CCII.—*Optical Activity and the Polarity of Substituent Groups. Part XIX.* l-*Menthyl Esters of Benzenesulphonic Acids, and of Benzoic Acids with Sulphur-containing* o-*Substituents.*

By H. Gordon Rule and Gordon Smith.

In so far as they have been examined, the rotatory powers of *l*-menthyl and β-octyl esters of substituted acetic acids vary with the polarity of the substituent, strongly electronegative groups producing the maximum rise in value and electropositive groups tending to bring about a fall. Similar results have also been obtained for octyl esters of *p*-substituted benzoic acids (*Trans. Faraday Soc.*, 1930, 321).

On the other hand, the menthyl and octyl esters of *o*-substituted benzoic acids present a number of unusual features. Although the highest rotations again result from the presence of the strongly electronegative nitro- and carboxyl groups, and electropositive groups in general cause a diminution in rotatory power, it has been observed that many substituents which are *o,p*-directive in benzene substitution also lead to low values, even when electronegative in type. Hydroxyl and occasionally the amino-group form exceptions to this statement, resulting in a very small rise which has been attributed to chelation with the ketonic group of the ester complex.

In order to obtain further evidence bearing on the abnormal behaviour of ortho-substituents, the *l*-menthyl esters have now been prepared of a number of methyl- and nitro-substituted sulphonic acids, and of benzoic acids containing the ortho-substituents SH, SMe, SO_2Me, $SO_2{\cdot}OH$, and $SO_2{\cdot}OMe$.

Sulphonic Esters.—The instability of *l*-menthyl benzenesulphonate (Patterson and co-workers, J., 1906, 332; 1927, 349) is repeated in the toluene- and nitrobenzene-sulphonic esters. The toluene derivatives do not decompose appreciably at the ordinary temperature, but the nitro-compounds are extremely unstable, decomposing rapidly at temperatures far below their melting points and darkening in a couple of days on standing at room temperature.*

An analysis of the rotatory powers shows the *o*- and *p*-toluenesulphonates to have normal and approximately simple dispersion, whilst that of the *m*- and *p*-nitrobenzenesulphonic esters is normal and complex. l-*Menthyl* o-*nitrobenzenesulphonate*, however, exhibits strongly anomalous dispersion, both in alcoholic and in benzene solution. The molecular rotations, $[M]_{5461}$, of these compounds are summarised in Table I; values for other wave-lengths of light will be found in the experimental section.

For the unsubstituted ester in alcohol, $[M]_{5461} = -250°$ (Patterson, *loc. cit.*).

The results obtained for the toluenesulphonates resemble those recorded by Cohen for the corresponding toluic esters. In each case a methyl group in the ortho-position brings about a slight depression in rotatory power. The somewhat low rotations of the

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* Prof. Patterson has informed the authors that he is continuing to investigate the thermal decomposition of these esters; the present communication therefore deals only with their optical properties.

TABLE I.

Values of $[M]_{5461}^{18^\circ}$ for *l*-Menthyl Esters of Substituted Benzenesulphonic Acids ($c = 5$).

	o-Compound.		*m*-Compound.		*p*-Compound.	
Substit.	EtOH.	C_6H_6.	EtOH.	C_6H_6.	EtOH.	C_6H_6.
CH_3	−228°	−202°	—	—	−247°	−214°
NO_2	−129	− 92	−232°	−204°	−231	−201

m- and *p*-nitro-derivatives also recall the properties of the *m*- and *p*-nitrobenzoic esters. On the other hand, the very high rotatory power of *l*-menthyl *o*-nitrobenzoate is not repeated in the case of the *o*-nitrobenzenesulphonic ester, the anomalous dispersion of which renders any comparison uncertain.

Ortho-substituted Benzoic Esters.—Among previously known esters of this type, *m*-directive groups (NO_2,CO_2H,COMe) were found to raise the rotatory power, whereas the majority of the *o,p*-directive groups led to a diminution. The values recorded in Table II for various sulphur-containing substituents reveal a number of further exceptions to this provisional classification.

TABLE II.

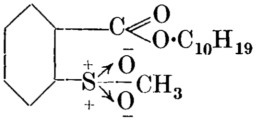
Values of $[M]_{5461}^{18^\circ}$ for *l*-Menthyl *o*-Substituted Benzoates.

Substituent ...	$S\cdot CH_3$	SH	*H*	$SO_2\cdot CH_3$	$SO_2\cdot O\cdot CH_3$	$SO_2\cdot OH$
In alcohol ...	−348°	−313°	*−275°*	−213°	−214°	−190°*
In benzene ...	−373	—	*−280*	−207	−191	—
Homogeneous	−372	—	—	−202	—	—

* This value was determined by adding hydrogen chloride to a solution of the potassium salt and does not represent the pure sulphonic acid.

