

LXXV.—*Optical Activity and the Polarity of Substituent Groups. Part III. Menthyl Acetophenone-o-carboxylate.*

By HAROLD GORDON RULE and JOHN SMITH.

IN certain cases it has now been established that the influence of substituents on the optical rotatory power of an organic compound is similar to their influence on acidity. This has been shown to hold true for the condensation products of an optically active base with substituted benzaldehydes (Betti, *Gazzetta*, 1923, **53**, 417) and for the menthyl esters of monosubstituted acetic acids (Rule and Smith, *J.*, 1925, **127**, 2188).

On the other hand, the menthyl esters of substituted benzoic acids prepared by Cohen reveal an influence of a quite different type. Here the relative changes in rotation produced by a number of simple

ortho-substituents (substitution in the *m*- or *p*-position has little effect) are given by $\text{NO}_2 > \text{CO}_2\text{H} > \text{H} > \text{I} > \text{CH}_3 > \text{Br} > \text{Cl} > \text{F} > \text{O}\cdot\text{CH}_3$. As has already been pointed out (Rule, J., 1924, **125**, 1122; Rule and Paterson, *ibid.*, 2159), this series is in very close agreement with the relative polarity of the groups as deduced from the molecular inductive capacities of compounds, and with the relative effect of the substituents on the nitration of benzene as we pass from the strongly positive (meta-directive) nitro-group to the strongly negative (para-directive) fluoro-group.

Only two positive groups occur in the above series and, unfortunately, few other simple groups of this type can be readily tested in the case of the menthyl benzoates. Acetophenone-*o*-carboxylic acid, however, is a comparatively accessible compound and figures are available relating to the influence of the acetyl group on benzene substitution.

It has been shown by Camps (compare Holleman, "Die direkte Einführung von Substituenten," 1910, p. 190) that when acetophenone is nitrated at 15° it yields a mixture of about 55% of the *m*-compound and 45% of the *o*-compound. Comparing these figures with those previously quoted for the nitration of nitrobenzene and of benzoic acid (Rule and Paterson, *loc. cit.*), we obtain :

	NO_2 .	CO_2H .	$\text{CO}\cdot\text{CH}_3$.
<i>m</i> -Compound.	93	76	55%

The determination of the relative polarity of the acetyl group from molecular inductive capacity data is inconclusive, as will be seen from the following values ($\text{X} = \text{CH}_3\cdot\text{CO}$) :

Series.		Dielec. const.	Density.	Mol. ind. capac.
HX.	Acetaldehyde.	18.5	0.80	10.1
EtX.	Methyl ethyl ketone.	17.8	0.81	15.8
$\text{C}_6\text{H}_5\text{X}$.	Acetophenone.	18.1	1.03	21.0

On comparing these figures with those calculated by Rule and Paterson (*loc. cit.*), it is found that the *m*-directive groups fall into the order :

Series	HX.	—	CN,	CO_2H ,	$\text{CO}\cdot\text{CH}_3$,	H.
	EtX.	NO_2 ,	CN,	$\text{CO}\cdot\text{CH}_3$,	CO_2H ,	H.
	$\text{C}_6\text{H}_5\text{X}$.	NO_2 ,	CN,	$\text{CO}\cdot\text{CH}_3$,	CO_2H ,	H.

From the evidence of the benzene substitution data, which is partly supported by that of inductive capacity, it may be concluded that the acetyl group falls between the carboxyl group and hydrogen.

The menthyl ester of acetophenone-*o*-carboxylic acid has now been prepared, and the optical properties of the compound have been

examined for sodium light and that of the three chief mercury lines. Owing to the slight yellow colour of the melt, the rotation of the fused ester could only be determined over the range λ_D to λ_{gr} , but the rotatory power in benzene and in acetone solution was examined over the range λ_D to λ_{vi} . The values of $1/\alpha$ when plotted against λ^2 gave straight lines. In addition, the dispersion ratio α_{gr}/α_D for the fused ester at 94° and for solutions in benzene and acetone at the ordinary temperature remained approximately constant in the neighbourhood of 1.213. It may therefore be concluded that the compound exhibits normal and apparently simple rotatory dispersion in this region of the spectrum. The molecular rotations were as follows: fused ester, $[M]_D^{94^\circ} = -261^\circ$; in benzene (5%), $[M]_D^{20^\circ} = -284^\circ$; in alcohol (2%), $[M]_D^{19.5^\circ} = -267^\circ$; in acetone (5%), $[M]_D^{18.5^\circ} = -253^\circ$.

