MENTHYL ESTERS OF THE ISOMERIC CHLOROBENZOIC ACIDS. 1213

CXVIII.—The Rotation of the Menthyl Esters of the Isomeric Chlorobenzoic Acids.

By JULIUS B. COHEN and SAMUEL HENRY CLIFFORD BRIGGS.

IN the course of a research on the chlorination of toluene (Cohen and Dakin, Trans., 1901, 79, 1111), the six isomeric dichlorobenzoic acids were obtained in a pure state by methods which, although tedious, gave without difficulty a satisfactory yield of each of the isomerides.

The rotation of the esters produced by condensing these acids with active alcohols seemed likely to throw some light on the effect of position isomerism on optical activity—a subject about which, from lack of data, our knowledge is at present very imperfect. We selected the esters of menthol as being most suitable for the purpose.

During the progress of the research, a paper by Tschugaeff (J. Russ. Phys. Chem. Soc., 1902, 34, 606) appeared giving the rotation of the three menthyl bromobenzoates. We have not been able to consult the original memoir, but the figures given in the abstract (Abstr., 1903, ii, 1) accord in the main with those obtained by us from the corresponding monochloro-compounds and are referred to below.

In preparing the chlorobenzoic acids and the corresponding menthyl esters, the following general method was adopted. The acids, obtained from the chlorotoluenes by oxidation with dilute nitric acid in sealed tubes, were purified by recrystallisation from water or dilute alcohol and converted into the acid chlorides by the action of phosphorus pentachloride. The products of this reaction were separated by distillation under diminished pressure, the phosphorus oxychloride being removed by heating on the water-bath, whilst the acid chloride was obtained at higher temperatures. A mixture of the acid chloride and menthol in molecular proportion was heated in the oil-bath at about 130-140° until the evolution of hydrogen chloride ceased, when the product was made slightly alkaline with aqueous sodium carbonate and distilled in steam until all the unaltered menthol and menthyl chloride were removed. The ester was isolated from a chloroform extract of the acidified residue after dehydration over calcium chloride and removal of the solvent by distillation under diminished pressure. At the beginning of the distillation, a small quantity of solid, which proved to be the free acid, was observed in the distillate from some of the esters; but the decomposition was very slight and did not appear to affect the rotation of the clear liquid, which remained unchanged after being repeatedly redistilled.

The esters which showed signs of decomposition were those of the

View Article Online

1214 COHEN AND BRIGGS : THE ROTATION OF THE

o- and p-chlorobenzoic acids and the 2:3-, 2:5- and 3:4-dichlorobenzoic acids.

Evidence of steric hindrance is very clearly indicated in the case of the 2:6-dichlorobenzoic acid, for whereas the acid chlorides as a rule react vigorously with menthol at $135-140^{\circ}$, no reaction occurs with 2:6-dichlorobenzoyl chloride until the temperature reaches 180° , and even then it proceeds very slowly.

The following table gives the boiling points of the six dichlorobenzoyl chlorides.

Dichlorobenzoyl chloride.	b. p.	Pressure in mm.	Dichlorobenzoyl chloride.	b. p.	Pressure in mm.
2·3 2·4 2·5	140° 150 137	$14 \\ 34 \\ 15$	2·6 3·4 3·5	$142-143^{\circ} \\ 159-160 \\ 135-137$	21 42 25

The following table gives the boiling points, specific gravities, specific and molecular rotations of the series of menthyl esters, together with the corresponding constants for menthyl benzoate, which are included for the purpose of comparison.

Ester.	Boiling or melting point.	Pressure in mm.	Specific gravity 20°/4°.	[α] ^{20°} .	[M] ^{20°} .
<pre>Menthyl o-chlorobenzoate , m-chlorobenzoate , p-chlorobenzoate , 2: 3-dichlorobenzo- ate , 2: 4-dichlorobenzo- ate , 2: 5-dichlorobenzo- ate , 3: 4-dichlorobenzo- ate , 3: 5-dichlorobenzo- ate , 3: 5-dichlorobenzo- ate , benzoate(Tschugaeff)</pre>	b. p. 225° ,, $218-219$,, 229 ,, $218-219$,, $243-245$ (m. p. $28-29$,, $134-135$ b. p. $244-245$,, $223-225$ m. p. 54	$ \begin{cases} 30 \\ 14 \\ 20 \\ 15 \\ 35 \\ \{ not \\ distilled \\ 35 \\ 20 \\ - \\ \} \end{cases} $	1.0870 1.0822 1.0804 1.1607 1.1546 1.1590 in CHCl ₃ solution 1.1548 1.1535 in benzene solution	$ = 66 \cdot 24^{\circ} \\ = 80 \cdot 45 \\ = 80 \cdot 60 \\ = 52 \cdot 57 \\ = 63 \cdot 72 \\ = 60 \cdot 62 \\ - 34 \cdot 4 \\ = 69 \cdot 16 \\ = 70 \cdot 89 \\ - 90 \cdot 92 \\ = 90 \cdot 92 $	$ \begin{array}{r} -195^{\circ} \\ -236 \cdot 9 \\ -237 \cdot 8 \\ -172 \cdot 9 \\ -209 \cdot 6 \\ -199 \cdot 4 \\ -113 \\ -227 \cdot 5 \\ -233 \cdot 2 \\ -236 \cdot 3 \end{array} $