Thus it will be seen that the *o,p*-directive groups $S\cdot CH_3$ and SH both bring about a considerable increase in rotatory power, and that the *m*-directive groups $SO_2\cdot CH_3$,$SO_2\cdot O\cdot CH_3$ and $SO_2\cdot OH$ result in a fall. Possibly co-ordination with the carboxyl group may contribute to the high rotation given by the thiol derivative, but the magnitude of the methylthiol value is in surprising contrast to the low rotation of *l*-menthyl *o*-methoxybenzoate.

Pending further information regarding the reason for these differences, the authors adopt an earlier suggestion (Rule, *Trans. Faraday Soc.*, 1930, 333) and assume that the effects are related to the electrical constitution of the substituent group and to its spatial disposition with respect to the asymmetric complex. The low rotation resulting from the presence of ·Cl, ·Br, ·I, $\cdot\overset{-}{O}$ or $\cdot CO\cdot\overset{-}{O}$ in the ortho-position has been attributed to the negative field exerted upon the menthyl complex by the negative end of the dipole present, or by the negative ionic charge. In all the above compounds containing the sulphone group, a dominant factor would similarly appear to be the electrical influence of the S→O dipoles, which will presumably resemble that exerted by the phenolic and carboxylic ions. As will be seen in the next section, this depressive effect is further reinforced by the ionic charge on the ionised sulphonic group. The high rotatory powers of the nitro- and non-ionised carboxylic derivatives are, however, not readily explained on this basis.



Influence of Ionisation.—Two of the benzoic esters under consideration, namely the thiol and sulphonic derivatives, may undergo changes connected with the ionisation of the substituent groups. The effect of such changes upon the rotatory power is shown below.

TABLE III.

Rotatory Powers in Alcohol, $c = 5$.

o-Substituent ...	SH	SK	*H*	SO_2·OMe	SO_2·OH*	SO_2·OK
$[M]^{18°}_{5461}$	−313°	−196°	*−275°*	−214°	−190°	−175°

* See Table II.

Ionisation of the thiol group thus converts an enhanced rotation into a diminished rotation, and, as was to be expected from the greater acidity of the group, the fall is of much greater magnitude than that undergone by the salicylic ester (Rule and McGillivray, J., 1929, 401), the molecular rotation $[M]_{5461}$ of which only drops from − 299° to − 246° on the addition of an equivalent of potassium ethoxide.

The lowest value recorded among the above compounds is that of the potassium sulphonate. After treatment of a solution of this salt with an equivalent of hydrogen chloride the rotation rises slightly, probably owing in the main to the formation of free sulphonic acid which is in a somewhat less complete state of ionisation. A much greater rise in rotation occurs when ionisation is suppressed by converting the sulphonate into the methyl ester. These changes are all in the direction to be anticipated from the properties of previously investigated menthyl and octyl esters of benzoic acids containing carboxyl and hydroxyl groups in the ortho-position (J., 1929, 401, 2274), among which it has been found that ionisation leading to the retention of a negative charge on the active ion invariably depresses the rotatory power.

Influence of Solvents.—In recent communications it has been indicated that the characteristic influence of a *peri*-substituent on the rotatory power of *l*-menthyl 1-naphthoate tends to be exhibited to the maximum degree in the presence of non-polar solvents, no matter whether the primary effect is to raise or lower the value (Rule, Bretscher, and Spence, J., 1929, 2516). Further, the influence of a large number of solvents on the rotatory power of *l*-menthyl methyl naphthalate has been found to vary with the polarity of the medium, the specific effect of the *peri*-substituent in raising the rotation being greatest in non-polar and least in highly polar solvents (Rule and McLean, this vol., p. 674).

No extended examination has been made of solvent influence in connexion with the esters discussed in the foregoing pages, but where possible the molecular rotation of each compound was determined in alcohol and benzene solutions.*

It is in agreement with the polar nature of these solvents that whether the ortho-substituents in Tables I and II raise or lower the rotatory power, the maximum change is observed in benzene solution. This generalisation holds without exception for the nine esters for which both measurements are available. In the case of the *o*-substituted benzoates it is probable that this regularity is due to the electrical influence of the ortho-groups upon the menthyl ester complex being diminished through association with alcohol (compare Rule and McLean, *loc. cit.*). But among the toluene- and nitrobenzene-sulphonates the differences in the molecular rotations for benzene and alcohol solutions respectively approximate to a constant value, and suggest that the solvent changes are to be traced to the strongly polar sulphonic group which is common to all the compounds. In the latter esters, therefore, the optical changes may be considered to be due primarily to association between alcohol and the dipoles of the sulphonic group.

