

CXCVII.—*Optical Activity and the Polarity of Substituent Groups. Part IX. Menthyl Esters of Methoxynaphthoic and of Diphenyl-2-carboxylic Acids.*

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IN earlier communications of this series emphasis has been placed on the influence of *o*, *p*-directive substituents in lowering the molecular rotation, when introduced into the *o*-position in an optically active ester of benzoic acid. In continuance of this line of investigation, the examination of a number of menthyl esters of methoxynaphthoic acids has now been undertaken, the methoxyl group having been selected as the substituent owing to the exceptionally large depression produced by this group in the rotatory powers of menthyl and *sec.*- $\beta$ -octyl benzoates.

The  $\alpha$ - and  $\beta$ -naphthoic acids, in comparison with benzoic acid, offer the advantage of several different *o*-positions. Moreover, the *peri*-compounds of the naphthoic series have many points in common with the *o*-derivatives, and it appeared probable that an examination

\* *l*-Menthol, when treated similarly, was found by Dr. Robertson to yield a partly racemised *d*- $\Delta^8$ -menthene, having  $[\alpha]_D^{18} + 22.3^\circ$ .

of compounds of this type might be of assistance in determining whether the peculiar *o*-effect in question is transmitted through the chain of carbon atoms or through space.

Very little information is so far available regarding the influence of substituents on the rotatory powers of active naphthoic esters. The unsubstituted menthyl 1- and 2-naphthoates have been investigated by Rupe (*Annalen*, 1903, **327**, 186), the rotatory power of menthyl 1-methoxy-2-naphthoate in the crude state was measured by Cohen and Dudley (J., 1910, **97**, 1748), and that of the 3-methoxy-2-naphthoate\* by these authors and by Pickard and Kenyon (J., 1915, **107**, 58). In the present work, the menthyl esters of 2-, 4-, 5-, and 8-methoxy-1-naphthoic acids have been prepared and examined, and the preparations of the unsubstituted 1-naphthoate and of the 1- and 3-methoxy-2-naphthoates have been repeated, the 1-methoxy-derivative having now been obtained in the optically pure state. In addition, the menthyl esters of diphenyl-2-carboxylic acid and of 2'-methoxydiphenyl-2-carboxylic acid have been prepared for the purpose of comparison.

An interesting and hitherto unrecorded feature of the crystalline 3-methoxy-2-naphthoic ester and of the newly prepared 8-methoxy-1-naphthoate is the powerful triboluminescence they exhibit. This was first observed on crushing a cake of the 3 : 2-derivative in a mortar in bright daylight. The deep violet flashes emitted were plainly visible and resembled a strong electric discharge. The 5-methoxy-ester also is triboluminescent, but the remaining crystalline esters, the 4 : 1- and the 2 : 1-compounds, do not possess this property.

Values of  $[M]_D$  obtained for the various menthyl esters, together with other values recorded in the literature, are summarised in Tables I and II. Molecular rotatory powers of the esters of diphenyl-2-carboxylic acid and of 2'-methoxydiphenyl-2-carboxylic acid in solution are given in Table III. Among the crystalline esters, only the 3-methoxy-2-naphthoate could be maintained in the supercooled condition. The 2-, 4-, 5- and 8-methoxy-1-naphthoates melted at comparatively high temperatures and solidified a few degrees below these points; the rotatory powers of these esters were therefore determined in solution.

\* There is some confusion in the literature regarding these acids. 1-Methoxy-2-naphthoic acid, described by Cohen and Dudley as  $\alpha$ -methoxynaphthoic acid, is listed in Stelzner's *Literaturregister* (1910—11, p. 705) as 4-methoxy-1-naphthoic acid. Similarly, the 3 : 2-acid, described as  $\beta$ -methoxynaphthoic acid, is listed as the 2 : 1-compound. The uncertainty is possibly due to the authors tabulating the ester of the  $\alpha$ -acid under the heading of *p*-compounds, and that of the  $\beta$ -acid under *o*-compounds (p. 1735), and is increased by the fact that the melting points quoted for both acids are too low.

TABLE I.