The series of esters was analysed by estimating the quantity of chlorine present, with the following results :

	Substance	AgCl	Percentage of chlorine.		
Ester.	taken.	found.	Found.	Calculated.	
Menthyl o-chlorobenzoate , m-chlorobenzoate , p-chlorobenzoate , 2:3-dichlorobenzoate , 2:4-dichlorobenzoate , 2:5-dichlorobenzoate , 3:4-dichlorobenzoate , 3:5-dichlorobenzoate	$\begin{array}{c} 0.2530\\ 0.2502\\ 0.2717\\ 0.2938\\ 0.2793\\ 0.2793\\ 0.2744\\ 0.2550\\ 0.2921\\ 0.2489\end{array}$	0 1235 0 1234 0 1317 0 2587 0 2423 0 2375 0 2235 0 2235 0 2490 0 2185	$\begin{array}{c} 12.06\\ 12.14\\ 11.98\\ 21.76\\ 21.44\\ 21.40\\ 21.67\\ 21.08\\ 21.70\\ \end{array}$	12.04 ,, 21.56 ,, ,, ,, ,,	

Analyses of the Chlorobenzoic Esters.

On reference to the properties of the isomeric dichlorobenzoic esters, it will be seen that the 2:6-compound is distinguished from the other isomerides by its high melting point; this substance is, nevertheless, monomolecular as indicated by a molecular weight determination by the cryoscopic method in benzene.

W	Δt	м.
10.3	0·151°	331
"	0.163	303
,,	0.169	319.
	W 10·3 "	$ \begin{array}{cccc} W & \Delta t \\ 10.3 & 0.151^{\circ} \\ , & 0.163 \\ , & 0.169 \end{array} $

Mean of 3 experiments, M = 318; Cal., $C_{17}H_{22}O_2Cl_2$ requires M = 329.

Owing to the high melting point, we were unfortunately unable to determine the rotation of the melted substance; moreover, it is so slightly soluble in all solvents that it was impossible to obtain strong solutions, and thus calculate the rotation of the pure substance by extrapolation. We had to be satisfied with finding the rotation in a chloroform solution containing 6.36 per cent. of the substance, which gave a specific rotation of $[a]_{D}^{20} = -34.4^{\circ}$, which may be regarded as an approximation. It seems reasonable to conclude, however, that the rotation would be low, and probably much lower than that of any of the other compounds of the series.

The order of magnitude, beginning with the ester of lowest rotation, is as follows:

$$2:6, 2:3$$
, ortho, $2:5, 2:4, 3:4, 3:5$, phenyl, meta, para.

Three conclusions may be drawn from the above experimental data. (1) The greatest effect in decreasing the rotation of the unsubstituted menthyl ester is produced when the halogen enters the ortho-position

1216 MENTHYL ESTERS OF THE ISOMERIC CHLOROBENZOIC ACIDS.

with respect to the ester radicle; the least alteration is observed when the halogen is in the meta- or para-position, the introduction of a single halogen atom in the latter position slightly increasing the rotation. (2) The monohalogen esters accord with the rule laid down by Frankland and Wharton (Trans., 1896, 69, 1320, 1583), and onfirmed by Guye and Babel (Abstr., 1899, 76, ii, 719) and by _'schugaeff (Abstr., 1903, 84, ii, 2), and follow the order :--ortho, phenyl, meta, para. (3) Two halogens attached to adjacent carbon atoms of the nucleus (2:3 and 3:4) produce a greater effect than either halogen singly.

The results obtained with the monochlorobenzoic esters show a general correspondence with the monobromobenzoic esters examined by Tschugaeff (*loc. cit.*).

1	Tschugaeff.	[M] ^{20°} .	C. and B.	[M] ^{20°} .
Menthyl bo ,, o- ,, m ,, P	enzoate bromobenzoate bromobenzoate bromobenzoate 	- 236·3° - 205·3 - 238·7 - 238·8	Menthyl benzoate ,, o-chlorobenzoate ,, m-chlorobenzoate ,, p-chlorobenzoate	236·3° 195·0 236·9 237·3

When compared with the rotation of the ortho-chloro-ester, the number for the ortho-bromo-ester seemed too high. We therefore repeated the preparation of this compound, and obtained a slightly lower result, namely, $[M]_{D}^{20^{\circ}} = -201.0^{\circ}$, but this is still much higher than the constant for the chlorine compound.

In regard to the dichlorobenzoic esters, it is of interest to notice the rotations of the 2:3- and 2:5-esters. In both compounds, the chlorine atoms occupy the ortho- and meta-positions, yet they show a wide difference in rotation. Instead of the rotations being approximately the same and lying between those of the ortho- and metacompounds, the constant for the 2:3-compound is much lower, and that of the 2:5-compound is slightly higher, than the value obtained for the ortho-compound. The difference might be attributed to the variation in the position of the centre of gravity of the masses in the two cases according to the theory of Guye, but the low rotation of the 3:4- and 3:5-isomerides is directly opposed to the principle of the lever-arm (Frankland and Wharton, *loc. cit.*).

A careful examination of the results obtained by different observers on the effect of position isomerism on optical activity leads to the conclusion that a satisfactory generalisation based on existing data has yet to be found.

THE YORKSHIRE COLLEGE, LEEDS.