The above relationship between the polarity of the solvent and the specific influence of the ortho-substituent appears to be repeated in the character of the dispersion. When the reciprocals of the rotations are plotted against the squares of the wave-lengths of the light employed, it is found that the deviations from the linear for the *o*-sulphomethoxy-derivative, which exhibits very complex dispersion, are more pronounced in benzene than in alcohol solution. Similarly the anomalous dispersion of *l*-menthyl *o*-nitrobenzenesulphonate is much more marked in benzene solution. The remain-

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* The present investigation was completed before the discovery of the above polar relationship.

ing esters show simple or only slightly complex dispersion, which is scarcely affected by the change of solvent. If, as has been assumed, the modifications in the optical properties are mainly due to the spatial influence of the ortho-substituent, it is to be expected that any anomaly in the dispersion will become more prominent in solvents of low polarity.

EXPERIMENTAL.

The following sulphonic esters were prepared from the corresponding acids by way of the acid chlorides and combination of the latter with *l*-menthol at a low temperature, pyridine being used as a condensing agent (Patterson and Frew, J., 1906, **89**, 332). The solids so obtained were purified by recrystallisation from methyl alcohol until of constant rotatory power. Patterson (*loc. cit.*) has already shown that esters of this type readily undergo decomposition.

l-*Menthyl toluene*-p-*sulphonate* was obtained from toluene-*p*-sulphonic acid, prepared by sulphonating toluene by the method of Rây and Dey (J., 1920, **117**, 1405). The ester separated in colourless needles, m. p. 91—92° (yield, 25%) (Found : S, 10·4. $C_{17}H_{26}O_3S$ requires S, 10·3%).

l-*Menthyl toluene*-o-*sulphonate*, from toluene-*o*-sulphonyl chloride, formed white prisms, m. p. 78° (yield, 50%) (Found : S, 10·4%).

l-*Menthyl* o-*nitrobenzenesulphonate* was obtained in a similar manner from potassium *o*-nitrobenzenesulphonate. This salt was prepared from *o*-chloronitrobenzene by converting it into *oo'*-dinitrodiphenyl disulphide by treatment with sodium disulphide and then oxidising the disulphide with nitric acid (Wohlfahrt, *J. pr. Chem.*, 1902, **66**, 551). The ester crystallises in white needles, m. p. 66° (yield, 20%). Signs of decomposition become evident after the ester has remained for 2 days at the ordinary temperature in air or in a vacuum desiccator (Found : S, 9·4. $C_{16}H_{23}O_5NS$ requires S, 9·4%).

l-*Menthyl* m-*nitrobenzenesulphonate* was prepared from sodium *m*-nitrobenzenesulphonate and isolated as a yellowish-white crystalline solid, m. p. 80°, which darkened slowly on standing (yield, 50%) (Found : S, 9·5%).

l-*Menthyl* p-*nitrobenzenesulphonate* was obtained from *p*-nitrobenzenesulphonic acid prepared in a similar manner to the *o*-compound (Wohlfahrt, *loc. cit.*). Recrystallisation gave fine white needles, m. p. 70·5° (yield, 40%) (Found : S, 9·5%).

l-*Menthyl* o-*thiolbenzoate*, prepared by direct esterification of *o*-thiolbenzoic acid in the presence of hydrogen chloride, was isolated as a liquid of greenish tint, b. p. 202—205°/0·2 mm., which oxidised very easily in air (yield, 10%) (Found : S, 11·2. $C_{17}H_{24}O_2S$ requires S, 11·0%).

l-*Menthyl* o-*methylthiolbenzoate*, prepared by the same method from *o*-methylthiolbenzoic acid (Friedländer, *Annalen*, 1907, **351**, 401), distilled as a pale greenish liquid, b. p. 210°/0·3 mm. (yield, 20%), slowly turning solid on standing; m. p. 48·5° (Found : S, 10·7. $C_{18}H_{26}O_2S$ requires S, 10·5%).

The l-*menthyl ester of* o-*carboxyphenylmethylsulphone.* Oxidation of *o*-methylthiolbenzoic acid in glacial acetic acid with hydrogen peroxide, and purification of the product from water, gave white needles of o-*carboxyphenylmethylsulphone monohydrate*, m. p. 73° (yield, 80%). After drying for 2 days at 130°, the anhydrous substance melted at 137° (Found for monohydrate : H_2O, 8·1 ; S, 14·7. $C_8H_8O_4S,H_2O$ requires H_2O, 8·2 ; S, 14·7%). The *ester*, prepared by direct esterification in presence of hydrogen chloride, formed a green-tinted viscous solid, distilling at 190—193°/0·2 mm. with slight decomposition (Found : S, 9·3. $C_{18}H_{26}O_4S$ requires S, 9·5%).

l-*Menthyl* o-*sulphobenzoate.* No yield of the desired ester could be obtained by heating *l*-menthol with *o*-sulphobenzoyl chloride (prepared from saccharin by the method of Kramich, *Ber.*, 1900, **33**, 3485). It was eventually prepared by treating the anhydride (15 g.) of *o*-sulphobenzoic acid (obtained by the action of acetyl chloride on the acid) with potassium menthoxide in warm toluene solution. The *potassium* salt of *l*-menthyl *o*-sulphobenzoate (7 g.) was extracted from the reaction mixture by shaking with water and purified by recrystallisation from methyl alcohol (Found : K, 10·3. $C_{17}H_{23}O_5SK$ requires K, 10·3%).