Like other positive *o*-substituents, the acetyl group therefore brings about an increase in the rotation of menthyl benzoate. The influence of various *o*-substituents in this case is summarised in the following table, in which the additional figures for the molecular rotations were determined by Cohen and those for the dispersion ratios by Pickard and Kenyon:

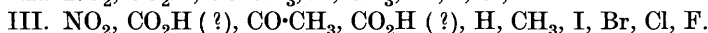
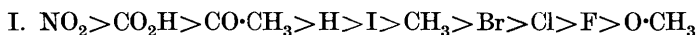
Substit.	NO ₂ .	CO ₂ H.	CO·CH ₃ .	H.	I.	CH ₃ .	Br.	Cl.	F.	O·CH ₃ .
$[M]_D$	-381*	332†	261‡	239	237	231	205	195	194	148
α_{gr}/α_D	1.26	1.21	1.21	1.18	1.19	—	—	—	1.18	—

* At 65° .

† In solution.

‡ At 94° .

The remarkably close correspondence between the effect of substituents on the rotatory power of menthyl benzoate (I) and on benzene substitution (II) is seen by a comparison of the series given below, in which the agreement is broken only by a slight displacement of the iodine atom. Series III represents the relative polarity of the substituents as determined from the inductive capacities of compounds.



EXPERIMENTAL.

Acetophenone-*o*-carboxylic acid was prepared by the method of Gabriel and Neumann (*Ber.*, 1893, **26**, 952). Phthalic anhydride, acetic anhydride, and potassium acetate were heated together to give phthalylacetic acid, and the latter, after purification, was converted into acetophenone-*o*-carboxylic acid by heating under pressure with water at 200° . After several recrystallisations from

water, the acid melted sharply at 112° (Gabriel and Michael, *Ber.*, 1877, **10**, 1554, quote 114—115°).

Menthyl acetophenone-o-carboxylate was prepared from the above acid by esterification in the presence of dry hydrogen chloride. The crude ester was freed from most of the excess menthol by heating at 200° under 10 mm. pressure, and was recrystallised from light petroleum until of constant rotation. The pure compound separated in colourless, odourless crystals, m. p. 92° (Found: C, 75.4; H, 8.6. $C_{19}H_{26}O_3$ requires C, 75.5; H, 8.6%).

The compound dissolves comparatively readily in benzene, but is not very soluble in other organic solvents at the ordinary temperature.

The following figures refer to the rotatory power of the ester in the fused state at 94° . All rotations were measured in a 50 mm. tube and were negative in sign. $D_4^{94} = 0.9898$ (α_{vi} could not be determined owing to the slight yellow tint of the liquid).

α_D .	α_{ye} .	α_{gr} .	α_{gr}/α_D .	$[\alpha]_D$.	$[\alpha]_{ye}$.	$[\alpha]_{gr}$.	$[M]_D$.
42.84	45.04	51.98	1.213	86.56	91.01	105.0	261.4

In addition, a number of measurements were made of the rotatory power in solution at about 20° . In each case the highest concentration quoted represents the maximum at which it is convenient to work, and is not far removed from the saturation point. All rotations are negative in sign.

Solvent.	G. of ester in 100 c.c.	α obs.	($l = 2$).	$[\alpha]_{\lambda}$.	α_{gr}/α_D .	$[M]_D$.
Benzene (20°).	5.000	α_D	9.42	94.2	1.216	284.5
		α_{ye}	9.90	99.0		
		α_{gr}	11.46	114.6		
		α_{vi}	22.03	220.3		
		α_D	37.68	94.15	1.211	284.3
Benzene (20.1°).	20.010	α_{gr}	45.60	113.9		
		α_D	8.48	83.9	1.211	253.4
		α_{ye}	8.90	88.1		
Acetone (18.8°).	5.054	α_{gr}	10.26	101.5		
		α_{vi}	18.85	186.5		
		α_D	3.54	88.46		
		α_D				267.0

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UNIVERSITY OF EDINBURGH.

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