*Menthyl 1-Naphthoates.*

Substit.	Solvent.	c.	$[M]_D^{20^\circ}$ .
None	CHCl <sub>3</sub>	4.990	-222° <sup>3</sup>
"	C <sub>2</sub> H <sub>5</sub> ·OH	9.090	-245.9 <sup>1</sup>
"	C <sub>6</sub> H <sub>6</sub>	4.938	-273 <sup>3</sup>
2-MeO	C <sub>6</sub> H <sub>6</sub>	5.000	+ 20.7
"	C <sub>6</sub> H <sub>6</sub>	20.00	+ 34.0
4-MeO	C <sub>6</sub> H <sub>6</sub>	5.000	-313.4
"	CHCl <sub>3</sub>	5.000	-250
5-MeO	C <sub>6</sub> H <sub>6</sub>	4.642	-262.9
"	CHCl <sub>3</sub>	4.663	-231
8-MeO	C <sub>6</sub> H <sub>6</sub>	4.987	-129.6
"	C <sub>2</sub> H <sub>5</sub> ·OH	4.995	-155.6
"	CS <sub>2</sub>	4.972	-114.9

TABLE II.

*Menthyl 2-Naphthoates.*

Substit.	Solvent.	c.	$[M]_D^{20^\circ}$ .
None	C <sub>6</sub> H <sub>6</sub>	11.11	-287.6° <sup>2</sup>
1-MeO	Homog.	—	-223.8 <sup>4</sup>
3-MeO	Homog. (100°)	—	-164.5 <sup>5</sup>
"	CHCl <sub>3</sub>	5.017	-123
"	C <sub>6</sub> H <sub>6</sub>	5.000	-174 <sup>6</sup>
"	CS <sub>2</sub>	5.000	-159.5 <sup>6</sup>

<sup>1</sup> Rupe, *Annalen*, 1910, **373**, 121. <sup>2</sup> Tschugaeff, C., 1902, II, 1238.

<sup>3</sup> See the experimental section of this paper. <sup>4</sup> Cohen and Dudley, *loc. cit.*, record  $[M]_D = -239^\circ$  for the crude ester. <sup>5</sup> Cohen and Dudley find  $[M]_D = -166.4^\circ$ . <sup>6</sup> Kenyon and Pickard, J., 1915, **107**, 58.

TABLE III.

*Menthyl Diphenyl-2-carboxylate and 2'-Methoxydiphenyl-2-carboxylate.*

Unsubstituted ester.	Substituted ester.
In C <sub>6</sub> H <sub>6</sub> (c = 5.194) $[M]_D^{20^\circ} = -201^\circ$ .	In C <sub>6</sub> H <sub>6</sub> (c = 5.63) $[M]_D^{20^\circ} = -323^\circ$ .
	In C <sub>2</sub> H <sub>5</sub> ·OH (c = 5.37) $[M]_D^{20^\circ} = -302^\circ$ .

TABLE IV.

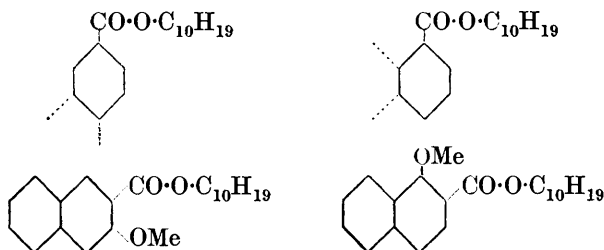
*Molecular Rotations  $[M]_D$  of Aromatic Esters<sup>7</sup> at 20°.*

Active alcohol.	Solvent.	Benzoate.	1-Naphtho-ate.	2-Naphtho-ate.
Menthol .....	C <sub>6</sub> H <sub>6</sub>	—	-273° <sup>8</sup>	-287.6° <sup>8</sup>
" .....	C <sub>2</sub> H <sub>5</sub> ·OH	-234.1°	-246	—
<i>d</i> -β-Octanol .....	C <sub>2</sub> H <sub>5</sub> ·OH	+ 91.9	+ 53.7	+ 129.4
<i>d</i> -γ-Nonanol .....	C <sub>2</sub> H <sub>5</sub> ·OH	+ 29.8	- 8.0	+ 68.4
<i>d</i> -Benzylmethylcarbinol	C <sub>2</sub> H <sub>5</sub> ·OH	+ 169.1	+ 104.5	+ 371.1

<sup>7</sup> Kenyon and Pickard, *loc. cit.*, p. 115. <sup>8</sup> Tschugaeff, *loc. cit.* <sup>9</sup> This paper.

