

CXXIX.—*The Relation of Position Isomerism to Optical Activity. III. The Rotation of the Menthyl Esters of the Isomeric Iodobenzoic Acids.*

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IN a former communication (Cohen and Briggs, *Trans.*, 1903, **83**, 1216), the rotations of the menthyl esters of the three monochlorobenzoic acids were given and compared with the constants obtained by Tschugaëff (*Abstr.*, 1903, **84**, ii, 2) for the three monobromobenzoic esters. It seemed desirable to complete the series by determining the constants of the esters of the three iodobenzoic acids, which has now been done with the results on p. 1272.

The results are somewhat remarkable. The rotation of the ester of *o*-iodobenzoic acid rises suddenly above that of the *o*-bromo-ester; the *m*-ester sinks slightly below that of the other two meta-compounds, whilst the para-ester shows the same gradual rise which differentiates the bromo- from the chloro-ester. But, whereas the meta- and para-esters exhibit among themselves differences not exceeding 4° and not above 5° between them and menthyl benzoate, the ortho-esters differ among themselves by more than 50°. If we compare the members of the ortho-series with one another and with menthyl benzoate, we see

*Molecular Rotations of the Menthyl Esters of the Chloro-, Bromo-, and Iodo-benzoic Acids.*Menthyl benzoate $[M]_D^{20} = 236.3^\circ$ (Tschugaeff).

Menthyl chlorobenzoate (C. and B.).	$[M]_D^{20}$.	Menthyl bromobenzoate (Tschugaeff).	$[M]_D^{20}$.	Menthyl iodobenzoate (C. and R.).	$[M]_D^{20}$.
ortho	-195.0°	ortho	-205.3°	ortho	-246°
meta	-236.9	meta	-238.7	meta	-234.5
para	-237.3	para	-238.8	para	-241.2

that the rotations vary on each side of the value for menthyl benzoate. If the effect of the three halogens on the ester group were the same in character but different in magnitude, we should expect a change—it might be gradual or abrupt—but a change in one direction.

This is not the case, and we are therefore compelled to recognise at least two factors simultaneously affecting rotation, namely, the chemical nature of the non-active group and its position in regard to the active group, which may act together or in opposite directions in increasing or diminishing the rotation of the active group.

EXPERIMENTAL.

o-Iodobenzoic acid was prepared from anthranilic acid by replacing the amino-group by iodine in the usual way. The acid was separated by filtration and crystallised from dilute acetic acid. Anthranilic acid gave about an equal weight of *o*-iodobenzoic acid melting at 162°. Prepared in this manner, the acid has a brown colour, which it does not lose on repeated crystallisation. In order to purify it, it was converted into the ethyl ester by Fischer and Speier's method, and then distilled under reduced pressure. Sixteen grams of the discoloured acid gave 13 grams of ethyl ester (b. p. 163—165°/23 mm.)

The ester was hydrolysed by heating it on the water-bath with the calculated quantity of methyl-alcoholic potash. It was then dissolved in water, acidified, and filtered. It now melted at 162—163° and was perfectly colourless.

o-Iodobenzoyl Chloride.—The acid chloride was prepared by heating equal weights of acid and phosphorus pentachloride at 130—135° in the oil-bath for half an hour. The phosphorus oxychloride was removed on the water-bath by distillation under diminished pressure, and the acid chloride was then distilled. It boils at 159°/27 mm., and solidifies on cooling; the melting point is 30—31°.

Menthyl o-Iodobenzoate.—The ester was prepared by heating the

acid chloride with an equal weight of menthol to 130—140° in the oil-bath until the evolution of hydrochloric acid ceased. The product was made slightly alkaline with sodium carbonate and the menthol removed by distillation in steam. The ester which remained in the distilling vessel was extracted with ether, dehydrated, and the ether removed by distillation, and finally by heating on the water-bath under reduced pressure. Ten grams of acid chloride gave 11 grams of ester. It is a colourless, viscid liquid, which decomposes on distillation even under reduced pressure.

0.1547 gave 0.0948 AgI. $I = 33.1$.

$C_{17}H_{23}O_2I$ requires $I = 32.9$ per cent.

The rotation observed in a 0.302 decimetre tube at 20° gave -26.46° ; sp. gr. 1.375 at 20°.

$$[\alpha]_D^{20} - 63.72^\circ; [M]_D^{20} - 246^\circ.$$

m-Iodobenzoic Acid.—The acid was prepared from *m*-aminobenzoic acid in precisely the same manner as the ortho-compound, and, like the ortho-compound, it was discoloured. It was purified in the same manner, by conversion into the ethyl ester and distilling under reduced pressure. The ethyl ester boils at 165—166°/24 mm.; it was hydrolysed with alcoholic potash, and the acid, when precipitated with hydrochloric acid, was recrystallised from acetone and melted at 187—188°.

m-Iodobenzoyl chloride was prepared like the ortho-compound and purified by distillation under reduced pressure; it boils at 159—160°/23 mm., and is liquid at the ordinary temperature.

Menthyl m-iodobenzoate was obtained by heating the acid chloride with menthol, as described under the ortho-compound, and purified in the same manner. The acid chloride gave nearly an equal weight of menthyl ester in the form of a viscid liquid, which had a pale amber colour, owing, no doubt, to some slight impurity.

0.1530 gave 0.0935 AgI. $I = 33.0$.

$C_{17}H_{23}O_2I$ requires $I = 32.9$ per cent.

The rotation in a 0.302 decimetre tube at 20° gave -24.95° ; sp. gr. 1.360 at 20°.

$$[\alpha]_D^{20} - 60.75^\circ; [M]_D^{20} - 234.5^\circ.$$

p-Iodobenzoic Acid.—The acid was prepared by oxidising *p*-iodotoluene in sealed tubes with dilute nitric acid at 135° for 3 hours. Some iodine was liberated. The acid was filtered off and the free iodine removed with sodium hydrogen sulphite solution. The product was then dissolved in sodium carbonate solution, filtered from any unchanged *p*-iodotoluene, and acidified; the acid was collected and

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crystallised from alcohol or acetic acid. Sixteen grams of iodotoluene yielded 11 grams of pure acid melting at 265° .

p-Iodobenzoyl chloride was obtained by the method already described, and purified by distillation under reduced pressure. The acid chloride boiled at $163\text{--}164^{\circ}/32$ mm.; on cooling, it solidified and melted at 71.2° .

Menthyl *p*-iodobenzoate was prepared in the ordinary manner. Nine grams of acid chloride yielded 10 grams of ester. This ester, like the two previously described, is a viscid liquid at the ordinary temperature.

0.1301 gave 0.0644 AgI. $I = 33.6$.

$C_{17}H_{23}O_2I$ requires $I = 32.9$ per cent.

The rotation in a 0.302 decimetre tube at $20^{\circ} = -24.74^{\circ}$; sp. gr. = 1.311.

$[\alpha]_D^{20} - 62.48^{\circ}$; $[M]_D^{20} - 241.2^{\circ}$.

The following table gives a summary of the constants of the compounds described above.

	Iodobenzoic acid, m. p.	Iodobenzoyl chloride.			Menthyl iodobenzoate.	
		B. p.	Pressure.	M. p.		$\Delta^{20^{\circ}}$.
ortho	162°	159°	27 mm.	$30\text{--}31^{\circ}$	viscid liquid	1.375
meta	187—188	159—160	23 "	—	"	1.360
para	265	163—164	32 "	71—72	"	1.311

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