion has been shown to be normal.

Effect of Solvents.

TABLE IX./

TABLE IX.

l-compounds	Et • OH	Acetone	Homogeneous	Ethyl Acetate	CHC13	CSs	CeHe	Toluene
(CgH <sub>5</sub> ) <sub>3</sub> C·COOCgH <sub>17</sub>	-33	-28		-	-29	+34	+0*6	•
(C <sub>8</sub> H <sub>5</sub> ) <sub>3</sub> C·OC <sub>8</sub> H <sub>17</sub>	+72	-	+59.6	-	-		+47	
(C6H2)3C.COOC10H18	-	-7		-	-19	+56	-	-15
Dielectric Constants	26.8	17.0	5 <b>-</b> 9 ®	6	5*2	2.6	2.3	2.3

① Tschugaeff (Ber., 45, 2759)

S Although quantitative determinations of the dielectric constants of the esters and ether have not been carried out, these probably fall between the limits, 5 - 9, by analogy with similar types of compounds, e.g., anisole (5.0), and ethyl acetate (6.0).

The marked influence of the triphenyl group on the rotatory powers of the octyl and menthyl esters and ethers investigated led to an examination of these compounds in various solvents. Although no definite rule is followed out, we see from a study of the foregoing table that the non-polar solvents, i.e., those of low dielectric constant, exert the greatest influence, the powerful depressing effect of the triphenyl group being clearly observed in benzene solution, whilst an actual reversal of the sign is exhibited in carbon disulphide. In the triphenyl octyl ester and ether the magnitude of the effect caused by the solvents is approximately in the order of their dielectric constants. In \( \ell \)-menthyl triphenyl acetate this agreement also holds approximately.

These results bear out the observations of Rule, Spence and Bretscher (loc. cit.) on the space effect of peri-substituents on the rotatory power of \( \ell-\text{menthyl l-naphthoate.} \)

## Influence of Substitution.

The results will be discussed with special reference to the general polar influence of the substituents as revealed in their effect upon the dissociation constant of an organic acid, and also from the point of view of the influence propagated directly through space.

#### Acidic Strength.

It was first attempted to deduce the polar effect of successively replacing the hydrogen atoms of the methyl group by phenyl radicals in esters and ethers of the type R.O.COCH, and R.OCH, from data referring to reaction velocity and acidity. Triphenylmethyl chloride dissolves in strongly dissociating solvents to give a yellow solution which conducts electricity well, giving values approximating to those of the quaternary ammonium salts. In this connection Straus and Hussy (Ber., 1909, 42, 2108) found that the successive replacement of a phenyl group of triphenylmethyl chloride by hydrogen diminishes the reactivity of the halogen to a very great extent. Since the degree of ionisation of halogen depends on the ease of transference of an electron from the adjoining carbon to the chlorine atom, it might therefore be assumed that the

introduction of phenyl groups leads to a shift towards the chlorine atom, thus facilitating the process:

CeHs · CH2 · Cl (CeHs) a CH · Cl (CeHs) a C · Cl

Direction of Electron Shift assisting ionisation.

The phenyl group, not only because of its size and weight, but also because of its unsaturated character, has a large effect in loosening neighbouring bonds. Three phenyl groups attached to a single carbon atom give the very extraordinary radical (CaHs) aC - which is capable of free existence and is never found firmly united to any other radical. Since the halogen atom of triphenylmethyl chloride possesses the power of attaching inorganic halides and other compounds to form highly coloured complexes (J. pr. Chem., 1921, [2], 103, 1) such as (CeH5) aC Cl, AlCls, this led Werner (Ber., 1906, 39, 1278) to the assumption that the three phenyl groups make such a demand on the affinity of the methane carbon atom that only a small surplus is left at the disposal of the fourth valency bond. Extending these views to triphenyl acetic acid, it will be seen that the carboxyl group is only loosely held by the triphenyl group, and according to the conclusion of Flurscheim (loc. cit.) this leads to a stronger linking between the carbon and oxygen and to a

weakening of the bond between the oxygen and the hydrogen, which should result in triphenyl acetic acid being a strong acid:  $(C_gH_g)_g$  C O H.