*Influence of Substitution on Rotatory Power.*—Before discussing the specific influence of the methoxyl group, it is instructive to compare the rotatory powers of 1- and 2-naphthoic esters with those of the corresponding benzoates. Reference to Table IV, which summarises the molecular rotatory powers recorded in the literature for the esters of menthol, *d*-β-octanol, *d*-γ-nonanol and *d*-benzylmethylcarbinol, shows that the substitution of the 2-naphthoyl group for the benzoyl group results in every case in a marked increase in the rotation. This increase cannot be due merely to the presence of the second unsaturated nucleus, since the rotatory powers of the

1-naphthoates are in general actually lower than those of the corresponding benzoates. All these differences, however, may be correlated with the changes in rotatory power following nuclear substitution in *sec.*- $\beta$ -octyl benzoate and other active derivatives of benzene. In such compounds *m*-substituents tend to raise the rotatory power and *p*-substituents to bring about a still greater increase, whether the substituent be *o*, *p*- or *m*-directive in type.\* Now the change from a benzoic ester to one of 2-naphthoic acid is equivalent to a 3:4-substitution in the benzene nucleus and thus is accompanied by an increase in rotatory power. On the other hand, the passage from the 2-naphthoic to the 1-naphthoic ester corresponds to the transference of a ring junction from the *p*- to the *o*-position with respect to the carboxylic complex. As the substituent is here of the *o*, *p*-directive type (leading to the formation of  $\alpha$ -derivatives in naphthalene), the change results in a reduction of rotatory power, owing to the characteristic influence of such groups in the *o*-position.



Returning now to the case of the methoxy-derivatives, it has previously been demonstrated that a methoxyl group in the *o*-position depresses the rotatory power of menthyl benzoate (Cohen and Dudley, *loc. cit.*) and of *sec.*- $\beta$ -octyl benzoate, whereas in the *p*-position it raises the value. The same regularity is now found to hold for the menthyl methoxynaphthoates (Tables I and II).

The simplest example is that of the 2-naphthoic ester, in which the *o*-substituent may occupy either of the positions 1 and 3. It will be observed that the depression in rotatory power is more

\* This generalisation holds for the substituents  $\text{NO}_2$ ,  $\text{Cl}$ ,  $\text{CH}_3\text{-O}$ ,  $\text{CO}_2\text{H}$ , and  $\text{CH}_3$ , when introduced into the nucleus in octyl benzoate (Rule, Hay, Numbers, and Paterson, this vol., p. 178). Similar changes occur in the nuclear-substituted methyl dibenzoyltartrates (Frankland, Carter, and Adams, J., 1912, **101**, 2470) and the substituted dianilides of tartaric acid (Frankland and Twiss, J., 1910, **97**, 155). The relation is also evident in the menthyl benzoates, although here the influence of *m*- or *p*-substitution on rotatory power is in some cases almost negligible (Cohen, J., 1914, **105**, 1892; 1918, **113**, 57).

pronounced in the case of the 3-methoxy-ester, which may be explained provisionally on the assumption of a screening effect exercised by the substituent. Each of the side chains attached to the ring bearing the carboxyl group has its own specific influence on the rotation, and following the generalisation formulated above it would be expected that the union of the second ring would depress the rotatory power in the *o*-position, but raise it to an increasing extent as it passes from the *m*- to the *p*-position. In menthyl 3-methoxy-2-naphthoate the elevating influence of the *p*-ring junction on the active complex appears to be partially screened by the substituents in the intermediate positions. The chief influences at work here are the depressive effect of the *o*-methoxy-group and the comparatively small elevating effect of the *m*-ring junction. In 1-methoxy-2-naphthoate the *m*-ring junction appears to be screened, whilst the stronger elevating influence of the *p*-junction has full play, thus leading to a higher rotatory power for this isomeride than for the 3-methoxy-derivative.