Methyl o-*carbomenthoxybenzenesulphonate*,

$$C_{10}H_{19}\cdot O\cdot OC\cdot C_6H_4\cdot SO_2\cdot O\cdot CH_3,$$

was prepared from the silver salt of the corresponding acid by treatment with methyl iodide. After removal of silver iodide, the acid filtrate was washed with sodium carbonate and dried with anhydrous sodium sulphate, and the excess of methyl iodide removed at the ordinary temperature under reduced pressure. The resulting pale yellow syrup was examined in the crude state, since considerable decomposition occurred when a portion was distilled under a high vacuum (Found : S, 9·3. $C_{18}H_{26}O_5S$ requires S, 9·0%).

Measurements of Rotatory Power.—The following observations were made at room temperature except those marked *, in which case the readings were taken at 70°. Where reference to hydrogen chloride or potassium ethoxide is made, one molecular equivalent was employed.

Solvent.	l.	c.	$[M]_{6708}$.	$[M]_{5893}$.	$[M]_{5461}$.	$[M]_{4358}$.
			l-*Menthyl toluene*-p-*sulphonate.*			
Alcohol	200	2·406	−165°	−215°	−247°	−399°
Benzene	200	5·002	−137	−182	−214	−353
			l-*Menthyl toluene*-o-*sulphonate.*			
Alcohol	200	2·865	−145	−196	−228	−376
Benzene	200	5·006	−132	−176	−202	−339
			l-*Menthyl* o-*nitrobenzenesulphonate.*			
Alcohol	200	4·995	−95·5	−115	−129	(−81·3)†
Benzene	200	5·006	−69·2	− 86·2	− 92·4	(−20·8)†
			l-*Menthyl* m-*nitrobenzenesulphonate.*			
Alcohol	200	1·006	−148	−198	−232	−371
Benzene	200	5·008	−132	−170	−204	−342
			l-*Menthyl* p-*nitrobenzenesulphonate.*			
Alcohol	200	4·565	−151	−195	−231	−372
Benzene	200	4·950	−131	−168	−201	−321
			l-*Menthyl* o-*thiolbenzoate.*			
Alcohol	100	4·856	—	—	−313	—
,, +KOEt	100	4·914	—	—	−196	—
			l-*Menthyl* o-*methylthiolbenzoate.*			
Homogeneous	50	$D_{4^\circ}^{17^\circ}$ 1·0724	−229·3	−307·6	−371·7	−678·5
Alcohol	200	5·000	−216	−288	−348	−612
Benzene	200	4·827	−232	−308	−373	−675
			l-*Menthyl ester of* o-*carboxyphenylmethylsulphone.*			
Homogeneous*	50	$D_{4^\circ}^{70^\circ}$ 1·107	−131	−174·8	−202·3	−372 †
Alcohol	200	4·955	−140	−178	−213	−365 †
Benzene	200	5·031	−134	−172	−207	−359
			l-*Menthyl* o-*sulphobenzoate.*			
Alcohol	200	2·001	−118	−152	−175	−292
,, +HCl	200	2·002	−126	−167	−190	−324
			Methyl o-*carbomenthoxybenzenesulphonate.*			
Alcohol	200	5·820	−137	−181	−214	−380
Benzene	200	5·200	−135	−150	−191	−375

† These figures are only approximate owing to the strong absorption of the violet light.

Summary.

The rotatory powers of a number of *l*-menthyl benzenesulphonates and *o*-substituted benzoates have been determined.

1. Except for the *o*-nitro-derivative, the toluene- and nitrobenzene-sulphonic esters resemble the corresponding benzoates and differ little from the unsubstituted ester. *l*-Menthyl *o*-nitrobenzenesulphonate, however, has a low rotatory power and strongly anomalous dispersion.

2. Among the *o*-substituted benzoic esters the relative effects are given by SMe>SH>H>SO_2Me>SO_2·OMe>SO_2·OH, of which the *o*-sulphomethoxy-compound exhibits very complex dispersion. The thiol and sulphonic derivatives have much lower rotations in the form of their potassium salts.

3. In agreement with the regularities previously established, the characteristic effect of the ortho-substituents is in every case more pronounced in benzene than in alcohol. Similarly, the dispersions of the *o*-nitrobenzenesulphonate and the *o*-sulphomethoxybenzoate are more abnormal in the non-polar solvent.

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