As has already been pointed out, on applying the modern idea of electron shifts in its simplest form, trisubstituted acid would be expected to have a very low dissociation constant, since ionisation depends on the ease with which an electron can be transferred from the carboxylic hydrogen to the adjacent oxygen, a movement in the opposite direction to that required for the ionisation of chlorine in triphenylmethyl chloride

(C<sub>5</sub>H<sub>5</sub>)<sub>3</sub>C - COO-----H

Direction of shift opposing ionisation.

This conclusion is apparently in agreement with the facts of experiment, for although no quantitative data for the dissociation constant of triphenyl acetic acid are available, it is recorded (loc. cit.) as being an exceedingly weak acid. Now from a study of the  $\ell$ -menthyl and sec- $\beta$ -octyl esters of monosubstituted acetic acids already discussed in the introduction of this thesis, it will be seen that the presence of a grouping which causes a shift of the electrons away from the asymmetric complex results in an increase in the rotatory power. A similar effect is observed in the following  $\ell$ -menthyl ethers.

TABLE X.
(Beilstein's Lexicon, Vol. VI, pp. 31 - 33).

# ←Menthyl Ethers, C<sub>1</sub> eH<sub>1</sub> eO • CH<sub>2</sub> • X in the homogeneous state.

	х	H	CHs	CaHs	CH3:CH · CH3	CoHs	COOC <sub>3</sub> H <sub>7</sub>	Cl
	[M]D	-163	179	183	193	233	234	353
k for	X . CH . COOH	1.8	1.4	1.5	2.1	5.3	45.1	155 × 10 <sup>5</sup>

The electron shift is towards the electronegative atom chlorine and thus away from the asymmetric complex, resulting in the chloromethyl menthyl ether having the greatest rotation and the corresponding acid having the largest dissociation constant. On this view. therefore, we would expect the negative rotation of the ethers and esters of  $\ell$ -menthol and  $\ell$ -octyl alcohol to be lowered by the presence of the triphenylmethyl group in the molecule. As will be seen from table II, in the sec-3-octyl esters of the substituted acetic acids the presence of the triphenylmethyl group causes a big depression when the rotatory power is measured in the solvents alcohol and acetone, whilst in benzene or carbon disulphide solution the influence of this group is so marked that there is a strong reversal of the sign of the rotation, particularly in the latter This change of sign due to the triphenyl group is very pronounced in the triphenylmethyl (-octyl ether, in which the rotation is reversed in all solvents.

It has been suggested by Forster and
Thornley (J.C.S., 1909, 95, 948) that accumulation of
identital radicals upon a carbon atom near the
asymmetric centre produces a kind of symmetry which
results in a diminution of rotatory power. In
support of this idea, Hilditch (Zeit. physikal. Chem.,
1911, 77, 486) quotes the following figures for
compounds in which the presence of two identical
groups linked to one and the same atom reduces the
optical activity.

#### TABLE XI.

Compound.	[ <u>w</u> ]	0
Benzylidene Camphor	R:CH·CeHs 1020	)
Phenylbenzylidene Car	mphor R:C(CoHs)2 907	7
Benzyl	" RH *CH <sub>S</sub> *C <sub>6</sub> H <sub>S</sub> 348	3
Diphenylmethyl	" RH • CH (CeHs) 2 197	7
Methyl Bornylamine	C10H17NH • CH3 160	)
Dimethyl "	C10H17N(CH3)2 108	3
Ethyl "	CloH17NH · CsHs 163	3
Diethyl "	C <sub>10</sub> H <sub>17</sub> N(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> 131	L

Although an increase in the rotatory power is observed in the above examples over that recorded for the corresponding less symmetrical compounds, this is not generally observed with other symmetrical

derivatives. For example, Rupe and Ahner (Trans. Farad. Soc., 1914, 10, 46) studied the substituted acetic esters and found that although the specific rotatory power diminishes slightly from the dimethyl to trimethyl acetic ester, the symmetry of the trimethyl acetic acid has no marked influence on the rotatory power of the asymmetric system.