Among the menthyl 1-naphthoates, a methoxyl group in the 2-position exerts so marked an influence that the rotatory power is actually reversed in sign. This is a rare phenomenon with 1-menthyl esters; a similar dextrorotation has also been recorded for menthyl triphenylacetate (Tschugaeff, *Ber.*, 1912, **45**, 2760), menthyl 1 : 4-dihydronaphthoate (Rupe, *Annalen*, 1903, **327**, 186), and certain complex thio-esters (Tschugaeff, *Ber.*, 1909, **42**, 2246). In the present instance the reversal appears to be due to the additive lowering influence of two groups, each of the *o*, *p*-directive type. The case is thus analogous to that of the 2 : 6-dibromobenzoic ester examined by Cohen (J., 1914, **105**, 1892), in which the combined effect of the two bromine atoms in the *o*-positions, although insufficient to reverse the sign of the rotation, reduces the value of  $[M]_D$  from  $-233^\circ$  to  $-19^\circ$ .

A special interest attaches to the 8-methoxy-1-naphthoate, in which the substituent also leads to a marked diminution in rotatory power. The resemblance between *peri*- and *o*-compounds as revealed in their chemical behaviour (*e.g.*, anhydride formation and steric hindrance) is therefore also evident in the optical activity of these compounds. This similarity lends further support to the view that the peculiar effect of *o*-substituents on the rotatory power of aromatic esters is transmitted through space and not through the carbon chain (compare also Rule, Hay, and Paul, this vol., p. 1347).

On the other hand, a comparison of the rotatory powers in benzene solution shows that when the methoxyl is introduced into the *p*-position with respect to the carboxyl group, as in the 4-methoxy-1-

naphthoate, it raises the value. In the 5-position, however, the substituent produces no observable change.

The derivatives of diphenylcarboxylic acid were prepared in order to discover whether the presence of a methoxyl substituent in the ortho-position to the common bond joining the two nuclei led to a depression in rotatory power as in the *peri*-compound of naphthalene. This was found not to be the case. In benzene solution the menthyl 2'-methoxydiphenyl-2-carboxylate ( $[M]_D - 323^\circ$ ) has a higher rotation than the unsubstituted ester ( $[M]_D - 201^\circ$ ). The influence of the methoxyl group in this case appears to be of the *general polar* type as in the acetic esters and in the *p*-substituted benzoic esters (compare Rule, Hay, Numbers, and Paterson, *loc. cit.*). This is readily understood in view of the comparatively free rotation of the two nuclei round the bond joining them, and of other observations relating to diphenyl compounds. Robinson (J., 1927, 2488), for example, comments on the fact that 2':2-dinitrodiphenyl is inactive towards alcoholic ammonia at  $150^\circ$ . Burton and Kenner (J., 1922, 121, 495) and Le Fèvre and Turner (this vol., p. 247) conclude that the two nuclei are independent systems joined by a bond which is not a link in a true conjugated system. In the *peri*- and *o*-derivatives the methoxyl group is maintained permanently in close proximity to the asymmetric complex. A comparison of the two diphenylcarboxylic esters with menthyl benzoate ( $[M]_D - 239^\circ$ ) is interesting. The introduction of the phenyl group into the *o*-position in the benzoate does not lead to an increase in rotatory power, as might have been anticipated from its cyclic and unsaturated character, but has the usual depressive effect of an *o*, *p*-directive grouping in this position.

*Influence of Solvents.*—The values recorded in Tables I and II show that the character of the solvent affects the rotatory powers of the naphthoic esters to a greater extent than those of the corresponding benzoic esters. In the case of menthyl 2-methoxy-1-naphthoate, the rotation is negative in chloroform and acetone but positive in benzene and in concentrated solutions in carbon disulphide. In each solvent examined, the rotatory power of this ester becomes increasingly positive with increasing concentration, thus indicating that the homogeneous ester has a comparatively high positive rotation. The highest positive rotations were observed in benzene ( $c = 20$  and  $c = 5$ ) and in carbon disulphide ( $c = 34$ ).

*Dispersion.*—With the exception of menthyl 2-methoxy-1-naphthoate, the above methoxynaphthoic esters proved to have normal dispersion under the conditions of experiment. When  $1/\alpha$  is plotted against  $\lambda^2$ , it is found that the deviations from the

linear, although very small, are systematic rather than casual. The dispersion of these compounds may therefore be described as normal and complex. The dispersion ratios,  $\alpha_{4358}/\alpha_{5893}$ , for the 1-naphthoates vary between 2.06 and 2.17. The 3-methoxy-2-naphthoate gives considerably lower ratios, varying from 1.95 in the homogeneous state to the surprisingly low value of 1.54 in chloroform solution.

Menthyl 2-methoxy-1-naphthoate exhibits a dispersion which is complex and under certain conditions anomalous. When the values obtained for this compound at various concentrations in different solvents are plotted in the form of a characteristic diagram (Armstrong and Walker, *Proc. Roy. Soc.*, 1913, *A*, **88**, 388), the points all lie on the diagram with the exception of those for the rotatory powers of 30% and 40% solutions in chloroform. Anomalous dispersion is observed in chloroform,  $c = 40$ , and in carbon disulphide,  $c = 5$ .

During the preparation of the menthyl ester of diphenyl-2-carboxylic acid by way of the acid chloride, it was found that under certain conditions a considerable proportion of fluorenone was formed. This point is being further investigated.

#### EXPERIMENTAL.

The menthol employed in the following preparations was specially purified and had  $[\alpha]_D^{20} = -49.75^\circ$  in alcohol,  $c = 10$ .

*Menthyl 2-Methoxy-1-naphthoate.*—The required methoxy-acid was obtained by a modification of Bodroux's method (*Compt. rend.*, 1903, **136**, 617). Magnesium, activated with iodine, was brought into reaction with 1-bromo-2-methoxynaphthalene, and the cooled ethereal suspension of the finely divided magnesium compound was treated with solid carbon dioxide at  $-40^\circ$ . The crude acid was dissolved in the minimum amount of alkali and dilute mineral acid was added drop by drop with vigorous shaking, a gummy impurity being precipitated. As soon as the methoxy-acid began to deposit as a white powder the liquid was filtered and acidified. After twice crystallising from alcohol, the methoxy-acid was pure, m. p.  $176^\circ$ . The yield was 63%. Bodroux obtained less than 20%, largely owing to his method of purification.

2-Methoxy-1-naphthoyl chloride, prepared by means of thionyl chloride, was purified by *rapid* distillation under diminished pressure (yield, almost quantitative).

*Menthyl 2-methoxy-1-naphthoate* was obtained from the acid chloride (23 g.) and menthol (16 g.) dissolved in benzene (100 c.c.), with the gradual addition of pyridine (17 g.). The reaction is very vigorous and the mixture should be well cooled to prevent the

formation of coloured products. The ester separates from ligroin in long needles, m. p. 122—123° (Found : C, 77·5; H, 8·3.  $C_{22}H_{28}O_3$  requires C, 77·6; H, 8·3%).

*Menthyl 4-Methoxy-1-naphthoate*.—4-Methoxy-1-naphthaldehyde (24 g.) was first prepared from  $\alpha$ -naphthyl methyl ether (25 g.) and hydrogen cyanide by Gattermann's method (*Annalen*, 1907, 357, 366). The aldehyde, in an equal weight of pyridine, was diluted with hot water, and the emulsion shaken until cold. Oxidation with potassium permanganate then gave the acid in 78% yield.

4-Methoxy-1-naphthoyl chloride, prepared by means of thionyl chloride, distilled at 210—215°/15 mm.

*Menthyl 4-methoxy-1-naphthoate* was obtained from the acid chloride and menthol, dissolved in a small amount of chloroform, pyridine being used as condensing agent. The ester was crystallised from ligroin until of constant rotatory power. M. p. 114—115° (Found : C, 77·4; H, 8·5.  $C_{22}H_{28}O_3$  requires C, 77·6; H, 8·3%).