TABLE XII.

Menthyl ester	[a] D	$[\mathtt{M}]_{\mathtt{D}}$	Dissociation Constant k
CH3 · CH2 · COOH	75.51	160.2	1.4 × 10 -8
(CHa) CH · GOOH	72.05	163 * 5	1.5 × 10 5
(CH <sub>3</sub> ) <sub>3</sub> C·COOH	67.30	161.5	0.98 × 10-5

Similar changes are observed in the rotatory powers of the n-, iso- and tert-butyl esters of mandelic acid investigated by Wood, Chrisman and Nicholas (J.C.S., 1928, 2180).

TABLE XIII.

Butyl esters	[α]D
CeH5 · CHOH · COO · CH2 · CH2 · CH2 · CH3	- 91.1
CeHs · CHOH · COO · CH2 · CH (CH3)2	-101.9
CeHs · CHOH · COO · C (CH3)3	- 78.0

All these results are in agreement with the general polar effect rather than with the symmetry hypothesis of Hilditch, since similar alternations are observed in the influence of the above butyl groups upon the dissociation constants of the corresponding valeric acids:

Valeric acids.	k			
CH3 · CH2 · CH2 · CH2 · COOH	1.60 × 10 -8			
(CHa)sCH·CHs·COOH	1.73 × 10 <sup>-6</sup>			
(CH <sub>3</sub> ) <sub>3</sub> C • COOH	0.98 × 10-5			

In addition, this view of Hilditch is not supported by the results of the present investigation, for the symmetrical triphenyl octyl ether has not merely a lower rotatory power of the same sign but exhibits a reversed molecular rotation of considerable magnitude. Also the rotatory power of the triphenylmethyl t-menthyl ether, although greatly diminished as compared with that of the diphenyl compound, is still much greater than that of the monophenyl derivative. With reference to the compounds in table XI, we see that the introduction of a second phenyl group results in a lowering of the rotation, whereas the reverse of this is found in the series of esters and ethers examined during the present investigation. influence of the (CeHs) aC - group, therefore, is not merely to lower but definitely tends to reverse the

sign of the rotation, a change which cannot be explained on the symmetry hypothesis.

powers of these esters and ethers, it was thought advisable to obtain some quantitative experimental evidence bearing on the strength of triphenyl acetic acid. The molecular conductivity of the mono-, diand tri- phenyl acetic acids was measured at different dilutions in 60% alcohol solution, on account of the very low solubility of the acids in water. Although the presence of the alcohol affects the ionisation of the acid, a comparison of the results which were obtained under similar conditions, shows the trisubstituted acid to be stronger than the mono or diphenyl derivative. The accompanying graph shows the order of magnitude of the acid strength to be

triphenyl > diphenyl > phenyl

The same order was found by employing a colorometric method of estimation.

The conclusions of Elbs and Tolle, and of Schmidlin and Hodgson (loc. cit.) are, therefore, incorrect, and the normal electron-attracting influence of the phenyl group must be assumed to

operate in the tri- as well as in the mono- and disubstituted acetic acids. An alternative view which
explains the behaviour of triphenylmethyl chloride
as well as that of triphenylacetic acid is that the
accumulation of bulky phenyl radicals around the
methane C-atom tends to hinder the recombination of
the ions in each case. A suggestion of this kind
was put forward by Flürscheim in a similar case.

It is therefore necessary to see whether some other explanation can be found for the low rotatory power of the triphenyl derivatives.

#### Space Effect of Substituents.

The abnormal effect produced by substituents on the rotatory power in the o-substituted benzoic esters has been attributed to the general polar effect of the group as transmitted through the chain being more than counterbalanced by the space effect of the phenyl group due to its proximity to the  $\ell$ -menthyl radical. This view is supported by numerous facts, particularly by the influence exerted by substituents in the peri-position in  $\ell$ -menthyl 1-naphtheate (Rule, Spence and Bretscher, J.C.S., 1929, 2516). The effect produced by a chlorine atom in the orthoposition in the  $\ell$ -menthyl and sec- $\beta$ -octyl benzoates or in the peri-naphtheates is the reverse of its

effect in the mono-substituted acetic esters or in the p-substituted benzoic esters. The chlorine atom lowers the molecular rotatory power in the ortho and peri compounds, whilst in the acetic esters it leads to an increase in the rotation.