*Menthyl 8-Methoxy-1-naphthoate*.—1 : 8-Naphtholactone (Eckstrand, *J. pr. Chem.*, 1888, 38, 159, 278) (8·5 g.), dissolved in *N*-aqueous sodium hydroxide (110 c.c.), was cooled with ice and mechanically shaken while methyl sulphate (28 g.) was added in four portions during  $\frac{1}{2}$  hour, and after 1 hour's shaking the product was heated at 100° to destroy any excess of the methylating agent. *Methyl 8-methoxy-1-naphthoate* was removed from the alkaline mixture by extraction with ether. It separated from light petroleum in colourless, rhombic plates, m. p. 51—52° (Found : C, 72·1; H, 5·7.  $C_{13}H_{12}O_3$  requires C, 72·2; H, 5·6%). 8-Methoxy-1-naphthoic acid, together with some unchanged hydroxy-acid, remained in the alkaline liquid. Addition of diazotised sulphanilic acid converted the hydroxy-acid into a dye. After 3 hours, the methoxy-acid and the dye were precipitated by means of hydrochloric acid as a viscous mass which soon solidified. This was dried on tile over phosphoric oxide and extracted with benzene, leaving the dye as a dark red powder. The methoxy-acid separates from benzene in glistening needles, which lose their lustre on standing. M. p. 162—163° (corr.) (Found : C, 71·2; H, 5·3.  $C_{12}H_{10}O_3$  requires C, 71·2; H, 5·0%).

Two separate methylations of 8·5 g. of the naphtholactone were carried out with sodium hydroxide as alkali, and two others with potassium hydroxide in the same proportion and concentration. The former gave a total of 9·5 g. of ester and 11·7 g. of acid; the latter gave 15·0 g. of ester and 6·3 g. of acid.

*Menthyl 8-methoxy-1-naphthoate* could not be prepared by way of the acid chloride, as the reaction with thionyl chloride did not



proceed smoothly and led to resinification. The methoxy-acid (12 g.) and menthol (36 g.) were heated for 42 hours at 120°, a few bubbles of hydrogen chloride being passed through the mixture at intervals. The mixture was worked up in the usual way and gave the ester as an oil (6.4 g.) which solidified on standing. On distillation under 0.09 mm. pressure it was obtained colourless. The ester separated from light petroleum in colourless prisms, m. p. 96—96.5° (Found: C, 77.3; H, 8.5.  $C_{22}H_{28}O_3$  requires C, 77.6; H, 8.3%). After two crystallisations from light petroleum the rotatory power remained constant. Some of the ester was hydrolysed; the liberated menthol was unchanged in optical rotation.

*Menthyl 1-Methoxy-2-naphthoate.*—Cohen and Dudley (*loc. cit.*) give 120—123° as the m. p. of the free acid, whereas Hübner (*Monatsh.*, 1894, **15**, 735) records 127°. For these and other reasons the preparation was repeated, but methyl sulphate was used in place of the iodide. A test methylation was carried out with aqueous alkali in the usual manner, but titration of the resulting acid with a standardised solution of benzenediazonium chloride (Fierz, "Farbenchemie," p. 245) showed that 63% of the hydroxy-acid had escaped reaction. Methylation of the dry disodium salt for 6 hours in boiling xylene was more successful. After the product had been washed with alkali and distilled under diminished pressure, an oil, b. p. 174—178°/15 mm., was obtained which, on hydrolysis with alcoholic alkali and subsequent acidification, gave an acid containing only 28% of the hydroxy-compound; the latter was removed by treatment with diazotised sulphanilic acid. The methoxy-acid crystallised from benzene in needles, m. p. 126—127°.

The crude menthyl 1-methoxy-2-naphthoate obtained from this acid had a rotatory power somewhat higher than that of the pure ester. The viscous oil was distilled under 0.02 mm. pressure, the main fraction boiling at 172—174°. Two further fractionations failed to alter the rotatory power of  $[M]_D^{100}$  —224° (Cohen and Dudley record  $[M]_D^{100} = -239$ ° for the crude ester).

Menthyl 3-methoxy-2-naphthoate was prepared from a methoxy-acid which melted at 133—134° (compare Lesser, Kranepuhl, and Gad, *Ber.*, 1925, **58**, 2120; Fries and Schimmelschmidt, *ibid.*, p. 2838). Its rotatory power agreed with that previously found by Cohen and Dudley.

*Menthyl 5-Methoxy-1-naphthoate.*—Laurent's acid was converted into 5-methoxy-1-naphthoic acid by the method of Royle and Schedler (*J.*, 1923, **123**, 1641) and Shoemith and Rubli (*J.*, 1926, 3241). Unchanged hydroxy-acid was removed by treatment with diazotised sulphanilic acid and the purified methoxy-acid (m. p.

229°) was esterified in the usual manner. The *menthyl* ester crystallises from methyl alcohol in colourless, glistening plates, m. p. 90.3°. It is readily soluble in ligroin, benzene and chloroform, but is less soluble in alcohol or light petroleum (Found: C, 77.8; H, 8.4.  $C_{22}H_{28}O_3$  requires C, 77.6; H, 8.3%).

*Menthyl Diphenyl-2-carboxylate*.—Diphenyl-2-carboxylic acid was prepared from fluorenone by fusion with potash. The purified and colourless acid (m. p. 110—111°) was carefully brought into reaction with thionyl chloride. The resulting acid chloride was treated with menthol, and the heating continued for 2 hours at 40°. The reaction mixture was extracted with ether, the extract washed with alkali, and the ether distilled off. Menthol was removed by distillation in steam. The resulting viscous oil was almost colourless and distilled at 175°/0.4 mm. Fractionation was repeated until no further change in rotatory power was observed (Found: C, 82.0; H, 8.4.  $C_{23}H_{28}O_2$  requires C, 82.1; H, 8.4%).

Under more vigorous treatment, the acid chloride underwent partial ring closure to yield fluorenone (see also Rule and Bretscher, J., 1927, 925). The above sample of ester, however, gave no reaction with *p*-nitrophenylhydrazine, a reagent with which it is possible to detect the presence of very small amounts of the ketone.

*Menthyl 2'-methoxydiphenyl-2-carboxylate* could not be prepared by way of the acid chloride (Rule and Bretscher, *loc. cit.*), but was obtained from the free acid by esterification at 120° in the presence of hydrogen chloride. After 30 hours' heating, 11 g. of acid and 33 g. of menthol gave 7.1 g. of crude ester,  $[\alpha]_D = -85.5^\circ$  in benzene ( $c = 5$ ). On distillation under 0.3 mm. pressure the ester came over at 171—173°. Fractionation was repeated twice more, after which the rotatory power was  $[\alpha]_D = -82.3^\circ$ . It is possible that this value might have undergone a further small change on continued fractionation, but the quantity was insufficient for this to be carried out (Found: C, 78.3; H, 8.2.  $C_{24}H_{30}O_3$  requires C, 78.6; H, 8.3%).

*Menthyl 1-naphthoate* prepared from purified naphthoic acid had the same rotatory power as previously found by Tschugaeff (*loc. cit.*).

#### *Rotations in the Homogeneous State.*

<i>t.</i>	<i>d.</i>	<i>l.</i>	$[M]_{6708}$	$[M]_{5893}$	$[M]_{5461}$	$[M]_{4358}$	$\alpha_{1358}/\alpha_{5893}$
Menthyl 1-methoxy-2-naphthoate.							
98°	1.0267	0.5	-166.5°	-223.8°	-267.8°	-488.9°	2.18
Menthyl 3-methoxy-2-naphthoate.							
20	1.083	0.5	—	-164.5	-193.5	-320.4	1.95
98	1.025	0.5	—	-154.7	-181.1	-297.0	1.85