Similarly, the introduction of a phenyl group into the ortho-position in menthyl benzoate results in a fall in the rotatory power,

$$[M]_D = -239^\circ$$
 $[M]_D = -201^\circ$  (in benzene)

instead of the more usual increase produced when a hydrogen atom is replaced by a phenyl group; thus

$$CH_3 \cdot COOC_{10}H_{19}$$
  $C_0H_5 \cdot CH_2 \cdot COOC_{10}H_{19}$   $[M]_D = -146 \cdot 2^{\circ}$   $[M]_D = -185^{\circ}$   $CH_5 \cdot COOC_{8}H_{17}$   $[M]_D = -11 \cdot 8^{\circ}$   $[M]_D = -43 \cdot 4^{\circ}$ 

A similar decrease has also been recorded at one particular point in the series of aliphatic esters studied by Rupe (loc. cit.), viz., in l-menthyl &-phenyl-valerate. In this compound we may suppose that the chain has returned upon itself and that in consequence the phenyl group approaches the carboxyl group in

space, evidence of which should be displayed in the molecular rotation of the menthyl ester. The space effect of the phenyl group here actually produces a remarkable lowering of the rotation, [M]D = -107°, as compared with the average fatty ester, [M]D = -157°, and [M]D = -185° for the phenyl substituted acetic ester above.

A study of tables I to IV shows that among phenyl substituted  $\ell$ -menthyl and sec- $\beta$ -octyl ethers and esters of the type under examination, the introduction of second phenyl group into the molecule results in every case in a rise in the molecular rotation. This increase in rotation follows the normal course of events, in that the electronegative phenyl group behaves in the same manner as other electronegative substituents, such as Cl. NO., COOH. It is only when a third phenyl group OMe, etc. is introduced into the molecule that any irregularity takes place, and then the depressing effect of the triphenyl group lowers the rotatory power to a value in general far below that of the monophenyl derivative. In the triphenyl compound there is an accumulation of bulky phenyl groups, which may be assumed to be forced into spatial proximity to the asymmetric earbon atom, resulting in a big decrease in the rotation similar to that observed with the -phenyl valerate or with the phenyl group in the ortho

position in 1-menthyl benzoate. This effect is greatest in the triphenyl octyl ether where the bulky phenyl groups are only separated from the asymmetric complex by an oxygen atom. In this case we have a very marked reversal of the sign of the rotation in all solvents.

In the corresponding \( \)-menthyl depivatives, however, we do not observe this powerful depressing effect of the three phenyl groups to the same extent, for although there is a considerable decrease in the rotation as compared with the diphenyl ether the value is still much greater than that observed for the monophenyl derivative. It is possible that the close packing of the phenyl groups in space affects unequally the partial rotations of the three asymmetric carbon atoms of the menthyl residue, and hence a secondary irregularity may result.

#### SUMMARY.

The investigation of a number of optically active menthyl and octyl esters and ethers of mono-, di- and tri-phenyl substituted derivatives has shown that whilst there is a progressive change as we pass from the phenyl to the diphenyl derivatives the direction of change is reversed when a third phenyl group is introduced. This irregularity can be best explained as a space effect, since a similar fall in rotation is observed with the  $\ell$ -menthyl ester of  $\delta$ -phenyl valeric acid and with the introduction of a phenyl group into the ortho position in  $\ell$ -menthyl benzoate.

The statements in the literature to the effect that triphenyl-acetic acid is a very weak acid are shown to be incorrect.

I take this opportunity of expressing my gratitude to Dr H. G. Rule whose wide practical knowledge and keen interest have been of exceptional value. To him also I am indebted for many helpful suggestions which have been greatly appreciated in this investigation.