*Rotations in Solution at about 20° (l = 2).*

Solvent.	c.	$[M]_{6708}$ .	$[M]_{5893}$ .	$[M]_{5161}$ .	$[M]_{4378}$ .	$\alpha_{4378}/\alpha_{5893}$ .
Menthyl 1-naphthoate.						
C <sub>2</sub> H <sub>5</sub> -OH...	8.991	—	-247°	—	—	—
C <sub>6</sub> H <sub>6</sub> .....	4.938	-201°	-273	-319°	-560°	2.05
CHCl <sub>3</sub> .....	4.990	-172	-222	-266	-451	2.02
Menthyl 2-methoxy-1-naphthoate.						
C <sub>6</sub> H <sub>6</sub> .....	5.000	+ 10.8	+ 20.7	+ 28.9	+ 92.5	4.46
C <sub>2</sub> H <sub>5</sub> .....	20.00	+ 21.9	+ 34.0	+ 45.3	+ 121	3.55
CS <sub>2</sub> .....	5.000	- 16.3	- 19.4	- 16.3	+ 7.82	—
CS <sub>2</sub> .....	34.00	—	+ 12.2	+ 20.6	+ 78.2	0.39
COMe <sub>2</sub> ..	5.00	- 45.8	- 55.9	- 62.2	- 78.8	1.40
CHCl <sub>3</sub> .....	5.00	- 54.4	- 68.0	- 76.2	- 105	1.54
CHCl <sub>3</sub> .....	30.0	- 36.0	- 43.9	- 48.0	- 49.1	1.12
CHCl <sub>3</sub> .....	40.0	- 27.7	- 33.0	- 39.9	- 22.4	0.68
Menthyl 4-methoxy-1-naphthoate.						
C <sub>6</sub> H <sub>6</sub> .....	4.994	—	-313	-374	-667	2.13
CHCl <sub>3</sub> .....	4.999	-190	-250	-302	-514	2.06
Menthyl 5-methoxy-1-naphthoate.						
C <sub>6</sub> H <sub>6</sub> .....	4.642	-198.6	-263	-325	-563	2.14
CHCl <sub>3</sub> .....	4.663	-182	-231	-287	—	—
Menthyl 8-methoxy-1-naphthoate.						
C <sub>2</sub> H <sub>5</sub> -OH...	5.000	-116.1	-156	-184.5	-326.5	2.10
C <sub>6</sub> H <sub>6</sub> .....	4.987	- 97.5	- 130	- 157	- 282	2.17
CS <sub>2</sub> .....	4.972	- 87.2	- 115	- 137.5	- 242	2.11
Menthyl 3-methoxy-2-naphthoate.						
CHCl <sub>3</sub> .....	5.017	—	-123	-139	-190	1.54
Menthyl diphenyl-2-carboxylate.						
C <sub>6</sub> H <sub>6</sub> .....	5.194	-151	-201	-233	—	—
Menthyl 2'-methoxydiphenyl-2-carboxylate.						
C <sub>6</sub> H <sub>6</sub> .....	5.630	-245	-323	-390	-692	2.14
C <sub>2</sub> H <sub>5</sub> -OH...	5.370	-223	-302	-362	-654	2.17

*Summary.*

The influence of the typically *o*-, *p*-directive methoxyl group on the rotatory powers of the menthyl naphthoates has been examined and found similar to that exerted in the case of menthyl benzoate.

1. In any position adjacent to the carboxylic complex the substituent depresses the rotatory powers of the 1- and 2-naphthoates. In menthyl 2-methoxy-1-naphthoate the combined effect of the two *o*-, *p*-directive groups in the 2- and 6-positions actually reverses the sign of the rotation, giving a dextrorotatory ester.

2. In 4-methoxy-1-naphthoate the *p*-substituent raises the rotation, but in the 5-position it has little or no effect.

3. A methoxyl group in the *peri*-position also produces a marked diminution in rotatory power, thus indicating that the peculiar

*o*-influence in question is transmitted through space and not through the chain of atoms.

4. A phenyl group in the 2-position in menthyl benzoate leads to the diminished rotation characteristic of *o*-, *p*-directive substituents. A 2-methoxyphenyl group in this position raises the rotation.

5. The relative magnitudes of the rotatory powers of optically active esters of benzoic acid, 1-naphthoic acid, and 2-naphthoic acid may be correlated with the known influence of *o*-, *m*-, and *p*-substituents on the benzoic esters.

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